APPENDIX

RESEARCH PUBLICATIONS
LIST OF PUBLICATIONS
(Published/Accepted/communicated)

1. Mixed ligand complexes with sulphur donor ligands and thiocyanato-N/cyanato-N -
   *Journal Indian Chemical Society*, 74(9) (1997) 718.

2. Spectrophotometric determination of lead(II) in water samples using benzil-α-monoxime isonicotinoylhydrazone -
   *Indian Journal of Chemistry, Section A* (Pub. SCCA 7003R) (Accepted for publication).

3. Analytical properties of diacetylmonoxime benzoylhydrazone (DMBH):
   Spectrophotometric determination of lead(II), cadmium(II), nickel(II) and copper(II)
   *Communicated to Indian Journal of Chemistry* (Ms No. 7228).

4. Analytical properties of diacetylmonoxime isonicotinoylhydrazone (DMIH):
   Spectrophotometric determination of lead(II) in water and industrial effluents -
   *Journal of Indian Chemical Society* (Communicated) - (ICS/4/N-32/99)
Mixed Ligand Complexes with Sulphur Donor Ligands and Thiocyanato-N/Cyanato-N

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In continuation of our earlier work1 on transition metal complexes of heterocyclic Schiff bases, we report here the synthesis of mixed ligand complexes of cobalt(n) and copper(ii) with \((\text{methylthiophen-2-yl})\text{methylene} \cdot \text{hydrazono-carbothioamide (1, MTHT) and hydrazinecarbothioamide (2, HT)}\) and thiocyanato-N (SCN)/cyanato-N (OCN).

Results and Discussion

All the complexes (Table 1) are stable at room temperature, non-hygroscopic, and insoluble in water and other common organic solvents such as methanol and ethanol but readily soluble in dimethylformamide and dimethylsulfoxide. The molar conductivity values of the complexes in DMF are in the range 6–12 Ω⁻¹ cm² mol⁻¹, indicating their non-electrolytic nature2.

The magnetic moments of \([\text{Co(HT)₂(SCN)₂]}\) and \([\text{Co(HT)₂(OCN)₂}]\) are found to be 4.8 and 5.0 B.M., suggesting their high-spin octahedral structure3. The values of 1.7 and 1.6 B.M. for \([\text{Co(MTHT)₂(SCN)₂}]\) and \([\text{Co(MTHT)₂(OCN)₂}]\) complexes are in favour of low-spin octahedral structure. The values of magnetic moment of the copper complexes are 1.82–2.10 B.M., normally observed for copperfn) complexes.

The electronic spectra of all the complexes are dominated by charge transfer bands tailed into visible regions. However, two distinct bands observed at 15 330–16 130 and 25 847–27 030 cm⁻¹ in the spectra of the cobalt complexes are attributable to \(4A_{2g} (F) \rightarrow 4T_{1u} (P)\) and \(4T_{1g} (F) \rightarrow 4A_{2g} (P)\) transitions respectively, which suggest an octahedral structure4. The \(v_1\) band is not observed in the spectra of the cobalt complexes. In the spectra of the copper complexes, the bands at 17 390–17 940 cm⁻¹ are assignable to d-d transitions.

The ir spectrum of HT shows bands at 3 372 and 3 329 cm⁻¹ assignable to \(\nuN-H\) stretching vibration of amino and imino groups respectively. The former band shifted (\(\Delta = -80\) enr1) towards lower wavenumber suggesting the participation of amino group in coordination. A strong ligand HT band observed at 1 268 cm⁻¹ (C=S) (\(\Delta = -50\) cm⁻¹) towards lower wavenumber in all the complexes indicating the involvement of thioketo sulphur5 in coordination.

### Table 1 - Analytical and Physical Data of Complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>Analysis % (Found/Calcd)</th>
<th>C</th>
<th>H</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co(HT)₂(SCN)₂ (Green)</td>
<td></td>
<td>14.39</td>
<td>2.83</td>
<td>32.77</td>
</tr>
<tr>
<td>Co(MTHT)₂(SCN)₂ (Green)</td>
<td></td>
<td>35.60</td>
<td>4.32</td>
<td>19.01</td>
</tr>
<tr>
<td>Co(HT)₂(OCN)₂ (Brown)</td>
<td></td>
<td>14.02</td>
<td>2.90</td>
<td>33.03</td>
</tr>
<tr>
<td>Co(MTHT)₂(OCN)₂ (Brown)</td>
<td></td>
<td>35.02</td>
<td>2.76</td>
<td>20.02</td>
</tr>
<tr>
<td>Cu(HT)₂(SCN)₂ (Yellow)</td>
<td></td>
<td>12.57</td>
<td>2.55</td>
<td>30.20</td>
</tr>
<tr>
<td>Cu(MTHT)₂(SCN)₂ (Yellow)</td>
<td></td>
<td>32.67</td>
<td>2.87</td>
<td>19.29</td>
</tr>
<tr>
<td>Cu(HT)₂(OCN)₂ (Brown)</td>
<td></td>
<td>13.96</td>
<td>2.98</td>
<td>34.02</td>
</tr>
<tr>
<td>Cu(MTHT)₂(OCN)₂ (Brown)</td>
<td></td>
<td>34.90</td>
<td>3.00</td>
<td>19.90</td>
</tr>
</tbody>
</table>

The high frequency bands in the spectra of MTHT observed at 3 408 and 3 242 cm⁻¹ are assigned to amino and imino groups. These bands are not affected in the spectra of the metal complexes, indicating the non-participation of terminal amino group in coordination. A strong ligand MTHT band at 1 606 cm⁻¹ (C=N) shifted (\(\Delta = -15\) cm⁻¹) shifted towards lower wavenumber in the spectra of all the complexes, suggesting the involvement of azomethine nitrogen in coordination. Strong and sharp ligand MTHT bands at 1 286 cm⁻¹ (C=S) of MTHT are assigned to \(v(C-S)\) stretching vibration. (\(\Delta = -40\) cm⁻¹) towards lower wavenumber suggesting the participation of thioketo sulphur in coordination. The spectrum of SCN ligands shows bands at 2 303 (C=N) and 748 cm⁻¹ (C=S). In the spectra of the complexes containing SCN the former band shifted (\(\Delta =
~80 cm⁻¹) towards higher wavenumber, which suggests that SCN ligand is binding the metal ion through nitrogen⁷. IR spectra of OCN complexes, similarly support OCN ligand binding through nitrogen donor atom.

**Experimental**

All the chemicals used were of AnalyR grade.

*Methylthiophen-2-yl [methylene]hydrazonocarbothioamide*: A mixture of equimolar amounts of 2-acetylthiophene and thiosemicarbazide (2) in ethanol containing a few drops of conc. HCl was refluxed for 3 h, then cooled to yield a light yellow coloured solid (45%), m.p. 152-54° (Found : C, 40.95; H, 4.56; N, 19.97. C₇H₉N₃S₂ calc. for : C, 42.22; H, 4.52; N, 21.10%); δ (CDCl₃) 8.94 (1H, s, imino), 6.72 (2H, s, amino), 7.04 (1H, dd, thiophene-5), 2.38 (3H, s, CH₃).

**Synthesis of complexes**: To a hot solution of MTHT or HT (0.01 mol) and SCN or OCN (0.01 mol), requisite quantity of the metal salt (0.05 mol) dissolved in minimum amount of water was added and the mixture was refluxed for 6-8 h under inert N₂-atmosphere. It was then cooled and the resulting solid was washed with cold methanol and hot water, and dried under reduced pressure over CaCl₂.

Molar conductivity, magnetic susceptibility, electronic, IR and 'H nmr spectra were measured as described earlier⁸.

**Acknowledgement**

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**References**

Spectrophotometric determination of Lead(II) in water samples using benzil-α-monoxime isonicotinoyl hydrazone
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ABSTRACT

The reagent benzil α-monoxime isonicotinoyl hydrazone has been used for the spectrophotometric determination of lead in water samples. The reagent gives yellow coloured solution with Pb(II) in basic medium. The maximum colour intensity is observed in 10-11 pH range. This colour reaction with molar absorptivity $1.18 \times 10^4 \text{ mol}^{-1} \text{ cm}^{-1}$ has been used for the determination of lead in different water samples.

Accepted for publication in Indian Journal of Chemistry, Section A (Pub. SCCA-7003R).
Analytical properties of diacetylmonoxime benzoyl hydrazone (DMBH): Spectrophotometric determination of lead(II) cadmium(II), nickel(II) and copper(II)

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Abstract

The reagent dicacetylmonoxime benzoylhydrazone has been proposed for the determination of lead(II) in water, industrial effluent and alloys. The reagent is characterized by IR, NMR and Mass spectra and its analytical properties were described. The reagent gives colour reaction with Pb(II), Cd(II), Ni(II) and Cu(II) in basic medium. The molar absorptivity and Sandell's sensitivity of lead, cadmium, nickel and copper systems are respectively found to be $1.25 \times 10^4$, $1.58 \times 10^4$, $2.13 \times 10^4$ and $1.36 \times 10^4$ L mol$^{-1}$ cm$^{-1}$; 0.0166, 0.0070, 0.00276 and 0.00467 cm$^{-2}$. These colour reactions have been studied for the determination of lead, cadmium, nickel and copper. Lead has been determined in water samples and industrial effluents.

Communicated to Indian Journal of Chemistry (Ms. No. 7228).
Analytical Properties of Diacetylmonoxime Isonicotinoyl hydrazone (DMIH); Spectrophotometric Determination of Lead(II) in Water and Industrial Effluents

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Abstract

Characterization and analytical properties of diacetylmonoxime isonicotinoyl hydrazone (DMIH) are described. The reagent gives yellow coloured solution with Pb(II) in basic medium. The maximum colour intensity is observed in pH 10.0-11.0 range. This colour reaction (molar absorptivity $1.25 \times 10^4$ L mol$^{-1}$ cm$^{-1}$ at 374 nm) has been used for the spectrophotometric determination of lead in water samples and industrial effluents.

Communicated to Journal of Indican Chemical Society (Ref. No. ICS/4/N-32/99)