

TABLE 1 — ELEMENTAL ANALYSES*, COLOUR AND MAGNETIC MOMENTS OF VANADIUM-DITHIOCARBAMATE COMPLEXES

Complex	Colour	Found (%)				Calc. (%)				μ_{eff} (BM) at 301°K
		C	H	N	S	C	H	N	S	
(Bu ₂ dtc) ₂ VO,	Grey-green	45.82	7.08	6.22	27.10	45.47	7.57	5.90	26.95	1.68
(pipdtc) ₂ VO,	do	37.52	5.29	7.08	32.95	37.21	5.17	7.23	33.08	1.72
(mordtc) ₂ VO,	Grey	31.03	4.33	7.50	33.01	30.69	4.09	7.16	32.73	1.69
[(cp) ₂ V(pyrdtc)] [Ph ₄ B]	Greenish brown	72.58	6.01	3.09	10.21	72.44	5.88	3.58	9.91	1.79
[(cp) ₂ V(mordtc)] [Ph ₄ B]	Light green	70.88	5.92	2.01	9.66	70.69	5.74	2.11	9.66	1.66
[(cp) ₂ V(pipdtc)] [Ph ₄ B]	Green	73.21	5.90	2.33	9.81	72.73	6.06	2.12	9.56	1.69

*By Dr Alfred Bernhardt's Microanalytical Laboratory, Germany.

(a d^1 system) in these chelates. These μ_{eff} values are comparable with the value of 1.73 BM observed for bis(acetylacetonato)oxovanadium(IV), or other V(IV) complexes.

It is very difficult to assign the electronic spectral bands in the present complexes, since in such systems neither of the energy schemes of Ballhausen and Gray⁹ or Vanquickenborne and McGlynn¹⁰ is likely to be applicable as such. Besides, much controversy is prevailing in assigning the electronic spectral bands observed for analogous dithiocarbamate-oxovanadium(IV) chelates^{4,5}.

The electronic spectra of [cp₂VL][Ph₄B] 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-complexes³. The bands are not well resolved and interpretations are difficult. Symmetry of these complexes may be C_{2v} 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 $\nu\text{V}=\text{O}$, $\nu\text{C} \dots \text{N}$, and $\nu\text{C} \dots \text{S}$ at 985, 1500 and 615 cm⁻¹ ($\pm 5-10$ cm⁻¹) respectively. The band assignments are tentative and have been made on the basis of previously published work on dithiocarbamate metal complexes³⁻⁵. The observed $\nu\text{V}=\text{O}$ is slightly lower than the $\nu\text{V}=\text{O}$ observed in VO(acac)₂. Thus, it is clear that an increased sulphur-to-vanadium metal π -bonding is present in the present L₂VO 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

1. DEY, K. & PODDAR, S. N., *Z. anorg. allg. Chem.*, **327** (1964), 104; DEY, K., RAY, M. M., PODDAR, S. N., SARKAR, S. C. N. & HALDER, J., *J. Indian chem. Soc.*, **47** (1970), 743; DEY, K. & CHATTERJEE, K. K., *Z. anorg. allg. Chem.*, **383** (1971), 199; DEY, K., CHATTERJEE, K. K. & SEN, S. K., *J. Indian chem. Soc.*, **50** (1973), 167; DEY, K., SEN, S. K. & MAITI, R. K., *J. Coord. Chem.* (communicated); DEY, K. & MAITI, R. K., *Z. Naturforsch.* (communicated).

*Detailed spectral data can be had from the authors on request.

2. DEY, K. & MAITI, R. K., *Z. anorg. allg. Chem.* (communicated).
3. CASEY, A. T. & THACKERAY, J. R., *Aust. J. Chem.*, **25** (1972), 2085; CASEY, A. T. & THACKERAY, J. R., *Aust. J. Chem.*, **27** (1974), 757.
4. McCORMICK, B. J., *Inorg. Chem.*, **7** (1968), 1965.
5. VIGEE, G. & SELBIN, J., *J. inorg. nucl. Chem.*, **31** (1969), 3187.
6. KLOPPING, H. L. & VANDERKERK, G. J. M., *Recl. Trav. chim. Pays-Bas. Belg.*, **70** (1951) 936; WELCHER, F. J., *Organic analytical reagents*, Vol. IV (Van Nostrand, New York), 1948, 82.
7. SKACHILOVA, S. YA., SAVITSKII, A. & VLASKINA, R. YA., *Zh. obsch. Khim.*, **36** (1966), 1059.
8. GEARY, W. J., *Coord. chem. Rev.*, **7** (1971), 81.
9. BALLAUSEN, C. J. & GRAY, H. B., *Inorg. Chem.*, **1** (1962), 111.
10. VANQUICKENBORNE, L. G. & MCGLYNN, S. P., *Theor. chim. Acta*, **9** (1968), 390.

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

R. C. AGGARWAL & R. B. S. YADAV

Department of Chemistry, Banaras Hindu University
Varanasi 221005

Received 10 November 1975; accepted 24 May 1976

Complexes of 1-isonicotinyl-4-phenyl-3-thiosemicarbazide (IPTSC) with VO(IV), Co(II), Ni(II) and Cu(II) having the compositions VOSO₄.IPTSC, CoCl₂.IPTSC, Ni(IPTSC-H)Cl, Cu(IPTSC-H)Cl and M(IPTSC-2H) [M=VO(IV), Co(II), Ni(II) or 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, thiocarbazine (an N-aminoderivative of thiosemicarbazide) and substituted thiocarbazine have generated considerable interest as revealed by a recent review on this subject by Akbar Ali and Livingstone¹. We thought it fit to prepare and characterize the nature of $3d$ 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 literature², m.p. 211° (lit.² m.p. 213°).

TABLE 1 — ANALYTICAL DATA, MAGNETIC MOMENTS AND SITE SYMMETRY OF 1-ISONICOTINYL-4-PHENYL-3-THIOSEMICARBAZIDE COMPLEXES

Complex	Colour	m.p. °C	Magnetic moment	Symmetry	Found (%) (Calc.)		
					M	N	S
VOSO ₄ .IPTSC	Brown	350	1.51	C _{2v}	12.6 (13.2)	14.7 (14.6)	15.1 (14.8)
VO(IPTSC-2H)	do	245	1.23	C _{2v}	14.9 (15.1)	17.0 (16.6)	10.0 (9.5)
CoCl ₂ .IPTSC*	do	250	4.57	T _d	15.4 (14.8)	13.8 (14.0)	7.6 (8.0)
Co(IPTSC-2H)	Green	350	4.01	O _h +T _d	18.4 (17.9)	17.1 (17.0)	10.5 (9.8)
Ni(IPTSC-H)Cl*	Oange	350	2.43	O _h +D _{4h}	15.4 (16.1)	15.1 (15.3)	8.4 (8.8)
Ni(IPTSC-2H)	Dirty yellow	350	2.45	O _h +D _{4h}	17.7 (17.9)	17.2 (17.0)	10.4 (9.8)
Cu(IPTSC-H)Cl*	Green	240	1.79	D _{4h}	17.4 (17.2)	14.9 (15.1)	8.5 (8.7)
Cu(IPTSC-2H)	do	350	1.86	D _{4h}	18.8 (19.0)	16.9 (16.7)	10.20 (9.6)

*Satisfactory Cl analyses have also been obtained.

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

Complex	Bands (kK), their assignments and values of some ligand field parameters
IPTSC	30.3 and 37.8L*
VOSO ₄ .IPTSC	12.9 <i>dxy</i> → <i>dyz</i> ; 14.8 <i>dxy</i> → <i>dxz</i> ; 25.0 <i>dxy</i> → <i>dx²-y²</i> ; 30.8 and 40.0L; 36.4 c.t.; D _q = 1482 cm ⁻¹
VO(IPTSC-2H)	12.9 <i>dxy</i> → <i>dyz</i> ; 15.4 <i>dxy</i> → <i>dxz</i> ; 25.0 <i>dxy</i> → <i>dx²-y²</i> ; 30.8 and 38.5L; 36.4 c.t.; D _q = 1539 cm ⁻¹
CoCl ₂ .IPTSC	4.76 ⁴ A ₂ → ⁴ T ₂ (v ₁); 7.81 ⁴ A ₂ → ⁴ T ₁ (F) (v ₂); 16.00 ⁴ A ₂ → ⁴ T ₁ (P) (v ₃); 30.3L; 25.0 and 36.4 C.t.; D _q = 476 cm ⁻¹ , B = 640 cm ⁻¹ , β° = 26.6%, LFSE = 16.3 kcal/mole
Co(IPTSC-2H)	4.88 ⁴ A ₂ → ⁴ T ₂ (v ₁); 8.16 ⁴ A ₂ → ⁴ T _{1g} (F) (v ₂); 16.4 ⁴ A ₂ → ⁴ T ₁ (P) (v ₃); 10.02 ⁴ T _{1g} → ⁴ T _{2g} (v ₄); 26.7 and 36.4 c.t. D _q = 488 cm ⁻¹ , B = 660 cm ⁻¹ , β° = 24.7%, LFSE = 16.7 kcal/mole
Ni(IPTSC-H)Cl	14.81 ³ A _{2g} → ³ T _{1g} (F) (v ₂); 23.53 ³ A _{2g} → ³ T _{1g} (P) (v ₃); 35.71L; D _q = 1018 cm ⁻¹ , B = 530 cm ⁻¹ , β° = 50%, LFSE = 32.0 kcal/mole
Ni(IPTSC-2H)	14.92 ³ A _{2g} → ³ T _{1g} (F) (v ₂); 23.93 ³ A _{2g} → ³ T _{1g} (P) (v ₃); 30.77 and 35.71L; D _q = 1015 cm ⁻¹ , B = 525 cm ⁻¹ , β° = 50.0%, LFSE = 31.9 kcal/mole
Cu(IPTSC-H)Cl	22.22 envelop of ² B _{1g} → ² A _{1g} , ² B _{2g} , ² E _g , 26.67 c.t.; 33.33 and 41.67L; D _q = 2200 cm ⁻¹
Cu(IPTSC-2H)	15.87 envelop of ² B _{1g} → ² A _{1g} , ² B _{2g} , ² E _g ; 25.33 c.t.; 35.70 and 41.67L; D _q = 1590 cm ⁻¹

*L stands for ligand and c.t. for charge transfer transition.

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 methanolic 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 were digested on a water-bath for 1 hr, filtered, washed with water/ethanol and dried at 60°.

The analytical data, magnetic moments³ 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 reported⁴ for tetrahedral complexes of Co(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 octahedral Ni(II) atoms in the unit cell⁵. The

magnetic moment 4.01 BM of Co(IPTSC-2H) is slightly below the lower limit of the tetrahedral complexes of Co(II), suggesting a tetrahedral structure with some metal-metal interaction.

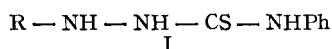
Electronic spectral studies—The electronic spectra (nujol, Cary 14) of all the complexes exhibited bands at 30.7-35.7 and 36.4-41.7 kK regions which correspond to 28.57 and 40.00 kK bands of IPTSC and hence may be assigned to intraligand transition (Table 2).

There has been a lot of controversy regarding the energy level sequence of the *d*-orbitals in VO(IV) ion in C_{2v} symmetry⁶⁻⁸. 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*→*dyz*, *dxz* and *dx²-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 coordination⁹ 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 arising 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 ($O_h + D_{4h}$) was proposed for Ni(II) complexes on the basis of magnetic moment data. The electronic spectra of these complexes show bands at about 10.00, 14.8 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 ν_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.



(R = isonicotinyI)

A negative shift in $\nu(\text{N}-\text{H})$ 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 $\text{>N}-\text{H}$ 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 >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 carbonyl oxygen as well as pyridine nitrogen in the latter¹⁰.

The $\nu(\text{C}=\text{S}+\text{C}-\text{N})$ mode¹¹ is either very weak or disappears completely in the spectra of condensation products M(IPTSC-2H) [M = VO(IV), Co(II), Ni(II) and Cu(II)] but shifts to the higher frequency side in the spectra of the adducts such as $\text{VOSO}_4 \cdot \text{IPTSC}$, $\text{CoCl}_2 \cdot \text{IPTSC}$, Ni(IPTSC-H)Cl and Cu(IPTSC-H)Cl indicating the destruction of the thioketo group in the former complexes and non-participation of the $\text{>C}=\text{S}$ group in the latter complexes.

The positive shift in the $\nu(\text{N}-\text{N})$ mode in the spectra of all the complexes indicates the involvement of one or both of the nitrogens in bonding¹².

The lower value of $\nu(\text{V}=\text{O})$ in VO-IPTSC complexes as compared with a number of VO(IV) complexes^{13,14} may be due to the existence of $\text{V}=\text{O} \cdots \text{V}$ 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 $\text{VOSO}_4 \cdot \text{IPTSC}$ may be attributed to the chelating sulphato group¹⁵.

The low frequency bands in 435-390 and 308-292 cm^{-1} regions in all the IPTSC complexes are tentatively assigned^{16,17} to $\nu(\text{M}-\text{O})$ and $\nu(\text{M}-\text{N})$ (ref. 16, 18) modes respectively. The 384-368 cm^{-1} region band in the uncharged complexes and 342-333 cm^{-1} region band in $\text{CoCl}_2 \cdot \text{IPTSC}$ and Cu(IPTSC-H)Cl may be attributed to $\nu(\text{M}-\text{S})$ (ref. 19) and $\nu(\text{M}-\text{Cl})$ (ref. 20) modes respectively.

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

References

- AKBAR ALI, M. & LIVINGSTONE, S. E., *Coord. Chem. Rev.*, **13** (1974), 10.
- KOROSI, J., *Egyesult Gyogyyszer es Tapszergyar (Hung.)*, **148** (1962), 949.
- FIGGIS, B. N. & LEWIS, J., cited in *Modern coordination chemistry*, edited by J. Lewis & R. G. Wilkins (Interscience, New York), 1962.
- KENT, BAREFIELD, E. BUSCH, D. H. & NELSON, S. M., *Q. Revs.*, **22** (1968), 457.
- KANEKAR, C. R. & CASEY, A. T., *J. inorg. nucl. Chem.*, **31** (1969), 3105.
- DRAKE, J. E., VEBRIS, J. & WOOD, J. S., *J. chem. Soc. (A)*, (1968), 1000.
- KUSKA, H. A. & YANG, P. H., *Abstract of the 5th Central Regional Meeting of the American Chemical Society, Cleveland, Ohio, 13-15 May 1973*.
- STOKLOSA, H. J., WASSON, J. R. & CORMIC, J. MC., *Inorg. Chem.*, **13** (1974), 592.
- SINGH, P. P. & RIVEST, R., *Can. J. Chem.*, **46** (1968), 2361.
- NAGANO, K., KINOSHITA, H. & HIRAKAWA, A., *Chem. pharm. Bull.*, **12** (1964), 1198; 1207.
- DUTT, N. K. & CHAKDER, N. C., *J. inorg. nucl. Chem.*, **32** (1970), 2303.
- BRAIBANTI, A., DALLVALLE, F., PELLINGHELL, M. A. & LAPARATI, E., *Inorg. Chem.*, **7** (1968), 1430.
- CORMIC, B. J. MC., BOZIS, R. A., *Inorg. Chem.*, **10** (1971), 2806.
- MATHEW, M., CARTY, A. J. & PALENIK, G. J., *J. Am. chem. Soc.*, **92** (1970), 3197.
- ESKENAZI, R., ROSKOWAN, J. & LEWITUR, R., *J. inorg. nucl. Chem.*, **28** (1966), 521.
- SPECA, A. N., KARAYANIS, N. M. & PYTLEWSKI, L. L., *Inorg. chem. Acta*, **9** (1974), 87; *J. inorg. nucl. Chem.*, **36** (1974), 3751.
- TEOTIA, M. P., RASTOGI, D. K. & MALIK, W. R., *Inorg. chim. Acta*, **7** (1973), 339.
- BEECROFT, B., CAMPBELL, M. J. M. & GREZESKOWIAK, R., *J. inorg. nucl. Chem.*, **36** (1974), 55.
- BROWALL, K. W. & INTERRANTE, L. V., *J. Coord. Chem.*, **3** (1973), 27.
- MASSACEST, M. & PONTICELLI, G., *J. inorg. nucl. Chem.*, **36** (1974), 2209.

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

R. C. PAUL, B. N. ANAND & R. KAPOOR

Department of Chemistry, Panjab University
Chandigarh 160014

Received 3 March 1976; accepted 3 June 1976

Substituted dimethylformamidyl tellurium(IV) chloride [$\text{TeCl}_3 \cdot \text{CON}(\text{CH}_3)_2 \cdot \text{DMF}$] and selenium(IV) chloride, $\text{SeCl}_4[\text{CON}(\text{CH}_3)_2]$ have been prepared by the reaction of TeCl_4 and 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 report¹ on the preparation of alkali metal dimethylformamidyls, we now report the preparation and characterization of substituted dimethylformamidyl compounds, $\text{TeCl}_3 \cdot \text{CON}(\text{CH}_3)_2 \cdot \text{DMF}$ and $\text{SeCl}_3 \cdot \text{CON}(\text{CH}_3)_2$ of Te(IV) and Se(IV) chlorides.

Preparation of $\text{TeCl}_3 \cdot \text{CON}(\text{CH}_3)_2 \cdot \text{DMF}$ (I)—On stirring an equimolar mixture of TeCl_4 and $\text{NaCON}(\text{CH}_3)_2$ in CCl_4 for 7-8 hr, a dark brown voluminous solid separated which was filtered, washed with