Chapter 2

Mixed valence (Co$^{II}_2$-Co$^{III}_2$) tetranuclear hydroxo defect dicubane clusters: Synthesis, crystal structures and magnetic studies of [Co$_4$(µ$_3$-OH)$_2$(µ$_2$-dea)$_2$(L-L)$_4$]4Cl·8H$_2$O [H$_2$dea = diethanolamine, L-L= 2,2’-bipyridine or 1,10-phenanthroline]
INTRODUCTION

Ligand bridged transition metal clusters with ancillary N- and O- donor ligands are of continuing interests for the synthetic inorganic chemists because of their diversified structural motifs, magnetic, optical, catalytic as well as biological relevance [1]. The design, synthesis, structural characterization and magneto structural correlations of new polynuclear coordination clusters of paramagnetic transition metal ions exhibiting ferromagnetic and antiferromagnetic spin interactions [2-7] have received much attention in the last decades. The spin coupled clusters have potential applications including their use in quantum computing and magnetic refrigeration etc [5,8-10]. The so called low-dimensional molecule-based magnets have also received considerable attention owing to their potential applications in data storage and memory devices [11,12]. Some of these low-dimensional systems display slow relaxation of the magnetization to give hysteresis effects, labelled as “single molecule magnet” (SMM) [10,13-29] and single chain magnets (SCM) [30-36] with the most famous example being [Mn$_{12}$O$_{12}$(CH$_3$COO)$_{16}$(H$_2$O)$_4$] [37,38]. Manganese is the most desirable transition metal to form the spin-coupled clusters (Mn$_4$ to Mn$_{84}$) exhibiting SMMs behaviour [30,39]. The number of SMM clusters containing metals other than manganese is very limited and these include Fe (Fe$_4$ to Fe$_{19}$) [40–48], Ni (Ni$_4$ to Ni$_{21}$) [49–51], V (V$_4$) [52] and Co (Co$_4$) clusters [23]. Many of the molecular based magnetic materials usually exhibit long range magnetic ordering at low temperature [53–56] and only a few display this behaviour at room temperature [57-61].
The study of molecule based magnetic materials has evoked considerable interest and off late has become one of the most active fields in inorganic and material chemistry [62]. Inorganic moieties specially big size metal ion clusters [63] or chains [64] may be formed and linked by multidentate organic bridging ligands. The discrete polynuclear clusters with a high symmetry are the excellent candidates [65,66] to explore and study their fundamental magnetic phenomena. The polydentate ligands which are capable to act as doubly or triply bridging moieties, have been of great help in the formation of the extended network structures in the systems. However, discrete polynuclear metal complexes as building blocks are limited. In magnetically spin coupled clusters with paramagnetic centers, the bridging ligands play a dominant role in determining the nature and the strength of the spin exchange interactions. Often the additional poly functional organic ligand systems in aqueous solution can arrest the formation of paramagnetic metal hydroxides yielding high nuclearity clusters as big as Fe$^{III}_{17}$ and Fe$^{II}_{19}$ crust molecules with high spin ground electronic state cores and adopt the analogous brucite structure [67,68]. The brucite like core structures is also generated in divalent transition metal ion cluster aggregates such as Co$^{II}_{24}$ [69] and Ni$^{II}_{21}$ [70,71] etc. The basic building block in the brucite structures usually identified as a defect cubane (with one metal ion vertex missing, i.e \{M$_3$(OH)$_4$\}$^{2+}$) stoichiometry. This may lead building up of the extended structures as a dicubane (with two missing vertices, i.e \{M$_4$(OH)$_6$\}$^{2+}$). Such a structural motif occurs often for the 3d divalent metal ions e.g. Ni(II) and Co(II) which adopt the brucite structures [70,71]. Specifically the Ni(II) system, with a large single ion zero field splitting, has been an attractive
candidate for the generation of single-molecule magnets [72–74] and many ferromagnetically coupled clusters are known, some with large spin ground states [75–77]. Similarly, Co(II) could generate interesting anisotropic systems through its d7 configuration [78–80].

In the last decade the number of bridged transition metal complexes has increased significantly. However, number of such complexes of Co(II), Co(III), Ni(II), and those especially with mixed valence viz Ni(II/III) and Co(II/III) etc, is still very limited [81]. The well known mixed valence cobalt(II/III) complexes involve hydroxy, alkoxy, oxo, or carboxylate bridging ligands are relatively more prevalent [82–84]. The tetranuclear Co(III) complex [85], tetranuclear [86] and octanuclear copper(II) complexes incorporating a bridged polyfunctional moiety, 2,6-bis[(2-hydroxy-ethylimino)-methyl]-4-methylphenol with 1D single chain and 2D sheet structures have recently been reported [87,88].

The tridentate ligand, bis(2-hydroxyethyl)amine trivial name (diethanolamine) has been chosen in this work due to its high degree of flexibility allowing for a variety of bridges through oxygen and nitrogen atoms, to provide modest values of the exchange coupling [89], with the possibility of supramolecular hydrogen bonding interactions [90]. The hydroxo bridged discrete tetramer defect dicubane mixed valency (CoII2-CoIII2) core, to the best of our knowledge are not so commonly known. Herein, the successful preparation of two novel mixed valence bridged discrete tetranuclear defect dicubane with stoichiometry [CoII2CoIII2(µ3-OH)2(µ2-dea)2(L-L)4]4Cl·8H2O [L-L = 2,2’-bipyridine (1) or 1,10-phenanthroline (2)] are described. The novel complexes have been characterized by single crystal X-
ray crystallographic studies. The magnetic susceptibility studies and genotoxic behaviours are also discussed.
EXPERIMENTAL

Materials

Diethanolamine (E. Merck), 1,10-phenanthroline and 2,2’-bipyridine (Merck) and CoCl$_2$.6H$_2$O (Aldrich) were used as received. The solvents used in the reactions were of AR grade.

Instrumentation

IR spectra were recorded on a Perkin–Elmer spectrum GX automatic recording spectrophotometer as KBr discs. The purity of the compounds was checked through silica gel chromatography and the melting points were non-corrected. Microanalysis for C, H and N were obtained from Microanalytical Laboratories, CDRI, Lucknow, India.

Synthetic procedures for the complexes [Co$^{II}_2$Co$^{III}_2$(µ$_3$-OH)$_2$(µ$_2$-dea)$_2$(L-L)$_4$]4Cl·8H$_2$O (L-L)= 2,2’-bipyridine (1) or 1,10-phenanthroline (2).

Synthesis of [Co$^{II}_2$Co$^{III}_2$(µ$_3$-OH)$_2$(µ$_2$-dea)$_2$(bipy)$_4$]4Cl·8H$_2$O (1)

The reaction of H$_2$dea (0.5 mL, 5 mmol) with 2,2’-bipyridine (0.78 g, 5 mmol) was carried out in methanol in a round bottomed flask. The reaction mixture was stirred and refluxed for 6 h. Then in the mixture aqueous solution of CoCl$_2$.6H$_2$O (1.18 g, 5 mmol) was added and the solution was refluxed for 8 h. The resulting brown coloured solution was kept in a fridge ($5^\circ$C) for about a week affording a good crop of dark red cubic crystals.

Molar conductance, $\Lambda_m$ (10^{-3} M, methanol): 263 ohm^{-1}cm^{2}mol^{-1}. IR spectra (KBr pellets, cm^{-1}): 3425, $\nu$(µ3-O-H); 2949, $\nu$(C-H); 1067, $\nu$(C-O); 945, $\nu$(Co-O-Co); 427, $\nu$(M-N).

**Synthesis of [Co^{II}Co^{III}_2(µ_3-OH)_2(µ_2-dea)_2(phen)_4]4Cl·8H_2O (2)**

The reaction of H$_2$dea (0.5 mL, 5 mmol) with 1,10-phenanthroline (0.98 g, 5 mmol) was carried out in methanol in a round bottomed flask. The reaction mixture was stirred and refluxed for 6 h. Then in the mixture aqueous solution of CoCl$_2$·6H$_2$O (1.18 g, 5 mmol) was added and the solution was refluxed for 8 h. The resulting brown coloured solution was kept in a fridge (5°C) for about a week affording a good crop of dark red cubic crystals.

[Dark Maroon, m.p 242°C, yield 68 %]. Anal. Calcd (%) of C$_{56}$H$_{52}$Cl$_4$Co$_4$N$_{10}$O$_{20}$: C 43.07; H 3.33; N 8.97. Found (%): C 43.14; H 3.11; N 8.85.

Molar conductance, $\Lambda_m$ (10^{-3} M, methanol): 260 ohm^{-1}cm^{2}mol^{-1}. IR spectra (KBr pellets, cm^{-1}): 3475, $\nu$(µ3-O-H); 2949, $\nu$(C-H); 1060, $\nu$(C-O); 943, $\nu$(Co-O-Co); 428, $\nu$(M-N).

**X-ray crystal structure determination and refinements**

Single-crystal X-ray data of (1) and (2) were collected using graphite monochromated Mo Kα radiation (λ=0.71073Å). The linear absorption coefficients, scattering factors for the atoms, and the anomalous dispersion corrections were taken from the International Tables for X-ray Crystallography [91]. The data integration
and reduction were processed with SAINT Software [92]. An empirical absorption correction was applied to the collected reflections with SADABS [93] using XPREP [94]. The structure was solved by direct methods using SIR-97 [95] and were refined on $F^2$ by the full-matrix least squares technique using the SHELXL-97 [96] program package. All non-hydrogen atoms were refined with anisotropic displacement parameters.

**Magnetic studies**

Magnetic susceptibility measurements were obtained with the use of a Quantum Design SQUID MPMS-XL susceptometer. Measurements were performed on polycrystalline samples of 16.48 mg (1) and 13.42 mg (2) in the temperature range 1.8–300 K and with fields up to 7 T. The magnetic data were corrected for the sample holder and the diamagnetic contribution calculated from Pascal’s constants [97]. Field dependence of the magnetization measurements on single crystals were performed with an array of micro-SQUIDs [98]. This magnetometer works in the temperature range between 0.03 and ~7 K and in fields up to 1.4 T with sweeping rates as high as 1 T s$^{-1}$, along with a field stability better than a microtesla. The time resolution is about 1 ms. The field can be applied in any direction of the micro-SQUID plane with a precision much better than 0.1° by separately driving three orthogonal coils. In order to ensure a good thermalization, a crystal of about $30 \times 10 \times 5 \mu m^3$ was fixed by using Apiezon grease. The field was applied approximately in direction of the easy axes of magnetization. Note that measurements performed with the micro-SQUID setup have been normalized on the data obtained with the Quantum Design SQUID MPMS-XL susceptometer.
RESULTS AND DISCUSSION

Diethanolamine (H$_2$dea) was reacted with CoCl$_2$•H$_2$O in presence of an α-diamoine viz. 2, 2’-bipyridine (Bpy) or 1,10-phenanthroline (Phen), affording fairly stable crystalline products, which have been characterized as tetranuclear species (1) or (2). The formation of (1) and (2) can be illustrated by Scheme 1.

Scheme 1. Synthetic route for the complexes (1) and (2).
The analytical data closely fit in the molecular formula (Experimental Section) consistent with the stoichiometry \([\text{Co}^{II}_2\text{Co}^{III}_2(\mu_3-\text{OH})(\mu_2-\text{dea})(\text{L-L})_4]\text{4Cl·8H}_2\text{O}\), where (L-L) = Bipy (1) and Phen (2). The compounds were soluble in water and usual organic solvents. The observed magnitude of molar conductivities \((\Lambda_m\sim260 \text{ ohm}^{-1}\text{cm}^2\text{mole}^{-1})\) indicate that in aqueous solution they ionized as strong electrolyte suggesting that the counter anion (Cl\(^-\)) is weakly bound to the bulky complex cation and preferably remains out of the coordination sphere. Suitable crystals of the compound (1) & (2) were obtained on slow evaporation of the mother liquor. The compounds were characterized by various spectroscopic techniques and single crystal X-ray diffraction of (1) & (2).

**FTIR Spectra**

The infrared spectrum of complexes show a sharp peak at in the high frequency range i.e. \(~3400 \text{ cm}^{-1}\) attributed to the coordinated \(\nu(\text{O-H})\) stretching vibration alongwith a strong broad band at 3389 \text{ cm}^{-1} characteristic of presence of lattice \(\text{H}_2\text{O}\) molecule(s) in the molecular unit [99]. The ligand \(\text{H}_2\text{dea}\) and its coordination complexes are reported to exhibit broad bands in the range 3320-3350 \text{ cm}^{-1} due to hydrogen bonded O-H bond stretching vibrations of unionized diethanolamine, which is, however, absent in the present tetranuclear complexes (1) and (2) indicating that the ligand binds the metal ions as an anionic moiety (dea\(^2-\)). A considerable negative shift in \(\nu(\text{N-H})\) frequency in the complexes relative to that of the free ligand moiety indicates the coordination from the nitrogen to the metal ion. The band appearing at \(~940\text{cm}^{-1}\) is assignable to the oxo-bridging \(\nu(\text{Co-O-Co})\)
stretching vibrations. The ligand dea², therefore, acts as bridging ligand behaving as a tridentate moiety [O,O,N]. The bands observed in the low frequency 400-550 cm⁻¹ region are characteristic of M-N bond stretching vibrations. The spectra contained other relevant frequencies including those arising from \( \nu(C-H) \) and \( \delta(CH_2) \) etc at the appropriate positions [100]. The involvement of the \( \alpha \)-diimine i.e 1,10-phenanthroline or 2,2’-bipyridine in the complex moieties was ascertained from the presence of characteristic \( \nu(C=C) \) and \( \nu(C=N) \) stretching vibrations.

\(^1\)H and \(^{13}\)C NMR Spectra

The \(^1\)H NMR spectra of the complexes contained a sharp resonance signal on the high field side (\( \delta \) 3.4-3.9 ppm) arising from the skeleton CH₂ proton of the ligand (dea). However, the low field side (\( \delta \) 9. ppm) contained broad signal arising from the N-H proton resonance, along with the sharp well splitted resonance in 7.5-8.4 ppm region characteristic of the aromatic protons of the \( \alpha \)-diimine moiety. There is a considerable shifts in the positions of the various signals compared to that of the uncomplexed ligands which is not an uncommon behaviour because of the coordination to the metal ion [101]. The \(^{13}\)C NMR spectra contained resonance signals in 34-41 and 121-150 ppm region assignable to the methylene (-CH₂-) and \( \alpha \)-diimine (2,2’-bipy & 1,10-phen) carbons, respectively [102,103].

X-ray Crystallographic Studies

The structures of the complexes (1) & (2) were determined by single crystal X-ray diffraction studies as shown in Figs. 1-7. Selected bond lengths between the
metal ions and the various binding sites i.e., Co-N and Co-O etc. are given in Fig. 1. The full crystallographic data and refinement parameters are available in Table 1. The structure of (1) is solved in the monoclinic system with C2/c and that of (2) in the monoclinic system with P2₁/n space groups.

It is apparent from Figs. 1(a) and (b) that the molecular unit of the present complexes contains four cobalts arranged in a manner that it generates a defect dicubane (Co₄) core [104]. Each cobalt metal has a six coordinate but distorted octahedral environment of the ligands. The dicubane cores (Co₄) are illustrated in an inset in Figs. 1(a) and (b), which also shows important various Co-O bond lengths of the constituent core. Furthermore, each core effectively contained four α-diimine (Phen or Bipy) chelator in addition to two dea²⁻ bridging moieties shared between the Co₄ unit of the dicubane. Each dea²⁻ anion here provides a strong alkoxo bridging (Co-O-Co) and the α-diimine chelators provide two N-sites listed as (N1, N2) or (N3, N4) bound or chelated to each cobalt atom. However, the secondary amine (NH) function of the dea²⁻ moieties (listed as N5) is apparently coordinated to the cobalt atoms listed as Co1 of the dicubane.

The investigations of the ortep view of the dicubane Co₄ core (Fig. 1c) reveals that the two cobalt atoms Co1 and Co2 are having different ligand environments. The octahedral coordination of Co1 is satisfied by two oxygens of dea²⁻ moiety, two N from α-diimine, one O from μ₃-OH and one N by secondary imine (NH) function. On the other hand the octahedral coordination of the Co2 ion is surrounded by two O atoms from two separately dea²⁻ moieties, two O from μ₃-OH and two N from α-diimine molecule.
It is interesting to note (Table 2) that there are two widely different Co-N bond lengths from the α-diimine coordinated to the metal ions, [i.e., d(Co1-N1 or Co1-N2) ~ 1.950 Å and d(Co2-N3 or Co2-N4) ~ 2.140 Å]. The observed magnitudes of the bond lengths Co1-N1 or Co1-N2 are close to that reported [105] for N-coordination to a trivalents (Co\textsuperscript{III}) ion where as the longer bond lengths (Co2-N3/N4) ~ 2.14 Å is indicative of a divalent (Co\textsuperscript{II}) oxidation state of the metal ion [106]. The dicubane core therefore has two sets (each with two cobalts) in different oxidation states of the metal ions. The one set with shorter bond length is apparently in higher (+3) oxidation state whereas the relatively longer bond distance corresponds to the lower (+2) oxidation state of the metal ion. Furthermore, the observed bond distances for secondary amine coordination of (dea\textsuperscript{2−}) i.e. d(Co1-N5) ~ 1.95 Å is comparable [107] to that of the Co\textsuperscript{III}-N bond lengths of the α-diimine coordination. The present defect dicubane is a combination of Co\textsuperscript{II} and Co\textsuperscript{III} (i.e., Co\textsubscript{2}\textsuperscript{III}-Co\textsubscript{2}\textsuperscript{II}) which is further ascertained from the various observed Co-O bond lengths for the complexes (1) and (2) [Figs. 1(a) and (b) (Insets)]. There are three different Co-O bond length (i.e. Co1-O ~1.90 and Co2-O ~2.1) due to presence of dissimilar oxidation states of the metal. This is in line with the reported [106] mixed valence cobalt complex corroborating that in present complexes (1) and (2) Co1 is in +3 state and Co2 is in +2 state.

In conclusion, the crystallographic data confirm that in present case, the Co1 with its symmetry related Co1’ is apparently in higher (Co\textsuperscript{III}) oxidation state while Co2 with its symmetry related Co2’ is in lower (Co\textsuperscript{II}) oxidation state. The tetranuclear discrete molecular unit is, therefore, an example of novel mixed valence
hydroxo-bridged defect dicubane cluster. The dicubane core in the present case contains two high-spin highly paramagnetic Co$^{II}$ ($t_{2g}^5e_g^2$ configuration) centres and the remaining two cobalt atoms in low spin diamagnetic Co$^{III}$ ($t_{2g}^6$ configuration). The four Cl- counter ions are held with the dicubane units through an extensive H-bonding (Figs. 3-7) such as N-H----Cl as well as C-H----Cl with bond distances 2.101(7)–2.440(4) and 2.624(3)–2.874(9) Å, respectively. The lattice water molecules are also held through H-bonding (Figs. 2-7) to produce a supramolecular architecture.
Fig. 1. (a) Molecular structure of 1 with its cubane core. (b) Molecular structure of 2 with its cubane core. The related atoms of the cubane are omitted for clarity. Green color for Co(II) and purple for Co(III). (c) Coordination of the cobalt atoms of the tetranuclear cation.
Thus by X-ray crystallographic studies we get two novel hydroxo bridged discrete mixed valent \([\text{Co}^{II}_2\text{Co}^{III}_2(\mu_3-\text{OH})_2(\mu_2-\text{dea})_2(L-L)_4]\) \(4\text{Cl}\cdot8\text{H}_2\text{O}\) tetranuclear cubane clusters supported via α-diimine chelator (1,10-phenanthroline or 2,2’-bipyridine) in which each cobalt acquires a coordinatively saturated hexacoordination.

![Diagram](image)

**Fig. 2.** Water molecules are bounded through hydrogen bonding (a) in compound 1 and (b) in compound 2.
Table 1. The crystallographic data and refinement parameters of complex (1) and (2).

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\[ R₁ = \frac{\sum |F₀| - |F₁|}{\sum |F₀|} \cdot R₂ = \frac{\{\sum w(F₀^2 - F₁^2)/\sum w(F₀^2)\}^{1/2}}{\sum w(F₀^2)^{1/2}}, \quad w = 1/[σ(F₀^2) + (αP)^2], \] where P = (F₀^2 + 2F₁^2)/3.
Fig. 3. (a) Tetranuclear units of complex 1 connected through hydrogen bonds between C-H—Cl and N-H----Cl. (b) Tetranuclear units of complex 2 connected through hydrogen bonds between C-H—Cl and N-H----Cl.
Fig. 4. Packing diagram of the complex (2).

Fig. 5. 3D cage network of the complex (1).
Fig. 6. Packing diagram of complex (1).

Fig. 7. 2D packing of the complex (1).
Fig. 8. ORTEP view of $[\text{Co}^{II}_{2}\text{Co}^{III}_{2}(\mu_{3}\text{-OH})_{2}(\mu_{2}\text{-dea})_{2}(\text{Bipy})_{4}]4\text{Cl}\cdot8\text{H}_{2}\text{O}$ (a) and $[\text{Co}^{II}_{2}\text{Co}^{III}_{2}(\mu_{3}\text{-OH})_{2}(\mu_{2}\text{-dea})_{2}(\text{Phen})_{4}]4\text{Cl}\cdot8\text{H}_{2}\text{O}$ (b).
Table 2. Selected Bond Lengths (Å) and Bond Angles(˚) of Complex (1) and (2).

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<td>C24-O3-Co1</td>
<td>113.7 (4)</td>
</tr>
<tr>
<td>C24-O3-Co2i</td>
<td>134.9 (3)</td>
</tr>
<tr>
<td>Co1-O3-Co2i</td>
<td>104.32 (17)</td>
</tr>
</tbody>
</table>

Symmetry code: (i) −x, −y, −z+1, (ii) −x, −y, −z+2.
MAGNETIC STUDIES

The $\chi T$ product at 300 K was 5.6 cm$^3$ K mol$^{-1}$ for complex (2) which is higher than the spin-only value of 3.75 cm$^3$ K mol$^{-1}$ ($S = 3/2$, $g = 2$ leads to $C = 15/8$ cm$^3$ mol$^{-1}$ per Co$^{II}$ ion). From this $\chi T$ product at room temperature we obtained $C = 2.82$ cm$^3$ mol$^{-1}$ per ion leading to $g = 2.45$. Such behavior is quite common for clusters containing Co$^{II}$ ions and shows the influence of the unquenched orbital angular momentum on the magnetic properties. On decreasing the temperature, $\chi T$ stayed constant down to a temperature of approximately 40 K. For further decreasing temperatures the $\chi T$ product increased to reach a maximum value of 6.3 cm$^3$ K mol$^{-1}$ around 10 K. At lowest measured temperatures the $\chi T$ product decreased again. Such a behavior of the $\chi T$ product is usually assigned to originate from weak ferromagnetic interactions together with magnetic anisotropy. However, such conclusions can be a pitfall for highly anisotropic systems like Co$^{II}$. The M vs B curves of complex (2) increased rapidly at low fields and more slowly at higher fields. However, no saturation was observed until 7 T. The magnetization value at the highest measured field (7 T) and the lowest temperature (2 K) was 4.11 $\mu_B$.

At 300 K the $\chi T$ product of complex (1) was observed as 5.8 cm$^3$ K mol$^{-1}$, which is also much higher than the spin-only value and would lead to $g = 2.48$. Again, the strong deviation from 2.0 shows the influence of the unquenched orbital angular momentum on the magnetic properties. With decreasing temperature the $\chi T$ product slightly increased. At around 40 K the increase was observed stronger with decreasing temperature and a maximum of 7.1 cm$^3$ K mol$^{-1}$ was reached around 9 K. With further decreasing temperature the $\chi T$ product decreased. Similar conclusions
as for complex (2) might be drawn from the curvature of $\chi T$. The M vs. B curves of complex (1) were observed as very similar as for complex (2) but with higher magnitudes. The magnetization value at the highest measured field (7 T) and the lowest temperature (2 K) was 4.27 $\mu_B$.

![Graph showing magnetic susceptibility vs. temperature](image)

**Fig. 9.** Magnetic susceptibility as $\chi T$ vs. T. The solid line in the main plot represents the best-fit with the L-S model to the magnetic data of 1. The inset show a magnified view of the low-temperature region (below 40 K) together with the best-fit simulations for both complexes obtained in the effective model.

Free Cobalt ions have a $^4F$ ground state, which is seven times degenerate in the orbital angular momentum. In an octahedral ligand field it splits into the three levels $^3A_2$, $^4T_2$ and $^4T_1$, with the latter being lowest. These levels are separated well by an energy difference in the order of ten thousand Kelvin. Thus, only the lowest level $^4T_1$ has to be regarded. The state $^4T_1$ consists of three orbital angular momentum states and can therefore be modeled by an effective orbital angular momentum $l = 1$, whose orbital angular momentum operator $\hat{l}$ is related to the
orbital angular momentum operator $\hat{L}$ of the $^4\!F$ ground state ($L = 3$) by $\hat{L} = -3/2 \hat{\mathbf{l}}$. As $^4\!T_1$ has the same symmetry as the higher state $^4\!P$, the ligand fields mixes in a portion of the higher state $^4\!P$ into the $^4\!T_1$. This can be represented by introducing an orbital reduction factor $k$, yielding an orbital angular momentum operator.

$$\hat{L} = -3/2 \hat{\mathbf{l}}$$

Where $k$ shall be of the order of but less than one.

Under the distortion of the ligand field and the spin-orbit coupling, the $^4\!T_1$ ground state splits further, yielding a sequence of Kramer’s doublets with splittings on the order of several 100 K. Below temperatures of about 40 K only the ground state Kramer’s doublet is thermally populated. Hence, the magnetic
Fig. 10. Magnetization as $M$ vs. $B$ for complex (1) (a) and complex (2) (b). The dots represents the measured data, while the solid lines represents the best fits using the effective model and the dashed lines in the upper panel represents the best-fit results with the $l$-$S$ model.

behaviour can be described by an effective spin Hamiltonian with an effective spin $\tau = 1/2$ for each Co$^{\text{II}}$ center [108]. The advantage of this model is the dramatic reduction of the dimension of the Hilbert space. In this effective description the magnetic couplings and g factors are anisotropic. To reduce the number of magnetic parameters, uniaxial anisotropy was assumed. As a further attempt to avoid over parametrisation, all $M$ vs. $B$ and the $\chi_T$ curve at temperatures below 40 K were fitted simultaneously to the following Hamiltonian:

$$
\hat{H} = -\left( J + \Delta J \right) \left( \hat{\tau}_{i,x} \hat{\tau}_{2,x} + \hat{\tau}_{i,y} \hat{\tau}_{2,y} \right) - J \hat{\tau}_{i,x} \hat{\tau}_{2,x} + \mu_B \sum_{i=1,2} \left( g_{i,xy} \hat{\tau}_{i,x} B_x + g_{i,y} \hat{\tau}_{i,y} B_y + g_{i,x} \hat{\tau}_{i,x} B_x \right)
$$
The magnetic data of each molecule were fitted separately. However, for both molecules we obtained excellent fits with nearly identical parameters. The magnetic parameters obtained from these fits were $J = 115(12) \text{ K}$, $\Delta J = -58.5(2.5) \text{ K}$, $g_{xy} = 3.34(5)$, and $g_z = 6.599(12)$ for complex (2) and $J = 115(6) \text{ K}$, $\Delta J = -57.0(1.2) \text{ K}$, $g_{xy} = 3.001(25)$, and $g_z = 7.214(7)$ for complex (1). The fits were stable in that sense, that we obtained from several fits with different start parameters the parameters shown above or the fitting routine failed completely to reproduce the experimental data.

| $|M = 1, P = 1 > = |\uparrow\uparrow>$ | E | E Complex (2) | E Complex (1) |
|---|---|---|---|
| $|M = -1, P = 1 > = |\downarrow\downarrow>$ | 0 | 0 | 0 |
| $|M = 0, P = 1 > = 2^{-1/2} (|\uparrow\downarrow> + |\downarrow\uparrow>)$ | $-\Delta J/2$ | 29(1) K | 28.5(6) K |
| $|M = 0, P = -1 > = 2^{-1/2} (|\uparrow\downarrow> - |\downarrow\uparrow>)$ | $J + \Delta J/2$ | 86(12) K | 87(6) K |

In the effective $\tau = 1/2$ model it was simple to calculate the Eigen states and the energies by hand. They are shown in the table below, where the states $|m_{e1} = \pm 1/2>$ (the two Eigen states of the operator $\hat{r}_{1z}$) are abbreviated as $|\uparrow>$ and $|\downarrow>$ respectively. Using a similar notation for $|m_{e2}>$ and the product states $|m_{e1},m_{e2} > = |m_{e1}> \otimes |m_{e2}>$ the Eigen states are written below and classified after the Eigen value M of the operator $\hat{r}_z = \hat{r}_{1z} + \hat{r}_{2z}$ and the parity P. The three states with even parity (P = 1) can be classified as the S = 1 multiplet, which is split up by the anisotropic
contribution to the exchange interaction. The odd state corresponds to $S = 0$. As one can see in the energy scheme shown below, the two ground states $|M = 1, P = 1>$ and $|M = -1, P = 1>$ are separated by an energy barrier of 29 and 28.5 K for complex (2) and (1) respectively. For such a, for dimers, remarkable high energy barrier for spin reversal one would expect slow relaxation of the magnetization and their indications should be observable in an AC susceptibility measurement even above 1.8 K. However, in such an experiment no out-of-phase signal was observed. A possible reason might be that the spin-phonon interaction, which is the process behind the thermal relaxation, allows transitions between states which differ in $M$ by two. Therefore the barrier might not be active for this process. The spin-phonon selection rule mentioned above is valid for the real spin. The selection rules for the effective model are less clear. Therefore, we decided to use a magnetic model which contains the real spin $S = 3/2$ of the Co$^{II}$ ion.

As already mentioned the magnetism of the Co$^{II}$ can be described using an effective orbital angular momentum $l = 1$. The corresponding Hamiltonian then reads:

$$
\hat{H} = -J \hat{S}_1 \cdot \hat{S}_2 + \sum_{i=1,2} \left( -\frac{3}{2} k \lambda \hat{l}_i \cdot \hat{S}_i \right) + \mu_B \sum_{i=1,2} \left( -\frac{3}{2} k \lambda \hat{l}_i + g \hat{S}_i \right) \mathbf{B} + \Lambda_i \left( \hat{l}_{1,z}^2 + \hat{l}_{2,z}^2 \right)
$$

where Heisenberg exchange coupling with coupling constant $J$ was assumed between the spin centers. The spin-orbit coupling is given by the second term with the spin-orbit coupling constant of Cobalt $\lambda = -259$ K and $k$ the reduction factor already mentioned. The same reduction factor was used in the Zeeman term for the
interaction with the magnetic field B, where g is 2.002. The splitting of the orbital angular momentum levels by the ligand field is described by the last term. This model contains only three free parameters J, k, and \( \lambda \). However, it turned out that fitting this model to the magnetic data was not a simple task, as the influence of the higher levels is only minor and it is therefore difficult to determine all parameters.

As we have observed in the effective \( \tau = 1/2 \) model, the low energy spectra of the two cluster are very similar and therefore we concentrate our efforts on only one, (1), of the two cluster. After several attempts in which the M vs B curves were fit alone or together with \( \chi_T \) or \( \chi_T \) alone (it turned out that fitting \( \chi_T \) only below temperatures of 150 K was essential) the following magnetic parameters were obtained: \( J = 13.07(22) \) K, \( \lambda = -1281 \) K, and \( k = 0.881(7) \). The error of \( \lambda \) could not be obtained from the fit but was found out by varying the parameters to be at most in the order of 10 K. Using this parameters the magnetization was excellently reproduced. However, the \( \chi_T \) curve was only reproduced from temperatures below 100 K. The deviation at higher temperatures can result from the influence of higher-lying ligand field levels or paramagnetic impurities in the sample holder. Both can be modeled by a temperature-independent paramagnetism, which just add a constant \( \chi_0 \) to \( \chi(T) \).

Including these parameter into our fit accounts we obtained: \( J = 14.21(17) \) K, \( \lambda = -1260(10) \) K, \( k = 0.929(7) \), and \( \chi_0 = -0.0029(1) \) cm\(^3\) mol\(^{-1}\). The obtained parameters are generally reasonable, even if the \( k \) is slightly larger than the usually reported values. Simulations with these parameters, which excellently agree with the measurements, are shown below.
The energy spectrum of this model is shown above (red bars) and compared to the energy scheme obtained from the best fit in the effective \( \tau = 1/2 \) model. The states are classified according to \( M_J \), the Eigen value of the operator

\[
\hat{J}_z = \hat{I}_{1,z} + \hat{I}_{2,z} + \hat{S}_{1,z} + \hat{S}_{2,z}
\]

(For the spectrum of the effective \( \tau = 1/2 \) model they are quantified according to \( M \)).

The inset shows a larger range of energies. The four lowest energies are well (327 K) separated from the higher lying energies. This validates the usage of the effective \( \tau = 1/2 \) model. However, the comparison between the energies obtained in both models reveal remarkable large differences. The ground state doublet in the effective model, \( |M = \pm 1> \) model a doublet of \( |M_J = \pm 1> \), which indeed have a more involved sub structure. The two higher lying energy levels differ in energy between the two models. From the energies obtained in the \( I-S \) model we could infer directly a set of parameters for the effective model (see Table 3). With \( J = 87.1 \) K and \( \Delta = -68.3 \) K a fit yield \( g_{xy} = 3.20(2) \) and \( g_z = 7.21(1) \). This fit does virtually reproduce the other fit with the effective model.
Fig. 11. Energy diagrams in zero fields as obtained from the best fits. In the main panel the energies obtained from the two models for complex (1) are compared. The right inset show the energies of complex (1) in the $l$-$S$ model, where a large gap $\Delta E$ was observed between the four lowest states and the higher lining energies. The left inset show the energies obtained in the effective models for the two complexes.

However, the relative order between the state with even and odd parity is the same for both (where the state with even parity is lower). Therefore the ground state is a $J = 1$ multiplet, splitted by the influence of the ligands on the orbital angular momentum. Also in this model a mechanism which allows transitions between states which differ in $M_J$ (or also in $M_{S1}$ or $M_{S2}$) by 2 can shortcut the energy barrier. This might be the explanation for the absence of out-of-phase signal down to 1.8 K in the AC susceptibility measurements, as thermal relaxation via spin-phonon coupling can allow such transitions.
Biological Studies

Plasmid Nicking Assay

DNA strand breaks in supercoiled DNA were analyzed by plasmid nicking assay which was performed as described by Lee et al. Reaction mixture (30 µl) contained 10 mM Tris-HCl (pH 7.5), 0.5 µg plasmid pUC19 DNA, testing compound in varied concentration. Incubation was performed at room temperature for 1 hour. After incubation, 10 µl of a solution containing 40 mM EDTA, 0.05% bromophenol blue tracking dye and 50 % (v/v) glycerol was added and the solution was subjected to electrophoresis in submarine 1% agarose gels at 50 V. Ethidium bromide stained gel was then viewed and photographed on a UV-transilluminator (109). Fig 12 show that at lower concentration there was no breakage to DNA while at higher concentration the small percentage of supercoiled plasmid was degraded to open circular form as depicted from lane 3 and 4.
Fig. 12. Shows no DNA breakage at lower concentration while supercoiled plasmid is degraded on higher concentration in lane 3 & 4.

Comet assay (single cell gel electrophoresis)

Comet assay was performed under alkaline conditions essentially according to the procedure of Singh et al [110] with slight modifications. Fully frosted microscopic slides pre-coated with 1.0 % normal melting agarose were used at about 50 °C (dissolved in Ca $^{2+}$ and Mg $^{2+}$ free PBS). Around 10 000 cells were mixed with 90 µl of 1.0 % low melting point agarose to form a cell suspension and pipetted over the first layer and covered immediately by a cover slip. The slides were placed on a flat tray and kept on ice for 10 min to solidify the agarose. The cover slips were
removed and a third layer of 0.5 % low melting point agarose (80 µl) was pipetted. Cover slips were placed over it and it

**Fig. 13.** The typical images of the comets of *Tetrahymena* cells. A, grade 0 (undamaged); B, grade 1 (soft damaged); C, grade 2 (middle damaged); D, grade 3 (high damaged); E, grade 4 (severely damaged).
was allowed to solidify on ice for 5 min. The cover slips were removed and the slides were immersed in cold lysis solution containing 2.5 M NaCl, 100 mM EDTA and 10 mM Tris, pH 10. 1 % Triton X-100 was added before use for a minimum of 1 h at 4 ºC. After lysis, DNA was allowed to unwind for 30 min in alkaline electrophoretic solution consisting of 300 mM NaOH and 1mM EDTA, pH >13. Electrophoresis was performed at 4 ºC in field strength of 0.7 V/cm and 300 mA current. The slides were then neutralized with cold 0.4 M Tris, pH 7.5, stained with 75 μl ethidium bromide (20 mg/ml) and covered with a cover slip. They were then placed in a humidified chamber to prevent drying of the gel and analyzed the same day. Slides were scored using an image analysis system (Komet 5.5; Kinetic Imaging, Liverpool, UK) attached to an Olympus (CX41) fluorescent microscope (Olympus Optical Co.,
Tokyo, Japan) and a COHU 4910-integrated CC camera (equipped with 510–560 nm excitation and 590 nm barrier filters) (COHU, San Diego, CA, USA). Images from 50 cells (25 from each replicate slide) were analyzed. The parameter taken to assess lymphocytes DNA damage was tail length (migration of DNA from the nucleus, µmeter).

**Isolation of lymphocytes**

Heparinized blood samples (2 ml) from a single healthy donor was obtained by venepuncture and diluted suitably in Ca$^{2+}$ and Mg$^{2+}$ free PBS of pH 7.5. Lymphocytes were isolated from blood using Histopaque 1077 and the cells were finally suspended in RPMI 1640 medium. A single donor donated blood for all experiments (author).

**Viability assessment of lymphocytes**

The lymphocytes were checked for their viability before the start and after the end of the reaction using Trypan Blue Exclusion Test [111].
CONCLUSION

Two novel hydroxo bridged complexes \([\text{Co}_4(\mu_3-\text{OH})_2(\mu_2-dea)_2(\text{L-})_4]4\text{Cl}_4\cdot8\text{H}_2\text{O}\) \([\text{H}_2\text{dea} = \text{diethanolamine}, \ \text{L-} = 2,2'-\text{bipyridine (1)} \text{ or } 1,10-\text{phenanthroline (2)}\) were synthesized and characterized. X-ray crystallography confirmed a hexa-coordinate geometry around each cobalt ion, and \(\alpha\)-diimine \((\text{L-}L)\) checks further polymerization to yield a discrete tetranuclear molecular unit with defect dicubane core. The X-ray data indicate that the \(\text{Co}_4\) molecular unit is held together via strong bridges provided by two dianionic dea\(^2\) ligand moieties forming two \(\text{Co}^{\text{II}}\) and two \(\text{Co}^{\text{III}}\) cores. Lattice water molecules adopt an unusual topology and play a crucial role forming supramolecule architectures. The observed magnetic moment data from variable temperature magnetic studies were analysed using the effective spin-1/2 Hamiltonian approach. The magnetic susceptibility parameter, \(J = 115(6)\ \text{K}, \ \Delta J = -57.0(1.2)\ \text{K}, \ g_{xy} = 3.001(25), \text{ and } g_{z} = 7.214(7)\) for 1 and \(J = 115(12)\ \text{K}, \ \Delta J = -58.5(2.5)\ \text{K}, \ g_{xy} = 3.34(5), \text{ and } g_{z} = 6.599(12)\) for 2 indicate that the exchange of ligands seems to influence only the effective \(g\) matrices. The two compounds have also been tested for genotoxicity employing DNA Nicking and Single cell gel electrophoresis (comet assay). Thus from plasmid nicking assay and Comet assay it can be concluded that the present compounds can be applied for industrial applications as it does not cause any genotoxic damage.
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