The electronic spectra of \([\text{CP}_2\text{VL}]\) complexes are approximately similar. Two overlapping bands are observed for these complexes around 16,000 and 19,000 cm\(^{-1}\). Spectra are similar to those of the corresponding xanthato- and dithiocarbamate complexes. The bands are not well resolved and interpretations are difficult. Similarity of these complexes may be Ca\(...\)r or lower, and in such a case none of the five vanadium \(d\) orbitals remains degenerate, and thus the possibility of four electronic transitions exists.

The infrared spectra (nujol mull) of all these complexes show bands for \(\nu_{\text{V=O}},\ \nu_{\text{C-S}}, \) and \(\nu_{\text{C-\cdots-N}}\) at 985, 1500 and 615 cm\(^{-1}\) respectively. The band assignments are tentative and have been made on the basis of previously published work on dithiocarbamate metal complexes. The observed \(\nu_{\text{V=O}}\) is slightly lower than the \(\nu_{\text{V=O}}\) observed in VO(acac). Thus, it is clear that an increased sulphur-to-vanadium metal bonding is present in the present \(\text{L}_2\text{VO}\) complexes.

One of the authors (R.K.M.) is thankful to the CSIR, New Delhi, for the award of a junior research fellowship. They are also thankful to Dr S. N. Poddar of Indian Association for the Cultivation of Science, Calcutta, for mull spectra.

References


Synthesis & Structural Studies of 1-Isonicotinyl-4-phenyl-3-thiosemicarbazide Complexes of VO(IV), Co(II), Ni(II) & Cu(II)

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Complexes of 1-isonicotinyl-4-phenyl-3-thiosemicarbazide (IPTSC) with VO(IV), Co(II), Ni(II) and Cu(II) having the compositions \(\text{VO}_2\text{IPTSC},\ \text{CoCl}_2\cdot\text{IPTSC},\ \text{Ni(IPTSC-H)}\cdot \text{CI},\ \text{Cu(IPTSC-H)}\cdot \text{Cl} \) and \(\text{M(IPTSC-2H)}\cdot \text{VO(IV)},\ \text{Co(II)},\ \text{Ni(II)} \) or \(\text{Cu(II)}\) have been prepared. The complexes are non-electrolytes in nitrobenzene. The magnetic susceptibility and the electronic spectral studies have been used to decide the geometry of the complexes. The subnormal magnetic moments in some of the complexes have been explained by assuming the presence of magnetically non-equivalent sites in the unit cell and/or metal-metal interaction. IR spectral studies have been used to infer the bonding sites in the complexes.

TRANSITION metal complexes of thiosemicarbazide, thiocarbamide (an N-aminoderivative of thiosemicarbazide) and substituted thiosemicarbazide have generated considerable interest as revealed by a recent review on this subject by Akbar Ali and Livingstone. We thought it fit to prepare and characterize the nature of 3f metal ion [VO(IV), Co(II), Ni(II) and Cu(II)] complexes with 1-isonicotinyl-4-phenyl-3-thiosemicarbazide (IPTSC).

All the metal salts used were of BDH quality, IPTSC was prepared as described in the literature, m.p. 211° (lit. 2 m.p. 213°).
methanolic solutions of the metal salts (15 mmoles) were prepared by mixing 50 ml of ethanolic or 
CoCl₂.IPTSC, Ni(IPTSC-H)Cl and Cu(IPTSC-H)Cl 
and IPTSC (10 mmoles). 
the reaction mixture using sodium acetate as in (i).
washed with water/ethanol and dried at 60°. 
The complexes are insoluble in CHCl₃, CCl₄ and 
symmetry of the complexes are given in Table 1. 
petroleum ether and slightly soluble in nitrobenzene 
and soluble in polar solvents like ethylenediamine 
and pyridine. All the complexes are nonelectrolytes 
as is evident from their molar conductance 
the ranges reported for tetrahedral complexes of 
Co(II) and square planar complexes of Cu(II). The 
H)Cl and Cu(IPTSC-2H) are normal and lie well in 
polymeric structures consisting of both planar and 

<table>
<thead>
<tr>
<th>Complex</th>
<th>Colour</th>
<th>m.p.</th>
<th>Magnetic moment</th>
<th>Symmetry</th>
<th>Found (%) (Calc.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>VOSO₄·IPTSC</td>
<td>Brown</td>
<td>350</td>
<td>1.51</td>
<td>C₂v</td>
<td>12-6</td>
</tr>
<tr>
<td>VO(IPTSC-2H)</td>
<td>do</td>
<td>245</td>
<td>1.23</td>
<td>C₂v</td>
<td>(13-2)</td>
</tr>
<tr>
<td>CoCl₂.IPTSC*</td>
<td>Green</td>
<td>350</td>
<td>4.01</td>
<td>O₆+T₄</td>
<td>(15-8)</td>
</tr>
<tr>
<td>Co(IPTSC-H)Cl*</td>
<td>Orange</td>
<td>350</td>
<td>2.43</td>
<td>O₆+D₄h</td>
<td>15-4</td>
</tr>
<tr>
<td>Ni(IPTSC-H)Cl*</td>
<td>Dirty yellow</td>
<td>350</td>
<td>2.45</td>
<td>O₆+D₄h</td>
<td>15-4</td>
</tr>
<tr>
<td>Ni(IPTSC-2H)</td>
<td>Green</td>
<td>350</td>
<td>1.79</td>
<td>D₄h</td>
<td>17-4</td>
</tr>
<tr>
<td>Cu(IPTSC-H)Cl*</td>
<td>do</td>
<td>350</td>
<td>1.86</td>
<td>D₄h</td>
<td>(17-2)</td>
</tr>
<tr>
<td>Cu(IPTSC-2H)</td>
<td>do</td>
<td>350</td>
<td>1.86</td>
<td>D₄h</td>
<td>(18-8)</td>
</tr>
</tbody>
</table>

*Satisfactory Cl analyses have also been obtained.

TABLE 2 — ELECTRONIC SPECTRAL BANDS, THEIR ASSIGNMENTS AND LIGAND FIELD PARAMETERS

<table>
<thead>
<tr>
<th>Complex</th>
<th>Bands (kK), their assignments and values of some ligand field parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>IPTSC</td>
<td>4-76 ²A₁g → ²T₁g (v.); 7-81 ²A₁g → ²T₂g (v.); 10-02 ²T₁g → ²T₂g (v.); 1015 cm⁻¹</td>
</tr>
<tr>
<td>VO(IPTSC-2H)</td>
<td>4-88 ²A₁g → ²T₁g (v.); 8-16 ²A₁g → ²T₂g (v.); 10-02 ²T₁g → ²T₂g (v.); 1015 cm⁻¹</td>
</tr>
<tr>
<td>Ni(IPTSC-H)Cl</td>
<td>14-92 ²A₁g → ²T₁g (v.); 23-93 ²A₂g → ²T₁g (v.); 30-77 and 35-71; D₄ = 1015 cm⁻¹</td>
</tr>
<tr>
<td>Cu(IPTSC-H)Cl</td>
<td>22-24 envelop of ²B₁g → ²A₁g, ²B₁g, ²E₂g; 25-33 c.t.; 35-70 and 41-67; D₄ = 1590 cm⁻¹</td>
</tr>
</tbody>
</table>

NOTES

Preparation of the complexes — (i) VOSO₄·IPTSC, 
CoCl₂.IPTSC, Ni(IPTSC-H)Cl and Cu(IPTSC-H)Cl 
were prepared by mixing ~50 ml of ethanolic or 
meatholic solutions of the metal salts (15 mmoles) 
and IPTSC (10 mmoles). 
(ii) M(IPTSC-2H) [where M = VO(IV), Co(II), 
Ni(II) or Cu(II)] were prepared by raising the pH of 
the reaction mixture using sodium acetate as in (i). 
The complexes thus precipitated in each case 
digested on a water-bath for 1 hr, filtered, 
washed with water/ethanol and dried at 60°. 
The analytical data, magnetic moments ⁸ and the 
symmetry of the complexes are given in Table 1. 
The complexes are insoluble in CHCl₃, CCl₄ and 
petroleum ether and slightly soluble in nitrobenzene 
and soluble in polar solvents like ethylenediamine 
and pyridine. All the complexes are nonelectrolytes 
as is evident from their molar conductance (<1-6 cm² 
mho/mole) in nitrobenzene. 
The magnetic moments of CoCl₂.IPTSC, Cu(IPTSC-
H)Cl and Cu(IPTSC-2H) are normal and lie well in 
the ranges reported for tetrahedral complexes of 
Ni(II) and square planar complexes of Cu(II). The 
subnormal magnetic moments of VO(IV) complexes 
are attributed to VO—V interaction while those of 
Ni(II) complexes are considered to be due to their 
polymeric structures consisting of both planar and 

Electronically spectral studies — The electronic spectra 
(nujol, Cary 14) of all the complexes exhibited bands 
at 30-7-35-7 and 36-4-41-7 kK regions which corre-
pond to 28-57 and 40-00 kK bands of IPTSC and 
hence may be assigned to intraligand transition. 

There has been a lot of controversy regarding the 
energy level sequence of the d-orbitals in VO(IV) 
on in C₄v symmetry⁴⁸. In the presently prepared 
VO(IV) complexes with IPTSC, the bands at 12-9, 
14-8-15-4 and 25 kK have been assigned to the 
transitions dxy → dxz, dxz and dyz → y² respectively 
in conformity with Wasson et al.⁸. 
The bands at 4-76, 7-80 and 16-00 kK in CoCl₂-
IPTSC are characteristic of tetrahedrally coordinated 
Co(II). The splitting of these bands gives further 
indication of tetrahedral coordination⁴¹ in the above 
complex. In addition to these bands the spectrum of 
Co(IPTSC-2H) shows bands at 10-00 and 16-40 kK 
characteristic of octahedral coordination. This 
indicates a certain amount of metal-metal interaction 
rising from dimeric or polymeric structure of the 
complex. This is supported by the magnetic moment 
value of 4-01 BM for this complex.
Mixed stereochemistry \((Q+S+Da)\) was proposed for Ni(II) complexes on the basis of magnetic moment data. The electronic spectra of these complexes show bands at about 1000, 148-8 and 23-5 kK characteristic of an octahedral geometry. The weak intensity band characteristic of Ni(II) in square planar environment appears to have submerged in the strong intensity \(v_2\) band of octahedrally coordinated Ni(II).

The 22-22 and 15-87 kK bands in the spectra of Cu(IPTSC-H)Cl and Cu(IPTSC-2H) indicate square planar and highly distorted octahedral geometries respectively for the two complexes.

\[
\text{R} - \text{NH} - \text{NH} - \text{CS} - \text{NHPh} \quad I
\]

\[
\text{R} = \text{isonicotinyl}
\]

A positive shift in \(v(N-H)\) bands in all the complexes except in the case of VO(IPTSC-2H), as compared with the solution spectrum (in acetonitrile) of the ligand indicates the involvement of at least one of the \(\geq N-H\) groups in bonding. The amide-I band suffers a negative shift in the spectra of the adducts as compared with the free ligand and disappears in the spectra of condensation compounds, indicating the involvement of the \(\geq C=O\) group of the ligand in coordination in the adducts and the destruction of this group presumably via enolization in the latter complexes.

A positive shift of about 30 cm\(^{-1}\) in the ring vibration in the spectra of the adducts and of about 60 cm\(^{-1}\) in those of condensation compounds as compared with the solution spectrum of the parent ligand suggests the involvement in coordination of the carbonyl oxygen in the adducts and carboxyl oxygen as well as pyridine nitrogen in the latter 10.

The \(v(C=S+C-N)\) mode\(^{11}\) is either very weak or disappears completely in the spectra of condensation products \(M\text{[IPTSC-2H]}\) \([M = \text{VO(IV)}, \text{Co(II)}, \text{Ni(II)} \text{and Cu(II)}]\) but shifts to the higher frequency side in the spectra of the adducts such as VO(IPTSC, Co(IPTSC, Ni(IPTSC-H)Cl) and Cu(IPTSC-H)Cl indicating the involvement of the thioketo group in the former complexes and non-participation of the \(\geq C=O\) group in the latter complexes.

The positive shift in the \(v(N-N)\) mode in the spectra of all the complexes indicates the involvement of one or both of the nitrogens in bonding\(^{12}\).

The lower value of \(v(V=O)\) in VO-IPTSC compounds as compared with a number of VO(IV) complexes\(^{13,14}\) may be due to the existence of \(V=O \cdots V\) interaction. This is in accord with the subnormal magnetic moments of these complexes discussed earlier. The bands at 1100-1125, 1025 and 975 cm\(^{-1}\) in the spectrum of VOSO\(_4\) ITPSC may be attributed to the chelating sulphato group\(^{15}\).

The low frequency bands in 435-390 and 308-292 cm\(^{-1}\) regions in all the ITPSC complexes are tentatively assigned\(^{16,17}\) to \(v(M-O)\) and \(v(M-N)\) (ref. 16, 18) modes respectively. The 384-368 cm\(^{-1}\) region band in the uncharged complexes and 342-333 cm\(^{-1}\) region band in Co(IPTSC-IPTSC and Cu(IPTSC-H)Cl may be attributed to \(v(M-S)\) (ref. 19) and \(v(M-Cl)\) (ref. 20) modes respectively.

One of the authors (R. B. S. Y.) is thankful to CSIR, New Delhi, for financial assistance.

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Synthesis of Substituted Dimethylformamidymyl 
Te(IV) & Se(IV) Chlorides

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Received 3 March 1976; accepted 3 June 1976

Substituted dimethylformamidymyl tellurium(IV) chloride \([\text{TeCl}_2\text{CON(CH}_3)_2\text{DMF}]\) and selenium(IV) chloride, \(\text{SeCl}_2\text{CON(CH}_3)_2\) have been prepared by the reaction of \(\text{TeCl}_4\) and \(\text{SeCl}_4\) with dimethylformamidyl sodium. The compounds have been characterized on the basis of elemental analyses, molar conductance and IR spectral data.

In continuation of our earlier report on the preparation of alkali metal dimethylformamidymyls, we now report the preparation and characterization of substituted dimethylformamidymyl compounds, \(\text{TeCl}_2\text{CON(CH}_3)_2\text{DMF}\) and \(\text{SeCl}_2\text{CON(CH}_3)_2\) of Te(IV) and Se(IV) chlorides.

Preparation of \(\text{TeCl}_2\text{CON(CH}_3)_2\text{DMF}\) (I) — On stirring an equimolar mixture of \(\text{TeCl}_4\) and \(\text{NaCON(CH}_3)_2\) in \(\text{CCl}_4\) for 7-8 hr, a dark brown voluminous solid separated which was filtered, washed with...