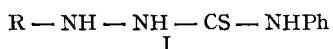


Mixed stereochemistry ( $O_h + D_{4h}$ ) was proposed for Ni(II) complexes on the basis of magnetic moment data. The electronic spectra of these complexes show bands at about 10.00, 14.8 and 23.5 kK characteristic of an octahedral geometry. The weak intensity band characteristic of Ni(II) in square planar environment appears to have submerged in the strong intensity  $\nu_2$  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  $\text{>C=O}$  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  $30 \text{ cm}^{-1}$  in the ring vibration in the spectra of the adducts and of about  $60 \text{ cm}^{-1}$  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 latter<sup>10</sup>.

The  $\nu(\text{C}=\text{S}+\text{C}-\text{N})$  mode<sup>11</sup> 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 bonding<sup>12</sup>.

The lower value of  $\nu(\text{V}=\text{O})$  in VO-IPTSC complexes as compared with a number of VO(IV) complexes<sup>13,14</sup> 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  $975 \text{ cm}^{-1}$  in the spectrum of  $\text{VOSO}_4 \cdot \text{IPTSC}$  may be attributed to the chelating sulphato group<sup>15</sup>.

The low frequency bands in 435-390 and 308-292  $\text{cm}^{-1}$  regions in all the IPTSC complexes are tentatively assigned<sup>16,17</sup> to  $\nu(\text{M}-\text{O})$  and  $\nu(\text{M}-\text{N})$  (ref. 16, 18) modes respectively. The 384-368  $\text{cm}^{-1}$  region band in the uncharged complexes and 342-333  $\text{cm}^{-1}$  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.

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

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

Department of Chemistry, Panjab University  
Chandigarh 160014

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Substituted dimethylformamidyl tellurium(IV) chloride [ $\text{TeCl}_3\text{CON}(\text{CH}_3)_2\text{DMF}$ ] and selenium(IV) chloride,  $\text{SeCl}_3[\text{CON}(\text{CH}_3)_2]$  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<sup>1</sup> on the preparation of alkali metal dimethylformamidyls, we now report the preparation and characterization of substituted dimethylformamidyl compounds,  $\text{TeCl}_3\text{CON}(\text{CH}_3)_2\text{DMF}$  and  $\text{SeCl}_3\text{CON}(\text{CH}_3)_2$  of Te(IV) and Se(IV) chlorides.

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

TABLE 1 — ANALYTICAL DATA OF THE COMPOUNDS

m.p. (°C)	Found (%) (calc.)				
	M	Cl	C	H	N
	TeCl <sub>3</sub> CON(CH <sub>3</sub> ) <sub>2</sub> .DMF				
100-102	32.9 (33.6)	28.0 28.1	17.9 19.0	3.3 3.4	7.8 7.4
	TeCl <sub>3</sub> CON(CH <sub>3</sub> ) <sub>2</sub> .Q				
195	29.0 (29.2)	26.0 24.4	31.8 33.2	2.8 3.0	6.0 6.4
	SeCl <sub>3</sub> CON(CH <sub>3</sub> ) <sub>2</sub>				
—	29.6 (30.7)	39.5 41.3	14.4 14.0	2.6 2.3	5.5 5.4

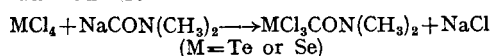
CCl<sub>4</sub> and dried. Sodium chloride formed and any unreacted NaCON(CH<sub>3</sub>)<sub>2</sub> were removed by treating the solid with DMF. The DMF solution on evaporation under reduced pressure yielded a mustard coloured powder analysing for TeCl<sub>3</sub>CON(CH<sub>3</sub>)<sub>2</sub>.DMF. Compound (I) is insoluble in CCl<sub>4</sub> and benzene but soluble in methylene chloride, nitrobenzene and nitromethane.

The suspension of I in CCl<sub>4</sub> on refluxing with quinoline (Q) yielded a white solid, TeCl<sub>3</sub>CON(CH<sub>3</sub>)<sub>2</sub>.Q, insoluble in CCl<sub>4</sub>, benzene and slightly soluble in methylene chloride, nitrobenzene and nitromethane.

**Preparation of SeCl<sub>3</sub>CON(CH<sub>3</sub>)<sub>2</sub> (II)** — It was prepared in a manner analogous to compound I. However, the separation of NaCl and unreacted NaCON(CH<sub>3</sub>)<sub>2</sub> could not be affected by treatment with DMF, as the compound disproportionated to give elemental Se. The compound dissolved in methylene chloride on prolonged stirring and insoluble NaCl and NaCON(CH<sub>3</sub>)<sub>2</sub> were removed by filtration. The solution on evaporation under reduced pressure yielded a yellow semi-solid, SeCl<sub>3</sub>CON(CH<sub>3</sub>)<sub>2</sub>. This compound is soluble in methylene chloride and slightly soluble in CCl<sub>4</sub>, nitrobenzene and nitromethane.

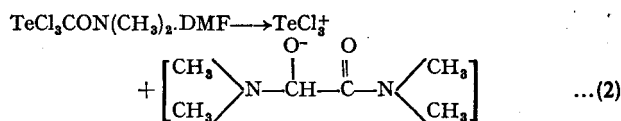
The analytical results are given in Table 1. All these compounds are highly sensitive to moisture.

Solvolytic reactions of metal halides do not take place in DMF due to the very low acidity of the proton on DMF. However, such reactions may be carried out by reacting metal halides with alkali metal dimethylformamidyls. The reactions may be visualized as:



Molar conductivities of the millimolar solutions of compound I (23 ohm<sup>-1</sup> cm<sup>2</sup> mole<sup>-1</sup>) and of its quinoline adduct (22 ohm<sup>-1</sup> cm<sup>2</sup> mole<sup>-1</sup>) in nitrobenzene indicate that they behave as 1:1 electrolytes in this medium<sup>2</sup>. Molecular weight of I as determined by freezing point method was found to be 192 (average of three measurements) which is about one-half of the required value of 379. The molecular weight of the quinoline adduct could not be determined due to its limited solubility. These observations can be explained in terms of Eqs. (1) and (2).

Equilibrium (1) can be justified, if it is assumed

$$TeCl_3CON(CH_3)_2.DMF \rightarrow [TeCl_2CON(CH_3)_2.DMF] + Cl^- \dots(1)$$


that Cl<sup>-</sup> ion and [CON(CH<sub>3</sub>)<sub>2</sub>]<sup>-</sup> ion have similar electronegativities. The other possibility is the ionization of solvated formamidyl anion (Eq. 2). The existence of this anion in the form of its alkali metal salts has been earlier proposed by Brederick *et al.*<sup>3</sup>.

Molar conductivity of the millimolar solutions of compound (II) in nitrobenzene (7 ohm<sup>-1</sup> cm<sup>2</sup> mole<sup>-1</sup>) shows it to be a non-electrolyte. Mol wt of the compound determined by freezing point method (255) tallies with the formula weight (257).

The IR spectra of the compound (I) and of its quinoline adduct show intense band at 1640 cm<sup>-1</sup> which may be assigned to νC=O. These compounds also show medium intensity band at 370 cm<sup>-1</sup> which is characteristic of Te-Cl bond in compounds containing TeCl<sub>3</sub><sup>+</sup> cation<sup>4</sup>. The IR bands at 1630 s, 1580 m and 1505 m in pure quinoline due to νC...C and νC...N are shifted to higher frequency region in the adduct (1635 m, 1590 s and 1555 m). This indicates the existence of coordinated quinoline, in agreement with our earlier work<sup>5</sup>. The IR spectrum of selenium compound, (II) could not be recorded as it will not form mull with nujol and it reacted with KBr and CsI plates.

Thermal behaviour of I as well as of its quinoline adduct shows that these decompose finally to be TeO<sub>2</sub> through the formation of some unstable intermediates. From the total loss in weight the composition of the compound was checked. The composition of the intermediate products could not be ascertained.

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#### Compounds of Thallium(III) Chloride with Some Lewis Acids

K. C. MALHOTRA & BALKRISHAN

Department of Chemistry, Himachal Pradesh University  
Simla 171001

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A number of adducts of thallium(III) chloride with Lewis acids have been isolated. On the basis of conductance, molecular weight and IR data, the adducts with phosphorus pentachloride, iodine trichloride and tetrachlorides of selenium and tellurium have been formulated as PCl<sub>5</sub>.TlCl<sub>3</sub>, ICl<sub>3</sub>.TlCl<sub>3</sub> and MCl<sub>4</sub>.TlCl<sub>3</sub> respectively; but in the case of trichlorides of phosphorus, arsenic and antimony, the adducts obtained have been characterized as halogen-bridged four-coordinated Tl(III) compounds.