Reprints
Anagostic interactions, revisiting the crystal structure of nickel dithiocarbamate complex and its antibacterial and antifungal studies

Ahmad Husain a, Shahab A.A. Nami b, Suneel P. Singh c, M. Oves d, K.S. Siddiqi a,⇑

⇑Corresponding author.
E-mail addresses: ahmad.chem786@hotmail.com (A. Husain), ks_siddiqi@yahoo.co.in (K.S. Siddiqi).

a Department of Chemistry, Aligarh Muslim University, Aligarh 202002, India
b Department of Kulliyat, Faculty of Unani Medicine, Aligarh Muslim University, Aligarh 202002, India
c Department of Chemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1
d Department of Microbiology, Faculty of Agriculture, Aligarh Muslim University, Aligarh 202002, India

A R T I C L E   I N F O

Keywords:
Anagostic interactions
Crystal structure
Square planar Ni(II) dithiocarbamate
Supramolecular synthons

A B S T R A C T

The synthesis of Ni(dtc)2 [dtc = diethyldithiocarbamate] has been achieved by the interaction of Ni(L)(ClO4)2 with sodium diethyldithiocarbamate. Although single crystal structure of this complex was already reported (R = 10.6%), we were able to refine crystal structure up to R = 2.99%. We also observed rare C–H–Ni anagostic interactions generally exhibited by d8 complexes which were overlooked previously. To investigate the structure of Ni(dtc)2 in solution, variable temperature NMR spectra in solution have also been recorded between 25 and −50 °C. Ni(dtc)2 was also tested for antibacterial and antifungal activities. It showed higher activity against the bacteria and fungi than the known antibiotics.

1. Introduction

Dithiocarbamate based coordination complexes have been thoroughly studied because of their ability to coordinate many common metal ions in different binding modes [1]. They have been shown to possess a broad spectrum of biological activities such as fungicidal [2,3] and bactericidal [4,5]. The antibacterial and antifungal activities of dithiocarbamates were reported to arise by the reaction with HS-groups of the physiologically important enzymes by transferring the alkyl group of the dithioester to the HS-function of the enzyme [5]. All dithiocarbamates contain the characteristic disulfur moiety that binds metal ions in monodentate or bidentate fashion. The nitrogen may be functionalized in various ways to modify the physico-chemical properties of the ensuing metal complex, particularly its solubility and lipophilicity [6]. The dithiocarbamate core, M–S2CNRR2 (M = Metal, R = Alkyl) could prove to be of great synthetic utility since a wide variety of organic substituents can be incorporated in this stable bidentate ligand system. It gives rise to the chemical ‘fine-tuning’ of the biological properties of the complex by variation of the substituent R in M–S2CNRR2 [7]. Recently, we have explored the chemistry of [Ni(L)][CoCl4] [where L = 3,7-bis(2-aminoethyl)-1,3,5,7-tetraazaacyclo[3.3.1]-nonane] complex [8]. As an extension of our previous findings, we report in this paper the reaction of NiL(ClO4)2 with sodium diethyldithiocarbamate which resulted in a ligand transfer reaction. The resulting compound was characterized as Ni(dtc)2 by single crystal X-ray diffraction and other spectroscopic studies and evaluated for antibacterial and antimicrobial properties.

2. Experimental

2.1. Materials and methods

Reagent grade sample of NiCl2·6H2O, sodium diethyldithiocarbamate (Fluka), ethylenediamine (Acros), Ammonia solution (25%) and formaldehyde (S.D. Fine) were used as received and all experiments were carried out in an open atmosphere. All solvents were purchased from Merck India and used after purification. Elemental analyses (C, H, N and S) were carried out with a Carlo Erba EA-1108 analyzer. IR spectra (4000–400 cm−1) were recorded with a RXI FT-IR spectrometer as KBr disc. The NMR spectra were recorded with a BRUKER AV-400 in CDCl3. Caution! Although our samples never exploded during handling, perchlorate metal complexes are potentially explosive: they should be handled with care.

2.2. Synthesis

[Ni(L)(ClO4)2] [where L = 3,7-bis(2-aminoethyl)-1,3,5,7-tetraazaacyclo[3.3.1]nonane] complex was synthesized as reported earlier [9]. To an aqueous solution of sodium diethyldithiocarbamate (10 mM, 1.69 g) were added dropwise with continuous stirring. The solution
immediately turned green followed by the formation of dark green precipitate which was filtered and washed several times with distilled water and dried in vacuo. The resulting compound was characterized as Ni(dtc)$_2$ (Scheme 1) by spectroscopic studies. In a competing process, the Ni(L)(ClO$_4$)$_2$ complex undergoes demetalation immediately due to sodium diethyldithiocarbamate to yield nickel(II) bis(N,N-diethyldithiocarbamate). X-ray quality crystals of Ni(dtc)$_2$ were grown by slow evaporation of chloroform solution at room temperature. Yield: 58%. M.p. 537 K. $^1$H NMR (CDCl$_3$; 400 MHz, $d$ ppm): 1.23 (t, $J$ = 7.2 Hz, 12H, CH$_3$), 3.6 (q, $J$ = 14.4 Hz, 8H, CH$_2$). IR (m cm$^{-1}$/KBr): $\nu$(CSS) 993, $\nu$(C–N) 1517; Anal. Calc. for C$_{10}$H$_{20}$N$_2$NiS$_4$: C, 33.83; H, 5.68; N, 7.89; S, 36.06; Ni, 16.54. Found: C, 33.40; H, 5.45; N, 7.76; S, 35.95; Ni, 16.65%.

2.3. Crystal structure determination

Single-crystal X-ray structural study was performed on a CCD Bruker SMART APEX Diffractometer equipped with an Oxford Instrument low-temperature attachment. Data were collected at 100(2) K using graphite monochromated Mo K$_\alpha$ radiation ($\lambda$) 0.71073 Å. The frames were indexed, integrated, and scaled using the SMART and SAINT software package [10] and the data were corrected for absorption using the SADABS [11] program. The structure was solved by direct method and refined using the SHELX-97 [12] suite of programs, while additional crystallographic calculations were performed by the program PLATON [13]. Figures were drawn using ORTEP-3.2 [14a] and MERCURY-2.3 [14b]. The hydrogen atoms were included at geometrically calculated positions in the final stages of the refinement and were refined according to the “riding model”. All non-hydrogen atoms were refined with anisotropic thermal parameters.

3. Results and discussion

3.1. Crystal structure description of [Ni(dtc)$_2$]

The molecular structure of the [Ni(dtc)$_2$] complex along with the atomic numbering scheme is shown in Fig. 1. Crystallographic

![Scheme 1. Synthesis of Ni(dtc)$_2$.](image)

![Fig. 1. Molecular structure of Ni(dtc)$_2$, depicting the Ni–H and S–H interactions. (MERCURY software has been used for the drawing, bond lengths have been measured in angstrom; only the atoms involving in the interactions are labeled for clarity).](image)
and 2. [Ni(dtc)2] was crystallized in monoclinic system with P2₁/c space group in body centered lattice. The unit cell contains two units of Ni(dtc)₂ (Fig. 2). The unit cell parameters were found to be a = 6.0080 Å, b = 11.441 (2), c = 11.543 (2) Å, β = 95.98° (3) which are considerably different from that reported by Bonamico et al. [15], Selvaraju and Panchanatheswaran [16] Khan et al. [17] and Hogarth et al. [1]. The major change takes place in the refinement factor, R which is improved from 10.6% to 2.9%. Two independent dithiocarbamate moiety coordinate to the nickel atom to form the complex. The nickel atom is four-coordinated with two sulfur atoms of each diethyldithiocarbamate ligand giving rise to a square planar arrangement. The bond angle of four-membered chelate rings around the Ni(II) is 109.75° which is in close proximity with a square planar Ni(II) ion. The near equality of the two Ni–S and two C–S distances confirm the isobidentate coordination of the dithiocarbamate group. The difference between the Ni–S₁ and Ni–S₂ bond lengths is only 0.001 (6). For comparison, the corresponding differences were 0.012 in the previous determination. The accuracy in the C₁–N bond length of 1.317 (3) is an order of magnitude higher than that reported earlier [1.33 (10)] Å. The Ni atom lies on a centre of symmetry and participates in two short symmetrically related Ni–H contacts of 2.665 Å with H3A atoms attached to C₃ [symmetry code: (i) –x + 1, –y + 1, –z + 1]. The torsion angles C₁–N₁–C₅–S₁ [5.2 (3)°], C₁–N₁–C₅–S₁ [174.6 (2)°], C₃–N₁–C₅–S₁ [–2.1 (3)°] and C₃–N₁–C₅–S₂ [178.0 (2)°] confirm the near planarity of the S₃CN₂ moiety.

In an attempt to understand the supramolecular arrangement of the Ni(dtc)₂ molecules, the packing and hydrogen bonding interactions between the molecules were analyzed in detail. The packing and Ni–H bonding interactions viewed along the a-axis are shown in Fig. 3. In addition to this, the hydrogen H3A of the methyl group is also involved in an S–H–C interaction propagating into a three dimensional hydrogen bonded network (Figs. 4–7).

Generally, there are three forms of C–H···M interactions including (i) hydrogen bond, (ii) agostic and (iii) agostic [18]. Hydrogen bonds (i) are 3-center–4-electron interactions with an almost linear geometry accompanied by a downfield 1H NMR shift of the participating protons. Although the origin of these interactions is still under debate it may involve donation of filled d orbital[28] of the metal to the empty 4s orbital of the metal. In the present case M–H distances is 2.665 Å and M–H–C bond angle is 142.4°. They are in between the hydrogen bonds and agostic interactions, with characteristic downfield shifts of the agostic protons. Although the origin of these interactions is still under debate it may involve donation of filled d orbital or dₓz/ᵧz orbitals of the metal center into the C–H σ* orbital [28]. The nature of the agostic M–H–C interaction in a variety of square planar d₈ compounds was recently addressed theoretically by Zhang et al. [29].

The methylene group to which the metal is attached through agostic-type bond, can be envisaged as a dative bond from the X–H σ bonding orbital to the empty 4s orbital of the metal, and a back-donation from the valence electron pairs of the metal into the X–H σ* antibonding orbital of the neutral species.

A specific interaction C–H···S (Figs. 4–6) apparently takes place between the hydrogen atom of the second methylene group and the thioureide sulfur. The existence of specific interactions C–H···S is manifested by anomalous downfield shift of the signal from the corresponding proton. This observed shift may be due to specific interaction C–H···S, or it may be due to the influence of anisotropy of the –CSS group [30], the interatomic S–H distance

### Table 1
Crystallographic data for nickel(II) bis(N,N-diethyldithiocarbamate).

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C₉H₁₅Ni₂S₄</td>
</tr>
<tr>
<td>Formula weight</td>
<td>355.25</td>
</tr>
<tr>
<td>Melting point (K)</td>
<td>317</td>
</tr>
<tr>
<td>Crystal system</td>
<td>monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P2₁/c</td>
</tr>
<tr>
<td>a (Å)</td>
<td>6.0080 (12)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>11.441 (2)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>11.543 (2)</td>
</tr>
<tr>
<td>β (°)</td>
<td>95.98 (3)</td>
</tr>
<tr>
<td>V (Å³)</td>
<td>781.1 (3)</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
</tr>
<tr>
<td>μ (mm⁻¹)</td>
<td>1.74</td>
</tr>
<tr>
<td>F(0 0 0)</td>
<td>372</td>
</tr>
<tr>
<td>Crystal size (mm)</td>
<td>0.25 x 0.12 x 0.09</td>
</tr>
<tr>
<td>θ Range for data collection (°)</td>
<td>2.2–25.5</td>
</tr>
<tr>
<td>Index ranges</td>
<td>–7 ≤ h ≤ 6; –13 ≤ k ≤ 13; –9 ≤ l ≤ 13</td>
</tr>
<tr>
<td>Number of reflections collected</td>
<td>4127</td>
</tr>
<tr>
<td>Number of independent reflections</td>
<td>1460 (0.038)</td>
</tr>
<tr>
<td>Number of observed</td>
<td>1361</td>
</tr>
<tr>
<td>Number of reflections</td>
<td>1460/0/81</td>
</tr>
<tr>
<td>Goodness-of-fit (GOF) on F²</td>
<td>1.14</td>
</tr>
<tr>
<td>wR(F²)</td>
<td>0.029</td>
</tr>
<tr>
<td>wR(F)</td>
<td>0.075</td>
</tr>
<tr>
<td>Δρ_max and Δρ_min (e Å⁻³)</td>
<td>0.45 and –0.45</td>
</tr>
<tr>
<td>Data completeness</td>
<td>0.593</td>
</tr>
</tbody>
</table>

### Table 2
Selected bond lengths (Å) and angles (°).

<table>
<thead>
<tr>
<th>Bond lengths</th>
<th>Ni–S₁</th>
<th>Ni–S₂</th>
<th>Ni–C₁</th>
<th>Ni–C₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni–S₁</td>
<td>2.2026 (8)</td>
<td>2.2026 (8)</td>
<td>1.478 (3)</td>
<td>1.525 (3)</td>
</tr>
<tr>
<td>Ni–S₂</td>
<td>2.311 (2)</td>
<td>2.311 (2)</td>
<td>1.525 (3)</td>
<td>1.478 (3)</td>
</tr>
<tr>
<td>Ni–C₁</td>
<td>1.719 (2)</td>
<td>1.724 (2)</td>
<td>1.467 (3)</td>
<td>1.478 (3)</td>
</tr>
<tr>
<td>Ni–C₂</td>
<td>1.719 (2)</td>
<td>1.724 (2)</td>
<td>1.467 (3)</td>
<td>1.478 (3)</td>
</tr>
</tbody>
</table>

Symmetry code: (i) –x + 1, –y + 1, –z + 1.

Data, selected bond lengths and bond angles are given in Tables 1 and 2. [Ni(dtc)₂] was crystallized in monoclinic system with P2₁/c space group in body centered lattice. The unit cell contains two
corresponding to the equilibrium geometry was found to be 3.0 Å, equal to the sum of the van der Waals radii of the hydrogen and sulfur atoms [31] and S⋅H–C bond angle was found to be 171.7°.

3.2. 1H NMR studies

To investigate the structure of Ni(dtc)₂ in solution, 1H NMR spectra of the complex was recorded in CDCl₃ solution at variable temperatures ranging from 25 °C to −50 °C (Fig. 8). All post acquisition data processing was performed with the MestReC NMR software package [32]. The 1H NMR spectrum at room temperature shows only a single set of signals, suggesting that the two ligands are equivalent in solution. In the 1H NMR spectrum of Ni(dtc)₂ the −CH₂− protons were observed at 3.54 ppm while in case of ligand it was reported at 4.02 ppm. Interestingly, upon cooling the sample to −50 °C the signals start to broaden. Similar observations have also been reported for C–H⋅⋅⋅M interactions in d₈ square-planar complexes of Pd(II) [33], Pt(II) [34] and Ni(II) [27,35] have been reported recently.

Fig. 2. Unit cell of Ni(dtc)₂. Molecules have been shown as ORTEP diagram with 50% thermal ellipsoids. All hydrogen atoms have been omitted for clarity.

Fig. 3. Two dimensional packing diagram depicting the Ni⋅⋅⋅H interactions bonded network along a-axis.
Fig. 4. Two dimensional packing diagram depicting the S·H interactions bonded network along $a$-axis. Hydrogen atoms except those involving in interaction have been omitted for clarity. Ni – green, S – yellow, N – sky blue, C – dark grey, H – light grey. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 5. 1D packing diagram depicting the S·H interactions bonded network along $b$-axis.
4. Biological activity

The antibacterial and antifungal activity of Ni(dtc)$_2$ was determined against three bacterial strains (Escherichia coli, Bacillus thuringiensisso and Pseudomonas aeruginosa) and three fungal strains (Aspergillus niger, Fusarium oxysporum and Penicillium chrysogenum) and the concentration of the complex was kept at 0.5 mg ml$^{-1}$ in DMSO and compared with known antibiotics viz...
Tetracycline and Nystatin (Table 3) at the same concentration. The biological activity of Ni(II) dithiocarbamate complexes is well documented [36–41]. The agar well-diffusion method [42] was used for antibacterial and antifungal studies in this assay and each
experiment was performed in triplicate. The radial growth of the colony was recorded on completion of the incubation, and the mean diameter was recorded. The complex showed higher activity against the bacteria and fungi than the known antibiotics. Area of zone of inhibition was used as a criterion to ascertain the biocidal activity. The screening data are reported in Table 3. The 20 mm zone of inhibition was used as a criterion to ascertain the biocidal activities against the bacteria and fungi than the slandered antibiotics. Ni(dtc)2 showed highest activity for bacterial and antifungal activities against these pathogens.

5. Conclusion

The crystal structure of nickel(II) bis(N,N-diethyldithiocarbamate) has been revisited and refined up to R = 2.99%. This paper reports a rare Ni–H anagostic interaction evidenced by the crystal structure of Ni(dtc)2. The complex showed higher antibacterial and antifungal activities than the slandered antibiotics. Ni(dtc)2 showed highest activity for B. thuringiensis and F. oxysporum.

Acknowledgements

Department of Chemistry, I.I.T, Kanpur India is gratefully acknowledged for providing single crystal X-ray facility. We are grateful to the Council of Scientific and Industrial Research, New Delhi (research scheme No. 21(0685)/07 EMR-II) for the financial support. One of us (SAAN) thanks Department of Science & Technology for financial assistance under SERC FAST Scheme, No. SR/FT/CS-031/2008, NewDelhi, India.

Appendix A. Supplementary data

CCDC 682361 contains the supplementary crystallographic data for Ni(dtc)2. This data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

References

[34] Y. Han, H.V. Huyhn, G.K. Tan, Organometallics 26 (2007) 4672.

Table 3

<table>
<thead>
<tr>
<th>Antibacterial assay</th>
<th>Antifungal assay</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bacteria</td>
<td>Ni(dtc)₂</td>
</tr>
<tr>
<td>E. coli (mm ± stdev)</td>
<td>25.5 ± 0.5</td>
</tr>
<tr>
<td>P. aeruginosa (mm ± stdev)</td>
<td>27.4 ± 0.6</td>
</tr>
<tr>
<td>B. thuringiensis (mm ± stdev)</td>
<td>31.0 ± 0.3</td>
</tr>
<tr>
<td>Fungi</td>
<td>Ni(dtc)₂</td>
</tr>
<tr>
<td>A. nigrus (mm ± stdev)</td>
<td>21.5 ± 0.5</td>
</tr>
<tr>
<td>F. oxysporum (mm ± stdev)</td>
<td>27.4 ± 0.6</td>
</tr>
<tr>
<td>P. chrysogenum (mm ± stdev)</td>
<td>24.0 ± 0.3</td>
</tr>
</tbody>
</table>

Acknowledgements

Department of Chemistry, I.I.T, Kanpur India is gratefully acknowledged for providing single crystal X-ray facility. We are grateful to the Council of Scientific and Industrial Research, New Delhi (research scheme No. 21(0685)/07 EMR-II) for the financial support. One of us (SAAN) thanks Department of Science & Technology for financial assistance under SERC FAST Scheme, No. SR/FT/CS-031/2008, NewDelhi, India.
Synthesis, spectroscopic, magnetic and thermal properties of bimetallic salts, \([\text{Ni}(L)][\text{MCl}_4]\) \{where \(\text{M} = \text{Co(II)}, \text{Zn(II)}, \text{Hg(II)}\) and 
\(L = 3,7\)-bis(2-aminoethyl)-1,3,5,7-tetraazabicyclo(3.3.1)nonane\}. X-ray structure of \([\text{Ni}(L)][\text{CoCl}_4]\)

Shahab A.A. Nami, Ahmad Husain, K.S. Siddiqi, Barry L. Westcott, Kristin Kopp-Vaughn

1. Introduction

A great deal of interest has been directed to the design and synthesis of macrocycles because of their chemical and biological applications [1–5]. Cyclam derivatives (1,4,8,11-tetraazacyclotetradecane) among various macrocyclic complexes are of cardinal importance [6–8]. These systems can be employed as models for protein–metal binding sites in biological systems [9,10] and as selective reagents for a variety of metal ions [11]. Of the various synthetic strategies the metal directed condensation of amines with formaldehyde yield saturated mono and bis(macrocyclic) complexes containing methyleneimine linkages (N–CH2–N) [12], although they are unstable unless both the nitrogen atoms are tertiary [13]. Large number of bis(macrocyces) joined through different functional groups, and their complexes have been reported [14,15]. These bis(macrocyclic) structures can be modulated by changing the organic groups and the central metal ion [16]. By changing the spatial orientation, flexibility and the carbon skeleton, diverse frameworks can be generated having specialized properties which find application in chemosensing and imaging [17], magnetic, nuclear waste treatment [18], sorption [19], ion exchange [20], nonlinear optics, catalysis [21], excited-state reactivity [22], mixed valency [23], and ionophoric activity [24].

During the course of our attempts to synthesize bis(tetraaza) macrocyclic systems, we observed facile reactions occurring between \([\text{Ni}(L)][\text{ClO}_4]_2\) and \([\text{MCl}_2(\text{PPh}_3)_2]\) \{where \(\text{M} = \text{Co(II)}, \text{Zn(II)}, \text{Hg(II)}\) and 
\(L = 3,7\)-bis(2-aminoethyl)-1,3,5,7-tetraazabicyclo(3.3.1)nonane\}. The complexes were characterized by IR, electronic spectra, TGA/DSC, magnetic moment and conductivity measurements. The X-ray crystal structure for \([\text{Ni}(L)][\text{CoCl}_4]\) clearly establishes the cationic–anionic interaction. It crystallizes in the space group \(P1\) with unit cell dimensions \(a = 7.1740(15)\) Å, \(b = 8.1583(16)\) Å and \(c = 8.3102(16)\) Å. A square-planar geometry is evident for the \([\text{Ni}(L)]^{2+}\) cation while the anion is found to be tetrahedral. A two-step thermolytic pattern is observed in the pyrolysis of the bimetallic complex salts.

2. Experimental

2.1. Material and methods

Hydrated metal (II) dichloride, perchloric acid (Merck India), ethylenediamine (E. Merck) were used as received; methanol was distilled prior to use. Elemental analyses (C, H and N) were carried out with Elementar Vario EL III (Carlo Erba 1108) analyzer. FTIR spectra (4000–400 cm\(^{-1}\)) were recorded with a PerkinElmer RXII FT-IR spectrometer as KBr disc while the 600–200 cm\(^{-1}\) range was scanned with CsI on a Nexus FT-IR Thermo Nicolet, spectrometer.
The conductivity measurements were carried out with a CM-82T Elico conductivity bridge in DMSO. The electronic spectra were recorded with a Cintra 5GBC spectrophotometer in DMSO. Magnetic susceptibility measurements were done with a Sherwood Scientific MSB Auto at room temperature. TGA/DSC was performed with a Universal V3.8 B TA SDT Q600 Build 51 Thermal Analyzer under nitrogen atmosphere using alumina powder as reference. The heating rate was kept at 20 °C/min and the metal contents were estimated by complexometric titration [25].

2.2. Synthesis of 3,7-bis-(2-aminoethyl)-1,3,5,7-tetrazabicyclo(3.3.1)nonane)-nickel(II) diperchlorate, Ni(L)ClO₄₂⁻ (1)

To a methanolic solution (100 mL) of NiCl₂·6H₂O (23.77 g, 100 mmol) neat ethylenediamine (13.6 mL, 200 mmol) was added dropwise with stirring to obtain a blue solution. To this mixture, 37% formaldehyde (30.1 mL, 400 mmol) and 25% ammonia (15 mL, 200 mmol) were added and left for three days yielding yellow crystals, which were subsequently filtered, washed with methanol and recrystallized from 1:1 water–methanol mixture at room temperature. Yield 61%. Anal. Calc. for C₂H₂Cl₄N₆O₂: C, 26.16; H, 5.36; N, 20.34. Found: C, 26.02; H, 5.18; N, 20.14.

2.3. Synthesis of [Ni(L)][CoCl₄] (2)

To 20 mL solution of [Ni(L)ClO₄]₂ (0.92 g, 2 mmol) in acetonitrile, was added dropwise CoCl₂(PPh₃)₂ (1.31 g, 2 mmol) solution in 20 mL THF to obtain a green solution. This mixture was refluxed for 6 h to obtain a blue-black solution. It was filtered to remove insoluble nickel hydroxide. An excess of perchloric acid (20 mL) was then added and left for three days yielding yellow crystals, which were subsequently filtered, washed with methanol and recrystallized from 1:1 water–methanol mixture at room temperature. Yield 74%. Anal. Calc. for C₉H₂₀Cl₄CoN₆Ni: C, 22.91; H, 4.14; N, 17.81; Ni, 12.44. Found: C, 22.73; H, 4.14; N, 17.94; Ni, 12.53.

2.4. Synthesis of [Ni(L)][ZnCl₄] (3)

To 20 mL solution of [Ni(L)ClO₄]₂ (0.92 g, 2 mmol) in acetonitrile a solution of ZnCl₂(PPh₃)₂ (1.32 g, 2 mmol) in the same solvent (20 mL) was added dropwise, with continuous stirring. A pinch of ammonium chloride was added and the mixture was refluxed for 6 h to obtain a yellow compound. It was filtered, washed with methanol and recrystallized from 1:1 mixture of water and methanol. Yield 74%. Anal. Calc. for C₉H₂₀Cl₄ZnN₆Ni: C, 22.91; H, 4.27; N, 17.81; Ni, 12.44. Found: C, 22.73; H, 4.14; N, 17.94; Ni, 12.53.

2.5. Synthesis of [Ni(L)][HgCl₄] (4)

To a well stirred solution (20 mL) of HgCl₂(PPh₃)₂ (1.59 g, 2 mmol) was added [Ni(L)ClO₄]₂ (0.92 g, 2 mmol) dissolved in acetonitrile. The reaction mixture was refluxed after about half an hour the solution became transparent; however, refluxing was continued for 8 h. The colored crystals were decanted, washed successively with methanol and acetonitrile and air-dried. Yield 65%. Anal. Calc. for C₉H₂₀Cl₄HgN₆Ni: C, 17.62; H, 3.28; N, 13.70; Ni, 9.57. Found: C, 17.49; H, 3.09; N, 13.59; Ni, 9.68.

2.6. X-ray crystallographic study and structure refinement

Green blocks with well-defined morphologies and uniform birefringence were selected for X-ray studies. The crystal was mounted on glass capillary, with all measurements done at 293 K using phi and omega scans with Oxford Diffraction CrysAlis CCD diffractometer equipped with a sealed-tube Mo Ka source (λ = 0.71073 Å), graphite monochromator, and CCD area detector. Data collection, integration, initial structure refinements and molecular graphics were carried out using the CrysAlis Red, SHELXS-97, and ORTEP3 software packages, respectively [26–28]. Cell dimensions were determined by least-square refinement of 14,888 reflections. Analysis of equivalent reflections indicated no sample decomposition during data collection. Intensity measurements were corrected for absorption using SADABS [29]. Extinction parameters were close to zero and were therefore, removed from refinements. Final structures were checked for missing symmetry in PLATON [30].

Crystal details are shown in Table 1. For structure solution, direct methods were used to locate the initial structural model that consisted of all non-hydrogen atoms. All ligand-based hydrogens were added during the refinement stage at idealized positions. All non-hydrogen atoms were refined anisotropically. The model converged to R = 0.0963, w = 0.096, and Goodness-of-fit on F² = 1.080. Final R indices (I/σ(I)) = R₁ = 0.0367, wR₂ = 0.0918. R indices (all data) = R₁ = 0.0405, wR₂ = 0.0963. Absolute structure parameter = −0.012(13). Largest diff. peak and hole = 0.913 and −0.720 e Å⁻³.

Table 1

<table>
<thead>
<tr>
<th>Crystal data and structure refinement of [Ni(L)][CoCl₄].</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
</tr>
<tr>
<td>Formula weight</td>
</tr>
<tr>
<td>Temperature</td>
</tr>
<tr>
<td>Wavelength</td>
</tr>
<tr>
<td>Crystal system</td>
</tr>
<tr>
<td>Space group</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
</tr>
<tr>
<td>Volume</td>
</tr>
<tr>
<td>Z</td>
</tr>
<tr>
<td>Density (calculated)</td>
</tr>
<tr>
<td>Absorption coefficient</td>
</tr>
<tr>
<td>F(000)</td>
</tr>
<tr>
<td>Crystal size</td>
</tr>
<tr>
<td>Theta range for data collection</td>
</tr>
<tr>
<td>Index ranges</td>
</tr>
<tr>
<td>Reflections collected</td>
</tr>
<tr>
<td>Independent reflections</td>
</tr>
<tr>
<td>Completeness to theta = 32.78 °</td>
</tr>
<tr>
<td>Absorption correction</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
</tr>
<tr>
<td>Refinement method</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
</tr>
<tr>
<td>Final R indices (I/σ(I))</td>
</tr>
<tr>
<td>R indices (all data)</td>
</tr>
<tr>
<td>Absolute structure parameter</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
</tr>
</tbody>
</table>

3. Results and discussion

The complex Ni[L][ClO₄]₂ was synthesized by one-pot condensation of ethylenediamine, formaldehyde and ammonia in 1:2:4:2 molar ratios followed by the addition of perchloric acid in excess. It was thermally stable and soluble in common polar solvents. The binuclear salts were conveniently obtained in accordance with the following equation:

\[ \text{Ni(L)[ClO₄]₂ + MCl₂(PPh₃)₂ → [Ni(L)][MCl₄]} \]
The complexes give satisfactory elemental analysis and are stable to heat and light. They can be stored in an open atmosphere without any decomposition. They are univalent electrolyte [31] in DMSO as evident by their room temperature molar conductivity (1 mM) data.

3.1. IR spectral studies

The infra red spectrum of Ni(L)(ClO4)2, exhibits two sharp absorptions at 1157 and 625 cm\(^{-1}\) characteristic of the ionic perchlorate [32]. These bands disappear in the [Ni(L)][MCl4] implying the interchange of counter ions. A strong absorption at 1157 and 625 cm\(^{-1}\) is characteristic of square-planar Ni(II) complex with (M–Cl) further ascertaining the presence of MCl4\(^{−}\) counter ion [35]. These bands disappear in the [Ni(L)][MCl4] implying the interchange of counter ions. A strong absorption at 1157 and 625 cm\(^{-1}\) is characteristic of square-planar Ni(II) complex with (M–Cl) further ascertaining the presence of MCl4\(^{−}\) counter ion [35].

### Table 2

<table>
<thead>
<tr>
<th></th>
<th>(U^{11})</th>
<th>(U^{12})</th>
<th>(U^{13})</th>
<th>(U^{14})</th>
<th>(U^{22})</th>
<th>(U^{23})</th>
<th>(U^{24})</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(2)</td>
<td>27(1)</td>
<td>43(2)</td>
<td>35(1)</td>
<td>−17(1)</td>
<td>2(1)</td>
<td>−15(1)</td>
<td></td>
</tr>
<tr>
<td>Ni(1)</td>
<td>24(1)</td>
<td>27(1)</td>
<td>26(1)</td>
<td>−8(1)</td>
<td>−2(1)</td>
<td>−6(1)</td>
<td></td>
</tr>
<tr>
<td>Co(1)</td>
<td>28(1)</td>
<td>37(1)</td>
<td>37(1)</td>
<td>−14(1)</td>
<td>−1(1)</td>
<td>−7(1)</td>
<td></td>
</tr>
<tr>
<td>Cl(4)</td>
<td>48(1)</td>
<td>43(1)</td>
<td>49(1)</td>
<td>−23(1)</td>
<td>0(1)</td>
<td>−2(1)</td>
<td></td>
</tr>
<tr>
<td>Cl(2)</td>
<td>50(1)</td>
<td>59(1)</td>
<td>46(1)</td>
<td>−26(1)</td>
<td>7(1)</td>
<td>−30(1)</td>
<td></td>
</tr>
<tr>
<td>Cl(3)</td>
<td>31(1)</td>
<td>39(1)</td>
<td>51(1)</td>
<td>−15(1)</td>
<td>2(1)</td>
<td>−3(1)</td>
<td></td>
</tr>
<tr>
<td>Cl(1)</td>
<td>55(1)</td>
<td>78(1)</td>
<td>51(1)</td>
<td>3(1)</td>
<td>−19(1)</td>
<td>−20(1)</td>
<td></td>
</tr>
<tr>
<td>N(4)</td>
<td>28(1)</td>
<td>27(1)</td>
<td>28(1)</td>
<td>−11(1)</td>
<td>0(1)</td>
<td>−8(1)</td>
<td></td>
</tr>
<tr>
<td>N(3)</td>
<td>44(2)</td>
<td>34(1)</td>
<td>34(1)</td>
<td>−9(1)</td>
<td>−14(1)</td>
<td>−11(1)</td>
<td></td>
</tr>
<tr>
<td>N(1)</td>
<td>32(1)</td>
<td>39(1)</td>
<td>24(1)</td>
<td>−9(1)</td>
<td>−3(1)</td>
<td>−14(1)</td>
<td></td>
</tr>
<tr>
<td>C(4)</td>
<td>43(2)</td>
<td>27(1)</td>
<td>33(1)</td>
<td>−4(1)</td>
<td>−3(1)</td>
<td>−12(1)</td>
<td></td>
</tr>
<tr>
<td>C(3)</td>
<td>57(2)</td>
<td>39(2)</td>
<td>25(1)</td>
<td>−8(1)</td>
<td>−7(1)</td>
<td>−14(2)</td>
<td></td>
</tr>
<tr>
<td>N(5)</td>
<td>49(2)</td>
<td>48(2)</td>
<td>38(1)</td>
<td>−21(1)</td>
<td>−4(1)</td>
<td>−17(2)</td>
<td></td>
</tr>
<tr>
<td>C(9)</td>
<td>25(1)</td>
<td>39(2)</td>
<td>41(2)</td>
<td>−15(1)</td>
<td>1(1)</td>
<td>−6(1)</td>
<td></td>
</tr>
<tr>
<td>C(5)</td>
<td>44(2)</td>
<td>36(2)</td>
<td>41(2)</td>
<td>−20(1)</td>
<td>−3(2)</td>
<td>−8(2)</td>
<td></td>
</tr>
<tr>
<td>N(6)</td>
<td>29(1)</td>
<td>46(2)</td>
<td>43(2)</td>
<td>−12(1)</td>
<td>−9(1)</td>
<td>−4(1)</td>
<td></td>
</tr>
<tr>
<td>C(8)</td>
<td>35(2)</td>
<td>39(2)</td>
<td>35(2)</td>
<td>−6(1)</td>
<td>−10(1)</td>
<td>−4(1)</td>
<td></td>
</tr>
<tr>
<td>C(2)</td>
<td>51(2)</td>
<td>34(2)</td>
<td>35(2)</td>
<td>−6(1)</td>
<td>0(2)</td>
<td>−17(2)</td>
<td></td>
</tr>
<tr>
<td>C(1)</td>
<td>54(2)</td>
<td>44(2)</td>
<td>30(2)</td>
<td>−7(1)</td>
<td>6(2)</td>
<td>−24(2)</td>
<td></td>
</tr>
<tr>
<td>C(7)</td>
<td>47(2)</td>
<td>56(2)</td>
<td>43(2)</td>
<td>−18(2)</td>
<td>−14(2)</td>
<td>−15(2)</td>
<td></td>
</tr>
<tr>
<td>C(6)</td>
<td>53(2)</td>
<td>51(2)</td>
<td>29(1)</td>
<td>−21(1)</td>
<td>2(1)</td>
<td>−20(2)</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 1. An ORTEP drawing of the centrosymmetric structure of [Ni(L)][CoCl4].

3.2. Electronic spectra and magnetic studies

The solution spectrum of Ni(L)(ClO4)2 displays a strong band at 17,800 cm\(^{-1}\) characteristic of square-planar Ni(II) complex with saturated tetra and hexa-aza macrocycles [36]. The field strength of the hexa-aza ligand in the present study does not vary much with that of the tetra-aza [37]. The diamagnetic behavior further confirms the square-planar geometry for the Ni(II) ion in Ni(L)(ClO4)2.

However, in case of [Ni(L)][CoCl4] two bands are observed at 14,430 and 21,400 cm\(^{-1}\) corresponding to \(4T_2(F)\) and \(4A_2(F)\) transitions, respectively, in addition to a charge transfer at 31,000 cm\(^{-1}\) characteristic of tetrahedral Co(II) complexes [38]. A slightly lower room temperature magnetic moment (4.12 B.M.) might be due the slight deviation from the regular tetrahedral geometry which is also evident from its crystal structure. Thus the ligand field spectrum and magnetic moment value suggest a tetrahedral environment around Co(II) ion [39].

3.3. Thermal studies

The numerous factors underlying the thermal stability of transition metal complexes are not well understood [40]. Generally, the stability follows the order Cu < Ni < Co, which is inverse of the Irving Williams series [41]. Our work indicates a two-step decomposition profile. The first step spans over 185–280 °C corresponding to the loss of four chlorine atoms as HCl (~31%). A sharp peak observed in the DSC curve implies the liberation of HCl as an exothermic process [42]. The second step continues from 300 to 440 °C indicating the decomposition of remaining organic moiety. This step is also exothermic in nature with a broad hump centered at 385 °C. Since the thermograms were obtained in an inert atmosphere the metal was left as residue [43].

3.4. Description of the crystal structure of [Ni(L)][CoCl4]

The ORTEP representation of the cation and anion is presented in Fig. 1. The bond lengths and angles are listed in Tables 1 and 2 and Table 3. The crystal structure of the cation was previously reported by Suh et al. [44]; however, there are several striking differences between their report and ours. First and foremost, they performed only an isotropic refinement on the complex and did not refine hydrogen position at all. The authors cited difficulty with thermal parameters as the primary reason for reporting only an isotropic refinement. Furthermore our complex has a CoCl42− counterion and crystallized in P1 as opposed to two perchlorate counterions and Imm2 space group reported previously. Perhaps the difficulty in the previous report arises from the disorder of the perchlorate groups, incorrect space group assignment, or small amount of usable data (482 unique reflections in the previous report versus 5064 in this report). Our improved data collection, refinement, and analysis leads to more accurate values for bond distances and angles in the cation.
The cation \([\text{Ni(L)}]^2+\), where \(L = 3,7\text{-bis}(2\text{-aminoethyl})-1,3,5,6\text{-tetraazabicyclo [3.3.1] nonane}\) has \(mm\) crystallographic symmetry. The \(\text{Ni(II)}\) is coordinated to two ethylenediamine moieties of the ligand giving square-planar structure. Although the Ni–N bond distances do not deviate much (1.922–1.926 Å) the geometry around \(\text{Ni(II)}\) ion is somewhat distorted. It may be due to the larger distance between the nitrogen donors at the open end of the ligand than those involving bicyclononane rings. The Ni–C(1) lie on twofold symmetry axis on the mirror intersecting planes. \(\{2\}–\{3\}–\{4\}–\{N(3)\}\) are located on the \(\{1\,0\,0\}\) mirror plane while \(N(1)\) is on the \(\{0\,1\,0\}\) mirror plane. The diagonally opposite bite angles \(N_1–N_i–N_2\) and \(N_4–N_i–N_3\) are almost equal measuring \(87.43(13)\) and \(87.73(13)\) Å respectively. However, the angle \(N_1–N_i–N_4\) \(98.86(12)\)–Å is substantially larger than the \(N_2–N_i–N_3\) \(94.88(13)\)–Å as \(N_2\) and \(N_3\) belong to the primary amino groups.

The \(\{\text{CoCl}_4\}^2–\) anion also exhibits a distorted tetrahedral geometry with unequal bond angles. The largest being \(\text{Cl}(1)–\text{Co}–\text{Cl}(2)\) measuring 111.68(5)° while the smallest being \(\text{Cl}(3)–\text{Co}–\text{Cl}(2)\) measuring 106.64(5)°. The average bond length of \(\text{Co}–\text{Cl}\) is found to be 2.27 Å.

A notable feature observed in the present case is the occurrence of hydrogen bonding. The \(\text{CoCl}_4^2–\) counter-ion was found to be connected to the cation \([\text{Ni(L)}]^2+\) by hydrogen bonding. The \(\text{C}1\) and \(\text{C}4\) atoms of \(\text{CoCl}_4^2–\) are connected to the hydrogen atoms \(\text{H}5\) of methylene group and \(\text{H}3\) of primary amine \(\text{N}3\) respectively. The bond lengths are 2.663 Å \([\text{Cl}1–\text{H}5\text{b}]\) and 2.525 Å \([\text{Cl}4–\text{H}3\text{b}]\).
Synthesis, characterization and biocidal activities of heterobimetallic complexes having tin(IV) as a padlock

Ahmad Husain a, Shahab A.A. Nami b, K.S. Siddiqi a,⁎

a Department of Chemistry, Aligarh Muslim University, Aligarh 202002, India
b Department of Kulliyat, Faculty of Unani Medicine, Aligarh Muslim University, Aligarh 202002, India

A R T I C L E   I N F O

Article history:
Received 20 October 2009
Received in revised form 2 February 2010
Accepted 19 February 2010
Available online 1 March 2010

Keywords:
Dithiocarbamates
Heterobimetallic complexes
Padlock
Square-pyramidal geometry
Organotin
Biological studies

A B S T R A C T

A mononuclear precursor complex, [(CH3)2Sn(tpdtc)] and several of its heterobimetallic derivatives of the type, [(CH3)2Sn(tpdtc)MCl2] have been synthesized by the simple addition reaction of transition metal chlorides, MCl2 nH2O where tpdtc = tetraethylenepentamine bis(dithiocarbamate) anion, M = Fe(II), Co(II), Ni(II), Cu(II) and Zn(II). The synthesized complexes have been systematically characterized by the physicochemical and spectroscopic techniques. A square-pyramidal geometry has been proposed for all the transition metal atoms with chloride ions occupying the axial while the three nitrogen atoms occupying the equatorial positions. A symmetrical bidentate coordination has been observed for the dithiocarbamato moiety leading to the formation of 18 member cavity. The thermal studies reveal that the mononuclear complex decomposes in three stages while its heterobimetallic analog exhibits a simple two-stage profile. The conductivity measurement data (1 mmol solution) implies a non-electrolytic behavior for all the complexes as evident by their low conductivity values obtained at room temperature. The heterobimetallic complexes have also been tested against the bacterial (Escherichia coli and Pseudomonas aeruginosa) and antifungal strains (Aspergillus niger and Fusarium oxysporum). All the complexes were found to be active against the test organisms and maximum activity was found for [(CH3)2Sn(tpdtc)]CuCl2 complex.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

There has been a continuous quest to synthesize prefabricated novel macrocyclic systems possessing various binding sites because of their vast biological and industrial significance. These systems selectively bind, transform and transfer a variety of substrate from charged species to neutral molecules [1]. Structural factors, such as ligand rigidity, type of donor atoms, and their disposition determine binding features of macrocycles toward metal ions [2]. Considerable attention has been paid to the synthesis of dinucleating macrocyclic complexes, particularly the heterobimetallic complexes owing to their potential use in photochemical molecular devices and as light sensitive probes in biological systems [3–5]. It has been observed that heterobimetallic complexes containing both electron deficient and electron rich transition metal ions behave in a cooperative manner leading to an enhanced reactivity [6]. These systems are of great interest because of their structural diversities, molecular magnetism, electrical conductivity and as complex initiators for photo-oxidation reactions [7–11]. In these heterobimetallic complexes each metal unit can impart, to the resulting macrocycle a specific property like the capability to absorb or emit visible light and to reversibly exchange electrons. These complexes, may thus find applications in molecular electronics [12] and information processing [4,12,13]. From a biochemical viewpoint the presence of two metal ions in close proximity mimic the active site of several metalloproteins, metallo-enzymes and offers an opportunity to study the metal–protein interactions in vitro. Such heterobimetallic complexes can therefore be used as biological models and probes for studying metal–proteins and metal–enzyme interactions [14,15].

Dithiocarbamates are ubiquitous sulfur donor ligands capable of binding nearly all metal ions in a variety of fashion for instance, monodentate, terminal bidentate and bridging bidentate moiety, which allows their complexes to be structurally organized [16]. Nowadays the dithiocarbamato moiety has been exploited as a useful structural motif for metal directed self-assembled systems having a range of structures like nano-sized resorcarene-based assemblies [17], catenanes [18], assorted macrocycles [19] and cryptands [20]. From a biochemical point of view they are used as antibacterial, antifungal and pesticidal agents. Recently, Fe(II)-diethylldithiocarbamate has been used for treating AIDS and neurodegenerative diseases [21,22] and also for monitoring nitric oxide in biological systems as they specifically bind NO [23,24]. The wide biological activity of dithiocarbamate systems may be attributed to their ability to fit into a receptor site and concurrently undergo...
reversible redox reactions [25]. Similarly Cu-dieathyldithiocarba-
mate is known to modify the cellular redox state by inducing a copper-dependent oxidative stress [26,27] and inhibiting the activity of cytosolic Cu/Zn superoxide dismutase. Dithiocarbamate anions may also act as therapeutic agents for the removal of intracellularly deposited metal ions [28]. Another peculiar feature of dithiocarba-
mates is their ability to stabilize unusually high oxidation states of several transition metal ions like Fe(IV), Cu(III) and Ni(IV) [29].

On the other hand organotin complexes of dieathyldithiocarba-
mates have been extensively studied because of their broad structural and biological applications. Particularly, the biological activity of tin dithiocarbamates has attracted much attention in terms of targeting fungi implicated in wood preservation, plant pathogens and in immuno-compromised patients [30–32]. They can also be used as efficient fungicides, because of their degrada-
tion in soil to give nontoxic inorganic tin. Organotin(IV) complexes have also been demonstrated to exhibit relatively high antitumor activity [33,34] but this field is still in infancy relative to Pt(II)-
based anti-neoplastic drugs.

In the present work, we have synthesized a new compartmental ligand by a simple metathesis bearing a (S4) and (N3) coordination
sites. Using this compartmental ligand, heterobimetallic com-
plexes were synthesized by the facile addition reaction of transi-
tion metal chloride, MCl2nH2O. The complexes have been charac-
terized by elemental analysis, FT-IR, NMR (1H, 13C and
119Sn), UV–vis spectroscopy, mass spectrometry, room tempera-
ture magnetic susceptibility measurement, EPR (RT and LNT), thermal
analysis (TGA and DSC) and molar conductivity data.

2. Experimental

Dimethyltin(IV)dichloride (Fluka), potassium hydroxide
(Merck), tetraethylenepentamine (Acros) and carbon disulfide
(s.d. fine) were used as received. Methanol was distilled prior to use. Elemental analyses (C, H, N and S) were carried out with a Carlo Erba EA-1108 analyzer. The metal contents were estimated by
complexometric titration [35]. IR spectra (4000–400 cm−1) were
recorded with a RXI FT-IR spectrometer as KBr disc while the
600–200 cm−1 range was scanned with CsI on a Nexus FT-IR Ther-
mico Nicolet, Wisconsin. The NMR spectra were recorded with a
Bruker AV-500 in DMSO. The conductivity measurements were
used to characterize the complexes. They are soluble in DMSO and DMF only and hence successive attempts to crystallize
the complexes were unsuccessful. Moreover on protonation of
amines of [(CH3)2Sn(tpdtc)] also yielded the powdery substance.
Their molar conductivity (10−3 M) in DMSO (Table 1) indicated
them to be non-electrolytes [36].

3.1. IR studies

The IR spectra of dithiocarbamato complexes consist of three principal regions; the first region spans from 1450 to 1500 cm−1
and accounts for the thioureide (NCSS) band whose position typi-
cally lies in between C–N and C=N band. The position of this sharp
band at 1481–1492 cm−1 in case of bimetallic complexes [39]. A slight
shift of this band towards lower wavenumber, in the range 1481–1492 cm−1 in case of bimetallic complexes [39]. A slight
shift of this band towards lower wavenumber may be attributed to the shift of electron cloud toward the imine nitrogen, which in turn,
is coordinated to the transition metal ion in bimetallic complexes [40]. The existence of metal nitrogen coordination bond is further
strengthening by the presence of new bands occurring in the far IR
region (414–410 cm−1). These bands may safely be assigned to
ν(M–N) in conformity with other workers [41] (Table 2). A strong
solitary ν(CSS) band has been observed throughout, indicative of a
symmetrical bidentate chelation of the dithiocarbamato group.

2.1. Synthesis of tetraethylenepentamine bis(dithiocarbamate)
dimethyltin(IV), [(CH3)2Sn(tpdtc)]

To a methanolic solution (50 ml) of tetraethylenepentamine (1.89 g, 10 mmol) carbon disulfide (1.22 ml, 20 mmol) was added
dropwise with continuous stirring in an icebath followed by the
addition of KOH (1.12 g, 20 mmol) dissolved in minimum amount
of aqueous methanol. The reaction mixture was then stirred for 3 h
at 4 ℃ which became transparent. A methanolic solution (50 ml)
of dimethyltin dichloride was added to it (2.20 g, 10 mmol) to obtain
an immediate precipitation (Scheme 1) which was further stirred for
3 h at room temperature. Excess of the solvent was removed under
reduced pressure and the product was washed with methanol,
diethy ether and dried over phosphorus pentoxide in vacuo.

2.2. Preparation of heterobimetallic complexes, [(CH3)2Sn(tpdtc)]MCl2

To a 20 ml methanolic suspension of [(CH3)2Sn(tpdtc)] (0.49 g, 1 mmol) hydrated metal chloride (1 mmol) dissolved in the same
solvent (20 ml) was added dropwise with continuous stirring for
4 h at room temperature which yielded the respective coloured
bimetallic complexes. It was filtered, washed with methanol,
diethyl ether and dried over phosphorus pentoxide in vacuo.

3. Results and discussion

The heterobimetallic dithiocarbamato complexes were obtained in high yield by the simple addition reaction of transition metal chlor-ide in the cavity generated by the addition reaction of carbon disul-
ride with tetraethylenepentamine as depicted in Schemes 1 and 2.

Elemental analysis (Table 1), TGA/DSC, 1H NMR, 13C NMR, 119Sn
NMR, ESI mass spectrometry, EPR, UV–vis and IR spectroscopy
were used to characterize the complexes. They are soluble in
DMSO and DMF only and hence successive attempts to crystallize
the complexes were unsuccessful. Moreover on protonation of
amines of [(CH3)2Sn(tpdtc)] also yielded the powdery substance.
Their molar conductivity (10−3 M) in DMSO (Table 1) indicated
them to be non-electrolytes [36].

3.1. IR studies

The IR spectra of dithiocarbamato complexes consist of three principal regions; the first region spans from 1450 to 1500 cm−1
and accounts for the thioureide (NCSS) band whose position typi-
cally lies in between C–N and C=N band. The position of this sharp
band at 1481–1492 cm−1 in case of bimetallic complexes [39]. A slight
shift of this band towards lower wavenumber, in the range 1481–1492 cm−1 in case of bimetallic complexes [39]. A slight
shift of this band towards lower wavenumber may be attributed to the shift of electron cloud toward the imine nitrogen, which in turn,
is coordinated to the transition metal ion in bimetallic complexes [40]. The existence of metal nitrogen coordination bond is further
strengthening by the presence of new bands occurring in the far IR
region (414–410 cm−1). These bands may safely be assigned to
ν(M–N) in conformity with other workers [41] (Table 2). A strong
solitary ν(CSS) band has been observed throughout, indicative of a
symmetrical bidentate chelation of the dithiocarbamato group.
The large negative shift in \(\nu(N-H)\) is attributed to the coordination of imino group to the transition metal ions [42]. All the complexes showed aliphatic C–H stretching bands due to methylene groups in the 2971–2965 cm\(^{-1}\) range for asymmetric stretch and \(\sim 2870\) cm\(^{-1}\) for symmetric stretch of the methylene group. Another strong band in the 1174–1185 cm\(^{-1}\) region (Fig. 2) is attributed to the N–C< bond[43].

Medium to weak intensity bands in the 364–348 cm\(^{-1}\) region [44] are assigned to M–S bond. We have also observed some very weak intensity bands in the far IR region (289–330 cm\(^{-1}\)) due to the M–Cl bonds which are found to be absent in the case of mononuclear analog.

### 3.2. Electronic spectra

Generally, the spectra of square-pyramidal complexes of Fe(II) are dominated by the intense charge transfer bands. In the case of [(CH\(_3\))\(_2\)Sn(tpdtc)]FeCl\(_2\) complex we have observed a strong broad band centered at 21,050 cm\(^{-1}\) which is quite close to the sor-t band observed in the spectrum of heme protein. A magnetic moment value of 4.78 BM further strengthens our proposal of square-pyramidal geometry for [(CH\(_3\))\(_2\)Sn(tpdtc)]FeCl\(_2\) [45].

The [(CH\(_3\))\(_2\)Sn(tpdtc)]CoCl\(_2\) exhibits two bands of moderate intensity at 9700 and 12,700 cm\(^{-1}\) corresponding to \(^3\)A\(_2\) \rightarrow \(^3\)B\(_4\) and \(^4\)A\(_2\) \rightarrow \(^4\)B\(_2\) transitions (Table 3), respectively. The square-pyramidal geometry of the Co(II) atom [46] further stems from the high molar absorptivity (~4601 cm\(^{-1}\) mol\(^{-1}\)) which is a characteristic feature of Co(II) complexes. The low magnetic moment value (2.16 BM) obtained in this case may be due to the presence of a main group element in close proximity with Co(II). Moreover, this low magnetic moment value may also be regarded due to the presence of one unpaired electron with appreciable orbital contribution. The origin or this large orbital contribution is however little understood. A similar behavior is also observed even for square-planar Co[(CH\(_3\))\(_2\)As\(_2\)C\(_6\)H\(_4\)]\(_2\)(ClO\(_4\))\(_2\) whose \(\mu_{eff}\) was found to be 2.1 BM at 300 K [47].

The distinction between trigonal-bipyramidal and square-pyramidal Ni(II) stereochemistry can only be made from the position and number of \(d\)–\(d\) bands. The former exhibits two bands while the later shows three to four well spaced bands in 6000–18,000 cm\(^{-1}\) region. In the present case, we have observed one broad band at 9700 cm\(^{-1}\) while the other two bands were observed at 15,150 and 17,750 cm\(^{-1}\) corresponding to \(^3\)B\(_1\) \rightarrow \(^3\)E + \(^3\)B\(_2\); \(^2\)A\(_2\) and \(^2\)E(P) transitions, respectively [48]. Another peculiar feature

### Table 1

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Yield (%)</th>
<th>Colour</th>
<th>M.P. (°C)</th>
<th>Molar conductance ((\Omega^{-1}) cm(^2) mol(^{-1}))</th>
<th>Analysis Found (Calcd.) %</th>
</tr>
</thead>
<tbody>
<tr>
<td>[(CH(_3))(_2)Sn(tpdtc)] 1</td>
<td>81</td>
<td>White</td>
<td>140</td>
<td>11.0</td>
<td>(29.52) (5.57) (14.34) (26.27) (24.30) –</td>
</tr>
<tr>
<td>[(CH(_3))(_2)Sn(tpdtc)]FeCl(_2) 2</td>
<td>78</td>
<td>Dark brown</td>
<td>&gt;300</td>
<td>17.1</td>
<td>(20.97) (3.96) (10.19) (18.66) (17.27) (8.12)</td>
</tr>
<tr>
<td>[(CH(_3))(_2)Sn(tpdtc)]CoCl(_2) 3</td>
<td>68</td>
<td>Pale green</td>
<td>260</td>
<td>11.1</td>
<td>(21.00) (3.90) (10.25) (18.75) (17.10) (8.10)</td>
</tr>
<tr>
<td>[(CH(_3))(_2)Sn(tpdtc)]NiCl(_2) 4</td>
<td>72</td>
<td>Light green</td>
<td>&gt;300</td>
<td>16.2</td>
<td>(19.84) (3.74) (9.64) (17.66) (16.34) (8.11)</td>
</tr>
<tr>
<td>[(CH(_3))(_2)Sn(tpdtc)]CuCl(_2) 5</td>
<td>70</td>
<td>Brown</td>
<td>205</td>
<td>15.7</td>
<td>(19.95) (3.69) (9.60) (17.70) (16.41) (8.02)</td>
</tr>
<tr>
<td>[(CH(_3))(_2)Sn(tpdtc)]ZnCl(_2) 6</td>
<td>82</td>
<td>White</td>
<td>168</td>
<td>20.2</td>
<td>(19.91) (3.77) (9.69) (17.71) (16.31) (8.00)</td>
</tr>
</tbody>
</table>

### Table 2

<table>
<thead>
<tr>
<th>Compounds</th>
<th>(\nu(C-S)) (cm(^{-1}))</th>
<th>(\nu(C-N)) (cm(^{-1}))</th>
<th>(\nu(N-H)) (cm(^{-1}))</th>
<th>(\nu(Sn-S)) (cm(^{-1}))</th>
<th>(\nu(M-N)) (cm(^{-1}))</th>
<th>(\nu(M-Cl)) (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>[(CH(_3))(_2)Sn(tpdtc)] 1</td>
<td>964</td>
<td>1501</td>
<td>3282</td>
<td>352</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>[(CH(_3))(_2)Sn(tpdtc)]FeCl(_2) 2</td>
<td>987</td>
<td>1492</td>
<td>3209</td>
<td>364</td>
<td>414</td>
<td>310</td>
</tr>
<tr>
<td>[(CH(_3))(_2)Sn(tpdtc)]CoCl(_2) 3</td>
<td>995</td>
<td>1492</td>
<td>3190</td>
<td>348</td>
<td>413</td>
<td>312</td>
</tr>
<tr>
<td>[(CH(_3))(_2)Sn(tpdtc)]NiCl(_2) 4</td>
<td>964</td>
<td>1492</td>
<td>3192</td>
<td>349</td>
<td>410</td>
<td>310</td>
</tr>
<tr>
<td>[(CH(_3))(_2)Sn(tpdtc)]CuCl(_2) 5</td>
<td>972</td>
<td>1488</td>
<td>3209</td>
<td>352</td>
<td>412</td>
<td>315</td>
</tr>
<tr>
<td>[(CH(_3))(_2)Sn(tpdtc)]ZnCl(_2) 6</td>
<td>987</td>
<td>1481</td>
<td>3186</td>
<td>364</td>
<td>410</td>
<td>310</td>
</tr>
</tbody>
</table>

### Scheme 1

Synthesis of [(CH\(_3\))\(_2\)Sn(tpdtc)].
of [(CH₃)₂Sn(tpdtc)]NiCl₂ complex is the high intensity of their d–d bands as compared to their Co(II) and Cu(II) analogs. It may be probably due to the similar nature of Ni–L bond as that observed in Ni(II) complex with thiosemicarbazone [49]. The room temperature magnetic moment value of 1.98 BM which is quite close to the spin-only value further supports a square-pyramidal geometry for Ni(II) atom in [(CH₃)₂Sn(tpdtc)]NiCl₂ complex.

Generally, the square-pyramidal Cu(II) complexes exhibit three spin allowed d–d bands in the 12,000–18,000 cm⁻¹ region. We have observed one broad band centered at 16,350 cm⁻¹ which may be due to the composite 2B₁ ↔ 2E₁ + 2B₂ transition while the low intensity band observed at 12,450 cm⁻¹ corresponds to the 2B₁ → 2A₁ transition [50] (Table 3). A low magnetic moment value (1.66 BM) further supports the C₄ᵥ symmetry for these complexes.

### 3.3. NMR studies

#### 3.3.1. ¹H NMR spectra

The ¹H NMR spectrum of the ligand, [(CH₃)₂Sn(tpdtc)] (Supplementary Information) in DMSO-d₆ exhibits only three different signals unlike the expected of eight signals. A singlet at 0.89 ppm corresponds to the methyl protons attached with the Sn atom of the heterobimetallic complexes while the NH protons in the bimetallic complexes were found to be shifted to lower field, i.e. at 3.9–4.5 ppm (Fig. 3) implying the partial drift of electron cloud of nitrogen atom towards the transition metal ion [52]. Such a behavior is also observed in other trimetallic complexes of the type Sn(tch)₂{M₂(dtc)₄} where tch = thiocarbohydrazide, M is divalent transition metal ion and dtc = diethyldithiocarbamate [53]. A notable feature is observed in case of heterobimetallic complexes where a small shoulder is observed along with the broad NH signal which may be attributed to the non-coordinating imine protons. Spectra of the Mn(II) and Cu(II) complexes were severely broadened due to the slow electron-relaxation time of these metal ions [54].

#### 3.3.2. ¹³C NMR spectra

In the ¹³C NMR spectra, the assignment of the ¹³C signal for –CSS group in both ligand and its heterobimetallic complexes is quite straightforward and is observed in the range of 198.5–203.2 ppm (Table 4) indicating coordination of sulfur atoms with the Sn atom [31]. The methyl groups attached to the tin atom gave signals in 8–12 ppm range in the ligand and its complexes [55]. The notable feature is the significant downfield shift observed for all the pentaamine carbons in case of heterobimetallic complexes as compared to the ligand which may be attributed to partial drift of electrons of amine nitrogen towards the transition metal ion which is consistent with our previous findings [56].

#### 3.3.3. ¹¹⁹Sn NMR studies

The ¹¹⁹Sn NMR spectroscopy is quite useful in ascertaining the nature of the coordination of organotin to dithiocarbamates [57].

---

**Table 3**

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Magnetic moment (BM)</th>
<th>Electronic bands (cm⁻¹)</th>
<th>Possible assignments (l mol⁻¹ cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[(CH₃)₂Sn(tpdtc)]FeCl₂ 2</td>
<td>4.78</td>
<td>21,050</td>
<td>Soret band</td>
</tr>
<tr>
<td>[(CH₃)₂Sn(tpdtc)]CoCl₂ 3</td>
<td>2.16</td>
<td>9,700</td>
<td>4A₂ → 4B₁</td>
</tr>
<tr>
<td>[(CH₃)₂Sn(tpdtc)]NiCl₂ 4</td>
<td>1.98</td>
<td>9,700</td>
<td>4A₂ → 4B₁</td>
</tr>
<tr>
<td>[(CH₃)₂Sn(tpdtc)]CuCl₂ 5</td>
<td>1.66</td>
<td>12,450</td>
<td>2B₁ → 2A₁</td>
</tr>
</tbody>
</table>

**Table 4**

<table>
<thead>
<tr>
<th>Compound</th>
<th>δ(–NH) ppm</th>
<th>δ(CH₃–Sn) ppm</th>
<th>δ(–NCH₂) ppm</th>
<th>δ(–CSS) ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>[(CH₃)₂Sn(tpdtc)] 1</td>
<td>3.01 (s)</td>
<td>0.89 (s)</td>
<td>2.85 (m)</td>
<td>198.5</td>
</tr>
<tr>
<td>[(CH₃)₂Sn(tpdtc)]FeCl₂ 2</td>
<td>3.9 (s)</td>
<td>0.83 (s)</td>
<td>2.84 (m)</td>
<td>202.8</td>
</tr>
<tr>
<td>[(CH₃)₂Sn(tpdtc)]CoCl₂ 3</td>
<td>4.0 (s)</td>
<td>0.84 (s)</td>
<td>2.85 (m)</td>
<td>200.0</td>
</tr>
<tr>
<td>[(CH₃)₂Sn(tpdtc)]NiCl₂ 4</td>
<td>3.9 (s)</td>
<td>0.86 (s)</td>
<td>2.84 (m)</td>
<td>201.4</td>
</tr>
<tr>
<td>[(CH₃)₂Sn(tpdtc)]CuCl₂ 5</td>
<td>4.4 (s)</td>
<td>20.89 (s)</td>
<td>2.84 (m)</td>
<td>203.2</td>
</tr>
<tr>
<td>[(CH₃)₂Sn(tpdtc)]ZnCl₂ 6</td>
<td>4.5 (s)</td>
<td>0.82 (s)</td>
<td>2.85 (m)</td>
<td>198.9</td>
</tr>
</tbody>
</table>

**Fig. 1.** EPR spectra of 5 [(CH₃)₂Sn(tpdtc)CuCl₂] and 2 [(CH₃)₂Sn(tpdtc)FeCl₂] at RT and LNT.
Only one signal was observed in the $^{119}\text{Sn}$ NMR spectra of the complexes, obviously due to one tin centre which was observed in 256–260 ppm region which is quite characteristic of the six coordinated Sn atom [58].
3.4. Electrospray ionization mass spectrometry

The electron ionization mass spectra of the ligand and its heterobimetallic complexes are in close proximity with the proposed structure (Schemes 1 and 2). Their fragmentation patterns are attached as supplementary information (Schemes 3 and 4). The mass spectrum of the ligand, [(CH₃)₂Sn(tpdtc)] exhibits a medium intensity molecular ion peak at m/z 488 (62%). However, the base peak was found at m/z 291 (100%) due to [C₅H₆N₃S₂Sn]+ fragment. Moreover some other peaks are also observed for which a possible fragmentation pattern is proposed. The notable feature of the mass spectrum of ligand is the absence of any peak above m/z 488 implying the formation of single cavity, i.e. locking of single dithiocarbamato-based pentamine moiety by one diorganotin dichloride (Scheme 1).

All the heterobimetallic complexes display molecular ion peaks corresponding to their molecular weight. The base peak for all the complexes, [(CH₃)₂Sn(tpdtc)]MCl₂ was observed at m/z 274 (100%) over some other peaks are also observed for which a possible fragmentation pattern is proposed. The notable feature of the mass spectrum of ligand is the absence of any peak above m/z 488 implying the formation of single cavity, i.e. locking of single dithiocarbamato-based pentamine moiety by one diorganotin dichloride (Scheme 1).

Scheme 2. Synthesis of heterobimetallic complexes [(CH₃)₂Sn(tpdtc)]MCl₂ where M = Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II).

Scheme 3. Fragmentation pattern of complex 1 [(CH₃)₂Sn(tpdtc)].
corresponding to the \([\text{SnS}_2\text{CNC}_2\text{H}_3\text{NC}_2\text{]}^+\) fragment. Akin to the ligand, the mass spectra of the complexes does not show any peak in the higher region supporting to the formation of 1:1 macrocycle [59], i.e. addition of one metal in the cavity generated by the addition reaction of carbon disulfide with tetraethylenepentamine subsequently locked by diorganotin dichloride (Scheme 2).

3.5. EPR studies

The EPR spectra of solid \([\text{CH}_3\text{Sn}\text{(tpdtc)}]\text{CuCl}_2\) and \([\text{CH}_3\text{Sn}\text{(tpdtc)}]\text{FeCl}_2\) recorded at room temperature (RT) and liquid nitrogen temperature (LNT) are shown in Fig. 1. They exhibit an isotropic intense broad signal with no hyperfine structure. The absence of any half field signal suggests the presence of only one transition metal atom. The EPR spectrum provides information about the coordination environment around the Cu(II) atom. There are two possibilities for five coordinated Cu(II) complex, i.e. trigonal-bipyramidal and square-pyramidal, which are characterized by ground states \(d_{x^2-y^2}\) and \(d_{x^2}\), respectively. The polycrystalline EPR spectra of Cu(II) complex at 298 K showed axial spectrum with well-defined \(g_\perp\) (2.124) and \(g_\parallel\) (2.083). The \(g_\parallel > g_\perp\) value suggests a distorted square-pyramidal structure [60]. The value of \(g_\parallel > g_\perp > (2.0023)\) in both complexes (Table 5) suggests that the ground state was \(d_{x^2}\) and is occupied by an unpaired electron [61].

3.6. Thermal studies

The TGA profile of the mononuclear precursor complex (1) shows three concurrent stages unlike its dinuclear analogs (2–6) which exhibit simple two step decomposition pattern. Such behav-
ior is quite rare since the increase in metal content makes a complex more resistant to decomposition [62]. Although on the basis of initial decomposition temperature (IDT) the dinuclear complexes are found to be thermally more stable (Table 6). A typical TGA profile of complex 3 is shown in Fig. 4. The first stage of thermal decomposition of the mononuclear complex claims about 6.4% weight loss (found 6.2%) corresponding to the decomposition of two exocyclic methyl groups which is quite common [63]. The sec-

Table 5
Temperature range and mass loss data of complexes.

<table>
<thead>
<tr>
<th>Complexes</th>
<th>First decomposition stage</th>
<th>Second decomposition stage</th>
<th>Third decomposition stage</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fragments</td>
<td>Temp. range (°C)</td>
<td>Mass loss data</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>found (calcd. %)</td>
</tr>
<tr>
<td>[(CH₃)₂Sn(tpdtc)]</td>
<td>Two methyl</td>
<td>100–130</td>
<td>6.41 (6.15)</td>
</tr>
<tr>
<td>1</td>
<td>group</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[(CH₃)₂Sn(tpdtc)]FeCl₂</td>
<td>2 Cl and</td>
<td>140–190</td>
<td>16.85 (17.24)</td>
</tr>
<tr>
<td>2</td>
<td>2CH₃ group</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[(CH₃)₂Sn(tpdtc)]CoCl₂</td>
<td>-do-</td>
<td>145–190</td>
<td>17.73 (17.15)</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[(CH₃)₂Sn(tpdtc)]NiCl₂</td>
<td>-do-</td>
<td>147–194</td>
<td>16.99 (17.15)</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[(CH₃)₂Sn(tpdtc)]CuCl₂</td>
<td>-do-</td>
<td>145–189</td>
<td>16.89 (17.04)</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[(CH₃)₂Sn(tpdtc)]ZnCl₂</td>
<td>-do-</td>
<td>160–198</td>
<td>17.16 (16.98)</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 6
EPR parameters of [(CH₃)₂Sn(tpdtc)]CuCl₂ and [(CH₃)₂Sn(tpdtc)]FeCl₂.

<table>
<thead>
<tr>
<th>Complexes</th>
<th>Temperature</th>
<th>g₁</th>
<th>g₂</th>
<th>g₃</th>
<th>G</th>
</tr>
</thead>
<tbody>
<tr>
<td>[(CH₃)₂Sn(tpdtc)]CuCl₂</td>
<td>RT</td>
<td>2.083</td>
<td>2.124</td>
<td>2.096</td>
<td>1.508</td>
</tr>
<tr>
<td></td>
<td>LNT</td>
<td>2.083</td>
<td>2.104</td>
<td>2.090</td>
<td>1.260</td>
</tr>
<tr>
<td>[(CH₃)₂Sn(tpdtc)]FeCl₂</td>
<td>RT</td>
<td>2.090</td>
<td>2.107</td>
<td>2.095</td>
<td>1.193</td>
</tr>
<tr>
<td></td>
<td>LNT</td>
<td>2.085</td>
<td>2.106</td>
<td>2.092</td>
<td>1.254</td>
</tr>
</tbody>
</table>

Fig. 4. Thermogravimetric curve of complex 4 [(CH₃)₂Sn(tpdtc)]NiCl₂.
ond stage of decomposition accounts for the weight loss of about 18% corresponding to the expulsion of NCS₂ group while the final stage of decomposition corresponds to the degradation of remaining part of the organic molecule. The mass percentage of the final residue, 37.6% was found to be in good agreement with the formation of tin sulfide, SnS₂. The DSC profile of the mononuclear complex also exhibits three peaks. The first small exothermic peak was obtained at 120 °C due to the expulsion of two methyl groups while the second endothermic peak was centered at 182 °C due to the decomposition of thiocyanate group. However, a broad exothermic hump ranging from 270 to 355 °C was obtained due to the formation of tin sulfide.

The heterodinuclear complexes 2–6 essentially decomposes in two steps. The first step is comparatively faster as compared to the second step. The first onset of decomposition begins at about 140 °C except for complex 6 which starts from 160 °C. The observed mass loss of about 17% corresponds to the degradation of two exocyclic methyl groups and two chlorine atoms. The evolution of chlorine gas was confirmed by the enhancement of fumes when a glass rod dipped in liquid ammonia is brought near to it. The second decomposition step is quite slow and ranges from 200 to 600 °C leading to the degradation of remaining organic moiety leaving behind a mixture of metal sulfide and tin sulfide [64]. This behavior is quite consistent as the decomposition is carried out under an inert atmosphere. However, the DSC profiles of the dinuclear complexes are not well explained. Although the first decomposition may be corroborated well with an exothermic peak while the second decomposition step is complex and consists of composite endotherms and exotherms. Moreover there is no well defined peak for the formation of metal sulfides.

4. Biological activity

The in vitro biocidal screening, antibacterial and antifungal activities of heterobimetallic complexes were carried out against Escherichia coli and Pseudomonas aeruginosa. The compounds were tested at the concentration of 0.5 mg ml⁻¹ in DMSO and compared with known antibiotics viz. ampicillin and ciprofloxacine at the same concentration. The agar well-diffusion method [65] was used in these assays and each experiment was performed in triplicate. It is observed that complexes show moderate activity against both the bacteria. Area of zone of inhibition is used as a criterion to ascertain the biocidal activities of the complexes. The mean values of three readings are shown in Table 7. The 20 mm zone of inhibition zone represents significant activity, for 10–12 mm inhibition activity is good, 7–9 mm is low, and below 7 mm the activity is non-significant. The values obtained for activity for compounds 3–6 represents good activity except for compound 2 which show low activity against two pathogenic strains. The higher activity in case of Cu-complex may be attributed to the good solubility of the complex as compared to its other metal complexes.

All the complexes were subjected to antifungal activity against Aspergillus niger and Fusarium oxysporum by using Agar tube dilution method [63]. The results are shown in Table 7. The 30–35 mm zone of inhibition zone represents significant activity, for 20–30 mm inhibition activity is good, 15–20 mm is low, and below 15 mm the activity is non-significant. Compounds 3–6 represents good activity except for compound 2 which show low activity against both fungi.

5. Structure simulations

Molecular geometry optimization was carried out using ChemBio3D Ultra 12.0 program package [66] which employs a modified version of Allinger’s MM2 force field [67] for molecular mechanical calculations. The structures of complexes were simulated by MM2 force field calculations in view of the reports that such computa-

![Fig. 5. Simulated structure of complex [(CH₃)₂Sn(tpdtc)].](image)
IR spectra and NMR, EPR spectra and elemental analysis, respectively. We are grateful to the Council of Scientific and Industrial Research, New Delhi (research scheme No. 21/0685/07 EMR-II) for the financial support. One of us (SAAN) thanks Department of Science & Technology for financial assistance under SERC FAST Scheme, No. SR/FT/CS-031/2008, New Delhi, India.

Appendix A. Supplementary data

The 1H NMR spectrum of the mononuclear ligand, [(CH3)2Sn(tpdtc)] has been attached as Supplementary Information. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2010.02.058.

References

Interaction of organotin with piperazine derived self-assembled cylindrical bisdithiocarbamates: Spectral and thermal investigations

Ahmad Husaina, Shahab A.A. Nami b, K.S. Siddiqia,∗

a Department of Chemistry, Aligarh Muslim University, Aligarh 202002, India
b Department of Applied Chemistry, Aligarh Muslim University, Aligarh 202002, India

1. Introduction

One of the ingenious ways to obtain supramolecular structures lies in the selection of a metal ion with appropriate coordination geometry and desiring a ligand system with predefined properties [1]. These supramolecular systems are gaining continuous attention due to their wide practical utility as catalysts, magnetic and optical materials [2,3]. Such systems can be conveniently generated by employing macrocyclic molecules with tunable properties via metal-directed self-assembling strategy [4,5]. The major advantages of self-assembly over conventional process are: the ease of formation of novel supramolecular structures, thermodynamic stability of the dative metal–ligand bonds and the modulation of the oxidation states of the metal ion involved which controls the stability and binding properties of the metal based assembly thus obtained [6].

Dithiocarbamato systems have been successfully used to generate polynuclear supramolecular structures having intriguing shapes and stereochemistry [7]. The metal directed self-assembling ability of dithiocarbamato ligand has been extensively explored by Beer and co-workers [8] leading to the formation of novel closed loop systems. Self-assembling is spontaneous where strong ionic interaction occurs between the electron rich sulfur atoms and the complexed metal ion. The bonded metal ion, in turn provides a set of coordination geometries with varying bond strengths [9]. The dithiocarbamato ligand is highly reactive and this unique feature is employed in building self-assembled novel supramolecular structures [10]. However, the dithiocarbamates generated from secondary amines are found to be more stable than those of primary amines because the later are susceptible to elimination reactions yielding isothiocyanates [6].

In addition, dithiocarbamato ligands better known as sulfur analogs of carbamates are one of the extensively studied classes of sulfur containing complexes due to their versatile chemical and biological applications. They can stabilize unusual oxidation states of a variety of metal ions [11]. However, some dialkyl dithiocarbamato salts have also been shown to possess fungicidal, herbicidal, pesticidal, bacteriological, anti-alkylating, anti-HIV and anti-cancer activities [12,13]. The application of dithiocarbamates depends on the amphiphilic properties of these ligands with metal ions with special reference to transition metal ions [14,15]. Recently, diethyl dithiocarbamates were demonstrated to act as chemoprotective agents against the cisplatin toxicity and are so termed “rescue agents” [16]. The Sn(IV) dithiocarbamato complexes are also gaining importance because of their wide application as antitumoral, biocide, antimalarial and schizonticidal agents [17,18]. They have shown promising cytotoxic activities against various types of tumor cells like lung, ovarian, melanoma, colon, renal, prostate and breast cancer [19,20].

Of the various nitrogen containing aliphatic heterocycles, piperazine owes a special place due to its hydrogen bonding ability which makes it very specific to generate novel supramolecular structures.
[21]. Of the two chair and boat conformations, piperazine and its
N,N-alkyl substituted derivatives generally exist in chair form due
to greater thermodynamic stability (17.2 kJ/mol) of the former over
the later [22].

Although the ability of transition metal ions to increase their
coordination number is well documented [23], the studies pertaining
to the increase in coordination number of Sn(IV) compounds are scanty. This property of Sn(IV) compounds has not yet been explored of self-assembled systems composed of substituted
dithiocarbamato derivatives. In view of the intensive synthetic and
biological applications of dithiocarbamato systems and the utility
of piperazinyl moiety in construction of supramolecular structures,
we have undertaken in this communication the synthesis, spectral
and thermal characterization of supramolecular systems involving
organotin moiety as a self-assembling agent.

2. Experimental

Dialkylltin(IV) dichlorides and anhydrous tin(IV) chloride (Fluka), potassium hydroxide (Merck), diethylenetriamine, thionyl
chloride, carbon disulfide (s. d. fine) and piperazine anhydrous
(Thomas Baker) were used as received. Methanol was distilled prior
to use. Elemental analyses (C, H, N and S) were carried out with a
Carlo Erba EA-1108 analyzer. The metal contents were estimated
by complexometric titration [24]. IR spectra (4000–400 cm
−1) were recorded with a RXI FT-IR spectrometer as KBr disc while
the 600–200 cm
−1 range was scanned with CsI on a Nexus FT-IR Thermo Nicolet, Madison Wisconsin. The NMR spectra were
recorded with a DPX-300 spectrometer in DMSO at room tem-
perature. The conductivity measurements were carried out with a
CM-82T Elico conductivity bridge in DMSO. TGA was per-
formed with a PerkinElmer (Pyris Diamond) thermal analyzer
under nitrogen atmosphere using alumina powder as reference.
The conductivity measurements were carried out with a
Carlo Erba EA-1108 analyzer. The metal contents were estimated
to use. Elemental analyses (C, H, N and S) were carried out with a
Carlo Erba EA-1108 analyzer. The metal contents were estimated
by complexometric titration [24]. IR spectra (4000–400 cm
−1) were recorded with a RXI FT-IR spectrometer as KBr disc while
the 600–200 cm
−1 range was scanned with CsI on a Nexus FT-IR Thermo Nicolet, Madison Wisconsin. The NMR spectra were
recorded with a DPX-300 spectrometer in DMSO at room tem-
perature. The conductivity measurements were carried out with a
CM-82T Elico conductivity bridge in DMSO. TGA was per-
formed with a PerkinElmer (Pyris Diamond) thermal analyzer
under nitrogen atmosphere using alumina powder as reference.
The weight of the sample was kept between 8 and 12 mg and
was added (10 mmol, 2.2 g) dimethyltin dichloride in 50 mL of the
same solvent. The reaction mixture was then stirred for 4 h at room
temperature which yielded the complex. It was filtered, washed
with methanol and anhydrous diethyl ether and dried in vacuo.

2.2. Synthesis of dimethyltin bis(2′,2′-dithiopiperazinato-
2′,2′-diaminoethylamine) dithiocarbamate, (CH3)2Sn2L2

To a stirred solution of K2L (10 mmol, 4.7 g) in 50 mL of methanol
was added (10 mmol, 2.2 g) dimethyltin dichloride in 50 mL of the
same solvent. The reaction mixture was then stirred for 4 h at room temperature which yielded the complex. It was filtered, washed
with methanol and anhydrous diethyl ether and dried in vacuo.

2.3. Synthesis of dibutyltin bis(2′,2′-dithiopiperazinato-
2′,2′-diaminoethylamine) dithiocarbamate, (C4H9)2Sn2L2

To a methanolic solution of the ligand (10 mmol, 4.7 g) (50 mL) was added (10 mmol, 3.0 g) dibutyltin dichloride 50 mL of the same
solvent to obtain an immediate precipitation. It was then stirred
for 4 h at room temperature. The product was filtered, washed with
methanol, anhydrous diethyl ether and dried in vacuo.

2.4. Synthesis of diphenyltin bis(2′,2′-dithiopiperazinato-
2′,2′-diaminoethylamine) dithiocarbamate, (C6H5)2Sn2L2

To the solution of the ligand (10 mmol, 4.7 g) in 50 mL of
methanol was added (10 mmol, 3.4 g) diphenyltin dichloride in
50 mL of the same solvent to obtain an immediate precipitation.
The product was separated by filtration, washed with methanol and
anhydrous diethyl ether and dried in vacuo.

2.5. Synthesis of dichlorotin bis(2′,2′-dithiopiperazinato-
2′,2′-diaminoethylamine) dithiocarbamate, Sn2L2Cl4

To a solution of the ligand (10 mmol, 4.7 g) in 50 mL of methanol
was added (10 mmol, 1.2 mL) tin tetrachloride in 50 mL of the same
solvent to obtain an immediate precipitation. After stirring for 4 h the product was filtered, washed with methanol and anhydrous
diethyl ether and dried in vacuo.

3. Results and discussion

The organotin bisdithiocarbamates [2–4] are conveniently
obtained in high yields as follows:

Table 2

| Complex               | ν(SN) (cm
−1) | ν(CN) (cm
−1) | ν(CN) (cm
−1) | ν(NH) (cm
−1) |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>K2L (1)</td>
<td>–</td>
<td>–</td>
<td>1408</td>
<td>3248</td>
</tr>
<tr>
<td>(CH3)2Sn2L2 (2)</td>
<td>352</td>
<td>999</td>
<td>1442</td>
<td>3244</td>
</tr>
<tr>
<td>(C4H9)2Sn2L2 (3)</td>
<td>364</td>
<td>995</td>
<td>1438</td>
<td>3244</td>
</tr>
<tr>
<td>(C6H5)2Sn2L2 (4)</td>
<td>348</td>
<td>999</td>
<td>1447</td>
<td>3244</td>
</tr>
<tr>
<td>Sn2L2Cl4 (5)</td>
<td>349</td>
<td>1010</td>
<td>1438</td>
<td>3244</td>
</tr>
</tbody>
</table>
The ligand and its complexes are stable in air but they are insoluble in water and common organic solvents but partially soluble in DMSO. It only because of this poor solubility they could not be recrystallized. The elemental analysis, another physical parameters are listed in Table 1. However, dichlorotin bis(2,2′-dithiopiperazinato-2,2′-diaminodiethylamine) dithiocarbamate, Sn₂L₂Cl₄ was obtained from SnCl₄ as shown below.

\[
2 \text{R}_2\text{SnCl}_2 + 2 \text{K}_2\text{L} \rightarrow \text{-4 KCl} \rightarrow \begin{array}{c}
\text{Sn} \\
\text{Cl} \\
\text{Cl}
\end{array}
\]

where R = -CH₃ (2), -C₆H₅ (3), -C₆H₃ (4)

The existence of the above structure was confirmed by the absence of higher peaks in mass spectrum of complex 5 which rules out the possibility of higher analogue. It is worth mentioning that the molar conductivity of complexes 2–5 falls in the range for non-electrolytes (Table 1) [26]. The presence of chlorine in complex 5 is also supported by a positive test with AgNO₃ forming a white curdy precipitate.
Fig. 1. IR spectra of complex (CH$_3$)$_4$Sn$_2$L$_2$ (2).

3.1. IR and UV spectral studies

The region 250–450 cm$^{-1}$ is quite diagnostic in ascertaining Sn–S bonds. Medium to weak intensity bands in 347–364 cm$^{-1}$ range corresponding to $\nu$(Sn–S) have been observed which are in accord with earlier results [27]. An additional band has also been observed at 280 cm$^{-1}$ in complex 5 which may safely be assigned to the Sn–Cl bond (Table 2).

The region 1000 ± 50 cm$^{-1}$ is considered very selective for $\nu$(C=S) of the dithiocarbamato group [28]. A single sharp band in the above region may be attributed to the presence of symmetrical bidentate coordination while the splitting of this band corresponds to the unsymmetrical monodentate coordination[29]. In the present study, we have observed a single sharp band in the 995–1010 cm$^{-1}$ region which confirms symmetrical bidentate coordination of the dithiocarbamate group.

Another interesting feature of the dithiocarbamato complexes is the presence of thioureide band which is simply a combination of $\nu$(C=N) and $\nu$(ETB)(C=N). Due to the presence of electron rich sulfur atoms delocalization of electrons occurs over the entire NCS$_2$ region [30]. It results in partial double bond character as depicted below.

We have observed a single strong band at 1408 cm$^{-1}$ corresponding to $\nu$(C–N), NR$_2$ band in case of ligand. This band is found to be red shifted (1438–1447) in case of complexes implying an increase in electron density over the entire NCS$_2$ region (Fig. 1). This increase in electron density may be attributed to the back donation of electron from metal d-orbital to vacant antibonding sulfur orbital [31]. The presence of piperazene moiety is confirmed by the appearance of a group of medium intensity bands in 1200–1300 cm$^{-1}$ and 300–350 cm$^{-1}$ range due to the ring vibrations [32]. However, a paltry change is observed in the complexes for the deformation and skeletal vibrational modes with respect to free ligand, which is consistent with only a slight distortion of the favoured chair conformation of the piperazine moiety upon coordination [33]. The almost equivalent values of the $\nu$(N–H) in the ligand and its complexes implies its non-involvement in the coordination [40].

Fig. 2. NMR spectra of complex (CH$_3$)$_4$Sn$_2$L$_2$ (2).

The electronic spectrum of K$_2$L exhibit two broad bands centered at 266 and 282 nm corresponding to $\pi \to \pi^*$ and $\tau \to \pi^*$ transitions of the thioureide group. On moving to the complexes these bands are found to be shifted to lower wavenumber implying the involvement of thioureide group in coordination [34].

3.2. NMR studies ($^1$H and $^{119}$Sn)

The $^{119}$Sn NMR spectroscopy is quite useful in ascertaining the nature of the coordination in organotin dithiocarbamato complexes [35]. R$_2$SnX$_2$ complexes having the same coordination can have a variety of $^{119}$Sn chemical shifts depending upon the number and nature of the R and dithiocarbamato groups attached to central Sn atom [36]. The $^{119}$Sn NMR chemical shifts can therefore be used as an aid to elucidate the nature of dithiocarbamato group. In the present study, we have observed $^{119}$Sn chemical shifts in the −485 to −501 for complexes 2–5 indicating a six coordinate environment around Sn-center [37]. This also implies a symmetrical bidentate coordination of bis(2,2’-dithiopiperezino-2,2’-diamino-1,4-diaminodiethylamine) moiety.

The $^1$H NMR spectrum of the ligand is in close accord with the previous findings [25]. It displays a sharp singlet at 2.30 ppm due to eight protons from four methylene groups of the piperazinium moiety while the methylene protons of diethylenetriamine were observed as a broad multiplet at 3.0–3.3 ppm (Fig. 2). The imine proton of the diethylenetriamine was observed at $\delta$ 3.88 ppm and remains unaltered throughout. However, amino protons of the diethylenetriamine were found to be shifted downfield at $\delta$ 4.8 ppm due to the attachment of piperazinium moiety [39]. These shifts remain undisturbed in the organotin complexes due to non-involvement of piperazinium and diethylenetriamine moieties with the Sn-center [40].
3.3. Electrospray ionization mass spectrometry

Electrospray ionization mass spectrometry is one of the most useful analytical techniques for the structural elucidation of organic as well as organometallic compounds [41]. Unlike the earlier report the mass spectrum of dipotassium bis[2,2'-dithiopiperazine-2,2'-diaminodiethylamine] shows molecular ion peak at $m/z$ 499. Its low intensity (16) implies lower stability. The base peak appears at $m/z$ 349 which is in accord with the previous findings [25]. The $m/z$ of other fragments along with their percent of occurrence is listed in Scheme 1. A typical electron mass ionization spectrum of complex 5 is shown in Fig. 3. A notable feature is the absence of any peak above $m/z$ 954 which completely obscures the presence of any polynuclear species [42]. Although, the molecular ion peak is not observed in this case, it satisfactorily explains the presence of other peaks and is completely different from its transition metal analogue. The base peak observed at $m/z$ 331 corresponds to three membered chelate ring on one side while the presence of an exopiperazine on the other side of Sn-atom (Scheme 2).

3.4. Thermal and differential scanning calorimetry

The thermal degradation data of the ligand, $K_2L$ and its organotin complexes are presented in Table 3. A perusal of thermogravimetric data of ligand reveals its stability up to 165 °C above which it undergoes pyrolysis in two well defined stages. A similar two step pattern is observed for the organotin complexes. The IDT (initial decomposition temperature) reveals a greater thermal stability (Table 3) of the complexes as compared to its precursor [43]. The first decomposition onsets at about 177 °C except for complex 5, which initiates at 171 °C accounting for the simultaneous loss of piperazinium moiety and carbon disulfide. The comparatively low IDT in case of complex 5 may be due to the presence of axially bonded chlorine which decomposes as HCl at relatively low temperature. The presence of axially positioned chlorine is also supported by the combinatorial study organotin complexes bearing substituted dioxime moieties [44]. Another notable feature inferred on the basis of IDT is the increase in thermal stability of complexes which follows the order $2 < 3 < 4$. This is common feature of organotin complexes [45]. The second decomposition stage onsets at about 280 °C, attributing a weight loss of about 50–60% which is consistent with the degradation of remaining organic moiety. In all the complexes we have

![Scheme 1. General fragmentation pattern of the complexes 2–4.](image)

![Fig. 3. Typical mass spectrum of complex 5.](image)
obtained SnS₂ as the end product since the TGA has been carried out under nitrogen atmosphere [46]. Furthermore, the formation of SnS₂ has also been ascertained by their microanalytical data.

Contrary to our previous findings, the DSC plots give reasonably good information on the different thermal aspects of ligand and its complexes. The free ligand decomposes endothermically exhibiting sharp peaks at 173 and 340 °C. The complexes also exhibit a broad endothermic peak centered at about 190 °C indicating the expulsion of piperazine, and carbon disulfide. The overall effect of decomposition in the complexes follows the counter effect due to the presence of Sn-atom. However, at higher temperatures only a slight hump is observed for the formation of SnS₂.

Table 3
Thermal degradation of ligand and its complexes.

<table>
<thead>
<tr>
<th>Compounds (molecular formula)</th>
<th>First decomposition stage</th>
<th>Second decomposition stage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fragments</td>
<td>Temperature range (°C)</td>
<td>Mass loss data, found (calcd.) %</td>
</tr>
<tr>
<td>Fragments</td>
<td>Temperature range (°C)</td>
<td>Mass loss data, found (calcd.) %</td>
</tr>
<tr>
<td>K₂L (1) C₂H₁₂N₄S₄</td>
<td>165–255</td>
<td>64.50 (64.17)</td>
</tr>
<tr>
<td>(C₅H₃)₂Sn₂L₂ (2) C₂₀H₃₂N₈S₄</td>
<td>177–280</td>
<td>44.98 (44.88)</td>
</tr>
<tr>
<td>(C₅H₃)₂Sn₂L₂ (3) C₂₀H₃₂N₈S₄</td>
<td>180–277</td>
<td>39.20 (39.11)</td>
</tr>
<tr>
<td>(C₅H₅)₂Sn₂L₂ (4) C₂₁H₂₀N₆S₄</td>
<td>186–281</td>
<td>36.56 (36.86)</td>
</tr>
<tr>
<td>Sn₂L₂Cl₄ (5) C₂₂H₁₂N₆S₄</td>
<td>171–276</td>
<td>41.63 (41.88)</td>
</tr>
</tbody>
</table>
4. Conclusion

The present manuscript describes the synthesis and characterization of some self-assembled dithiocarbamates of the type $R_4SnL_2$. This facile synthesis is good yielding and good purity complexes are obtained which are confirmed from their elemental analysis. These complexes are very well characterized by elemental analysis and by a host of spectral techniques like FT-IR, UV–vis, $^1H$ NMR, $^{119}Sn$ NMR, ESI-MS. The paper describes the formation of novel cylindrical type dithiocarbamates which offers an avenue to study the host guest relationship. Due to the presence of dithiocarbamo and organotin moiety these complexes can prove to be effective herbicide, fungicide and insecticide. Moreover, they can also be tested clinically for their cytotoxicity.

Acknowledgement

SAIF Punjab University, Chandigarh is gratefully acknowledged for providing ESI-MS and $^{119}Sn$ NMR spectra.

References