Bull.Chem.Soc.Ethiop.,4(1), 39-44 (1990).

METAL COMPLEXES OF VANILLIN - AND 2-FURALDEHYDE-4-PHENYLTHIOSEMICARBAZONES

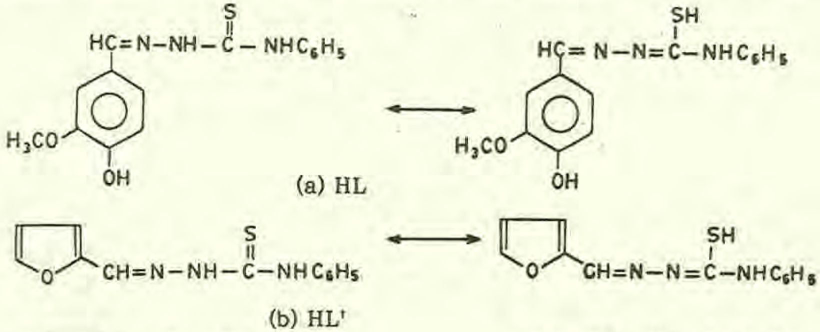
Mrs. Papia Chatterjee and B.V. Agarwala[*][§]
Chemical Laboratories, University of Allahabad
Allahabad-211002, India

(Received September 7, 1989; revised February 16, 1990)

ABSTRACT. The interaction of two Schiff bases (L) derived by the condensation of vanillin or 2-furaldehyed and 4-phenylthiosemicarbazide with several bipositive cations (M) have been investigated. The complexes of the general formula $ML_2.2H_2O$ are formed where the metal ion is coordinated via azomethine N and thiolo S atoms. On the basis of elemental analysis, IR, DRS, magnetic susceptibility measurements at varying current and thermal studies, structures have been proposed for the new octahedral complexes. The calculated ligand field parameters are found to be consistent with the proposed geometry.

INTRODUCTION

4-Phenylthiosemicarbazide, $H_2NNH(CS)NHC_6H_5$ possesses a thioketo and two secondary amine groups, giving rise to large number of metal chelates of structural and biological interest (1). Their proven antitumor carcinostatic and other biochemical activities aroused interest to several investigators (2,3). Metal complexes of 4-phenylthiosemicarbazone exhibit various stereochemistry as reported by Mostafa and coworkers (4). Cobalt(II) and nickel(II) complexes are octahedral whereas copper(II) complex has a square planar geometry as ascertained by IR and diffuse reflectance spectroscopic studies. Potentiometric studies of 4-phenylthiosemicarbazide, thiozolidones, salicylaldehyde derivatives and their metal complexes have also been described (5). Significant work on their structural characteristic has also been reported from these laboratories (6-8).



thione form (in solid state) thiolo form (in solution)

Fig. 1. Tautomeric forms of: (a) VPTSC (HL); (b) FPTSC (HL').

[§] Present address: Department of Postgraduate Studies and Research in Chemistry, R.D. University, Jabalpur - 482001, India.

In the present paper, two Schiff bases are synthesised by the interaction of 2-furaldehyde or vanillin with 4-phenylthiosemicarbazide (PTSC) to yield vanillin-4-phenylthiosemicarbazone (VPTSC) and 2-furaldehyde-4-phenylthiosemicarbazone (FPTSC). Their metal complexes with Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and UO_2(II) are characterized and the structural features are discussed.

EXPERIMENTAL

Materials. 4-Phenylthiosemicarbazide (Fluka), vanillin (Loba), 2-furaldehyde (Loba) and metal acetates of BDH Analar grade were employed.

Synthesis of vanillin - (VPTSC) and 2-furaldehyde-4-phenylthiosemicarbazone (FPTSC). To an ethanolic solution of 4-phenylthiosemicarbazide (19.24 g; 0.1 M), 0.1 M vanillin or 0.1 M 2-furaldehyde was added slowly with vigorous shaking. The mixture was then heated under reflux on a water bath for 3-4 h and left overnight. Vanillin-4-phenylthiosemicarbazone (VPTSC) and 2-furaldehyde-4-phenyklthiosemicarbazone (EPTSC) were obtained as white crystals and brown needles respectively. The products were filtered, washed several times with cold ethanol followed by ether and finally dried in vacuo over silica gel. Each product was recrystallised from ethanol.

Preparation of metal(II)-VPTSC and metal(II)-FPTSC complexes. (a) The cobalt complex was prepared by heating under reflux VPTSC (1.20 g, 0.004 M) in water (10 cm^3) with cobalt acetate (0.49 g, 0.002 M) in water (10 cm^3) for 2-3 hr. The brown complex which precipitated was filtered, washed and dried. The black Ni(II), brown Cu(II), white Zn(II), yellow Cd(II) compounds were made similarly. (b) The metal complexes of FPTSC were obtained in an identical manner using ligand (1.91 g, 0.004 M) and metal acetates as in (a) above. The black Co(II), black Ni(II), green Cu(II), yellow Zn(II), yellow Cd(II), and dirty yellow UO_2(VI) were synthesised. Their respective yields are given in Table 1.

All the complexes were insoluble in common organic solvents, viz. ethanol, dioxane, ether, DMF, DMSO and THF. Physicochemical measurements were made as described earlier (8).

Characterization of ligands. The Schiff bases VPTSC and FPTSC were analysed for C, H and N by microanalytical method and the data along with other physical characteristics are shown in Table 1. Their IR spectra show characteristic bands due to ν (C=N) and ν(C=S) at 1645-60 and 760-80 cm^{-1}. The presence of N-C-N, N-C=S and C=S bands in the ligands suggest that they exist in thione form [1(a)] in the solid state as represented by structures which shows tautomeric character (Fig. 1).

Composition and characterization of complexes. The analytical data of the complexes (Table 1) indicate that the complexes have the general formula $ML_2 2H_2O$. Where HL represents the ligand (VPTSC or FPTSC) and M is Co(II), Ni(II), Cu(II), Zn(II), Cd(II) or UO_2(II).

The metal complexes are characterized by the presence of IR spectral bands in the range 1600-1560 cm^{-1} in each case, assignable to azine group (9). The C=N stretching of the ligands shows a downward shift on complexation by 30-20 cm^{-1} indicating their definite involvment in coordination through azomethine nitrogen (10). The N-N stretching vibration observed at 1000 cm^{-1} in the ligands shows a positive shift of 30-40 in each complex. This shift indicates that nitrogen of the N-N bond takes part in coordination (11,12). New bands observed in the metal sensitive region around 500-460 cm^{-1} in the complexes may be assigned to M-N stretching vibrations (13), and thus provide further support to the fact that

Table 1. Physical characterization and analytical data of complexes.

Compound	Yield (%)	Decomposition temperature (°C)	Metal found (calcd.)	Carbon found (calcd.)	Hydrogen found (calcd.)	Nitrogen found (calcd.)
HL (VPTSC)		201*	-	59.0 (59.8)	4.5 (4.9)	13.2 (13.9)
$CoL_2 2H_2O$	78	260	7.8 (8.5)	53.0 (53.2)	4.6 (4.4)	13.0 (12.4)
$NiL_2.2H_2O$	62	320	8.7 (8.5)	54.0 (53.2)	4.6 (4.4)	13.0 (12.4)
$CuL_2.2H_2O$	69	340	9.6 (9.3)	52.0 (52.8)	4.0 (4.4)	12.0 (12.3)
$ZnL_2.2H_2O$	78	340	10.0 (9.5)	51.6 (52.6)	4.0 (4.3)	11.8 (12.2)
$CdL_2.2H_2O$	85	300	17.6 (15.3)	49.0 (49.3)	3.8 (4.1)	10.0 (11.5)
HL' (FPTSC)		153*	-	59.9 (58.7)	4.5 (4.4)	17.0 (17.1)
$CoL_2.2H_2O$	85	250	10.2 (10.4)	48.3 (49.4)	4.0 (4.1)	15.4 (14.4)
$NiL_2.2H_2O$	72	280	10.0 (10.3)	48.5 (49.5)	4.1 (4.1)	14.9 (14.4)
$CuL_2 2H_2O$	78	320	11.0 (10.8)	49.1 (49.0)	4.0 (4.1)	13.9 (14.3)
$ZnL_2.2H_2O$	58	280	10.0 (11.1)	49.0 (48.9)	4.1 (4.1)	14.2 (14.2)
$CdL_2.2H_2O$	85	280	16.6 (17.6)	45.6 (45.2)	3.7 (3.8)	13.0 (13.2)
$UO_2L_2.2H_2O$	62	360	28.2 (29.9)	36.6 (36.3)	3.0 (3.0)	10.4 (10.5)

HL = VPTSC (Vanillin-4-phenylthiosemicarbazone).
HL' = FPTSC (2-Furaldehyde-4-phenylthiosemicarbazone).
* = Melting point.

metals coordinate to the ligands by azomethine nitrogen. The formation of metal chelates through the enolic form [1(b)] of the three 4-phenylthiosemicarbazone ligands is evidenced from: (i) the absence of N-C=S stretching band at 1380 (14); (ii) the appearance of new bands due to $>C=N-N=C<$ at 1580; (III) new bands due to C-S stretching at 670 (15) and (iv) the appearance of a new band due to ν (M-S) in complexes at 270 cm^{-1} (16, 17).

The $-OCH_3$ in VPTSC and the furan O in FPTSC do not participate in coordination as their respective stretching band appearing at 2840 and 1510 cm^{-1} remains unaltered in both the ligands and complexes. A new band at 1640-1620 cm^{-1} in the complexes of VPTSC and FPTSC appears due to the deformation vibration of coordinated water (12,18). This is further confirmed by the appearance of a band in 660-680 cm^{-1} range assignable to the rocking mode of vibration of coordinated water (19).

Magnetic susceptibility measurements. The magnetic susceptibility measurements for Co(II) complexes formed by VPTSC and FPTSC have been made at various magnetic fields (employing 5,10,15 amp current) and the magnetic moment values are found to be 4.81 and 4.92 B.M. respectively. These values are well within the range (4.7-5.2 B.M.) reported for octahedral cobalt(II) complexes (20,21), similarly Ni(II) and Cu(II) complexes also show octahedral stereochemistry and μ_{eff} values are found to be 1.81 and 1.87B.M. in the latter case. Other values are incorporated in Table 2. Zn(II), Cd(II) and UO_2(II) complexes are diamagnetic.

Diffuse reflectance spectra. The diffuse relectance spectra of the samples were obtained by intimately grinding the samples with MgO and a thin film of the mixture was placed for spectral measurement. Different metal complexes show respective transition bands due to the electronic transition in the atom. For example, Co(II) complexes exhibit only two bands (ν_1, ν_3) out of the expected three transitions in the region of octahedral complexes (22). The position of ν_2 band could not be experimentally found but can be anticipated by the relation $\nu_2 = \nu_1 + 10$ Dq. The 10 Dq values have been evaluated by using the expression:

$$10\ \mathrm{Dq} = 2\nu_1 - \nu_3 + 15\ \mathrm{B}$$

where B is the Racah parameter and is 971 cm^{-1} for free Co(II) ion. The 10 Dq values are calculated to be low, indicating that the ligands produce a weak field in each case.

Table 2. Band position ligand field parameters and magnetic moment of complexes.

Complex	Band position (cm^{-1})	10 Dq (cm^{-1})	B'	β	β° (%)	ν_2	ν_2/ν_1	μ_{eff} (B.M.)	$E_{h.s.} - E_{l.s.}$*
$CoL_2.2H_2O$	10256, 23255	11585	893	0.91	8.0	21789	2.10	4.81	- 10920
$NiL_2.2H_2O$	10309, 14492, 23255	10309	662	0.63	37.0	14491	1.40	2.81	
$CoL'_2.2H_2O$	10416, 23255	11520	929	0.95	4.3	21936	2.10	4.92	- 10980
$NiL'_2.2H_2O$	10416, 15151 25000	10416	648	0.61	39.0	15151	1.45	2.92	

Abbreviations given in Table 1.

* Denotes the difference in energy between high-spin and low-spin complexes.

The octahedral nature of Co(II) complexes is well supported from the value of ν_2/ν_1 and is found in the octahedral range 2.1-2.2 (23). The covalency factor B' degree of covalency β and percentage degree of covalency β° have been calculated and shown in Table 2.

On the basis of magnetic and DRS studies it can be concluded that the Co(II) complexes of VPTSC and FPTSC are high-spin type involving octahedral symmetry around the metal ion.

The Ni(II) complexes show three absorption bands as expected for octahedral configuration and lie between 8000-13000, 15000-19000 and 25000-29000 cm^{-1} (24, 25). 10 Dq, B', β and β° values have been calculated and are listed in Table 2. The low values of 10 Dq (26, 27) suggest that the ligands employed produce a weak field. Also the low values of 15 B' as compared to the 15 B for free Ni(II) ion (15840) indicate the covalent nature of the metal-ligand interaction in the complexes. Moreover the ratios ν_2/ν_1 lie well within the reported range (1.7-1.4) (28) for Ni(II) octahedral complexes.

For a perfect octahedral Cu(II) complex, only one band is expected due to $^2T_{2g} \leftarrow {}^2E_g$ transition (29). Undistorted octahedral Cu(II) complexes are rather uncommon due to Jahn Teller distortion, giving rise to one band (30) or a broad envelope of bands (31). Among the two 4-phenylthiosemicarbazone complexes Cu(II)-VPTSC and Cu(II)-FPTSC complex show only one band (at 15384 and 13888 cm^{-1} respectively) corresponding to the above transition in distorted octahedral region (32) and recorded in Table 2. The 10 Dq values have been evaluated from the expressions already elaborated and are also given in this table.

Thermogravimetry. The thermograms of the metal complexes show that they lose two water molecules at 160-300° (33,34). This is in conformity with earlier observation made by analytical and IR spectral investigations. The complexes remain quite stable up to 160° and thereafter gradually decompose up to ∿300° (Table 3). The amount of weight-loss between 160°-300° correpond to the percentage weight of two molecules of water. The complexes show rapid degradation after this temperature range presumably due to the decomposition of organic constituent of the complex molecules (35). The stability of VPTSC and FPTSC complexes with respect to temperature lie in the order: Cu(II)≈ Zn(II) = Cd(II) < Co(II) < Ni(II) for VPTSC complexes and UO_2(II) < Co(II) ≈ Cu(II) < Ni(II) < Cd(II) < Zn(II) for FPTSC complexes.

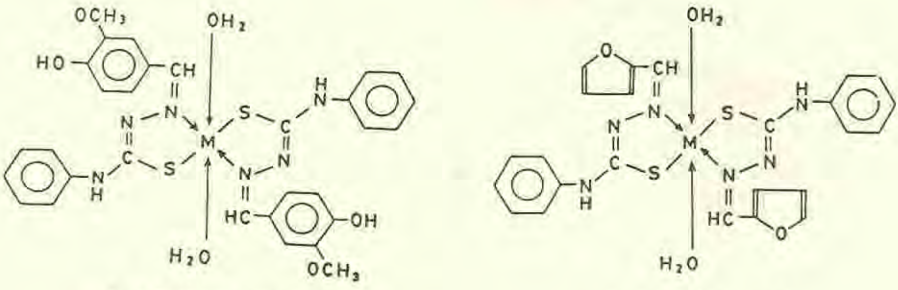
Table 3. Thermal characteristics of VPTSC complexes.

Complex	Total wt for ig (mg)	Temp. of water loss °C	% water loss obs.	calcd.	Decomposition temp. °C	% wt of residue obs.	calcd.
$CoL_2.2H_2O$	86	160-240	4.0	3.6	260	11.1	11.29
$NiL_2.2H_2O$	100	160-280	4.2	3.6	300	11.5	11.35
$CuL_2.2H_2O$	128	160-220	3.0	2.6	240	-	-
$ZnL_2.2H_2O$	172	160-220	3.5	2.5	240	12.1	12.3
$CdL_2.2H_2O$	116	120-220	2.8	2.4	240	18.2	17.9
$CoL'_2.2H_2O$	125	120-240	3.5	3.1	280	15.6	16.0
$NiL'_2.2H_2O$	102	120-280	4.0	3.1	320	12.4	12.8
$CuL'_2.2H_2O$	186	160-240	4.6	3.1	280	18.0	16.7
$ZnL'_2.2H_2O$	129	160-360	4.2	3.3	400	20.0	18.3
$CdL'_2.2H_2O$	150	160-320	3.2	2.9	360	25.0	23.3
$UO'_2L'_2.2H_2O$	146	120-240	3.8	3.9	240	-	-

HL = VPTSC, HL' = FPSTC.

CONCLUSION

The elemental analysis, infrared spectra, diffuse reflectance spectra and magnetic studies and thermal stability of the VPTSC and FPTSC complex lead to the conclusion that the ligands are bidentate through azomethine nitrogen and thiolate sulphur. The two vacant positions in the coordination sphere are occupied by water molecules to produce 6- coordinated complexes.



(a) $[ML_2 \cdot 2H_2O]$ (b) $[ML'_2 \cdot 2H_2O]$

Fig. 2. Proposed structures of 4-phenylthiosemicarbazone complexes
M = Co(II), Ni(II), Zn(II), Cd(II), UO_2(II)
HL = VPTSC (vanillin-4-phenylthiosemicarbazone)
HL' = FPTSC(2-furaldehyde-4-phenylthiosemicarbazone).

ACKNOWLEDGEMENT

The authors are grateful to Professor A.K. Dey for his keen interest in the work and to the University Grants Commision New Delhi for partial financial support to one of them (PC).

REFERENCES

1. M. Das and S.E. Livingstone, Inorg. Chim. Acta, **5**, 19 (1976).
2. E.M. Hodnett, C.H. Moore and F.A. French, J. Med. Chem., **1121**, 14 (1971).
3. A. Chirioc, O. Dragomir, F. Motoc and T. Motoc, Ser. Chim., **3**, 1 (1979).
4. M.M. Mostafa, A.M. Shallaby and A.A. El-Asmy, J. Inorg. Nucl. Chem., **2992**, 43 (1981).
5. Y.N. Bhatt, K.K. Patil, K.J. Shah and R.S. Patel, J. Indian Chem. Soc., **1214**, 52 (1975).
6. P.L. Maurya, B.V. Agarawala and A.K. Dey, Polym. Bull., **631**, 1 (1979); J. Indian Chem. Soc., **418**, 55 (1978).
7. P. Chatterjee, H.K. Duggal and B.V. Agarwala, Radiochem. and Radiation Chem. Symp. Tiruupati (1986).
8. P.S.N. Reddy and B.V. Agarwala, Transition Met. Chem., **585**, 17 (2987).
9. C.N.R. Rao, "Chemical Application of Infrared Spectroscopy", Academic Press, New York, 1976.
10. S.S.P. Rao and A. Manohar, Indian J. Chem., **455**, 25A (1986).
11. D.M. Wiles and T. Suprunchuk, Canadian J. Chem., **1087**, 47 (1969).
12. K. Nakamot, "Infrared Spectra of Inorganic and Coordination Compounds", John Wiley, New York, 1978.
13. J. Csaszar and L. Kiss, Acta Chim. Acad. Sci. Hung., **17**, 78 (1973).
14. K. Burger, I. Ruff and F. Ruff, I. Inorg. Nucl. Chem., **646**, 38 (1976).
15. L.F. Lindoy, S.E. Livingstone and T.N. Lokyer, Inorg. Chem., **652**, 6 (1967).
16. D.M. Adams,"Metal Ligand and Related Vibrations", Arnold, London, 1976.
17. T. Ojima, T. Onishi, T.I. Wamoto, Ni. Inamot and K. Tamaru, Inorg. Nucl. Chem. Lett., **65**, 6 (1970).
18. P.S. Zacharias and K.N. Reddy, Indian J. Chem., **244**, 25A (186).
19. T.S. Lobana, H.S. Cheema and S.S. Sandhu, Polyhedron, **717**, 1 (1985).
20. F.A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry,"Wiley, New York, 1976.
21. R.C. Aggarwal, N.K. Singh and P. Singh, Indian J. Chem., **384**, 25A (1986).
22. N.N. Greenwood and A. Earnshaw,"Chemistry of Elements", Pergamon Press, Oxford, 1985.
23. N.B. Colthup, L.H. Dey and Siberley, "Introduction to Infrared and Raman Spectroscopy", Academic Press, New York, 1964.
24. A.B.P. Lever, "Inorganic Electronic Spectroscopy", Elsevier, Amsterdam, 1968.
25. R.L. Carlin, Transition Met. Chem., **3**, 1 (1961).
26. E.C. Alyea and P.H. Merell, Inorg. Chim. Acta, **91**, 28 (1978).
27. G. Devote, M. Masaceri, G. Ponticelli and C. Preti, J. Inorg. Nucl. Chem., **271**, 39 (1977).
28. N. Saha and S. Sinha, Indian J. Chem., **203**, 24A (1985).
29. C.M. Dani and A.K. Das, J. Indian Chem. Soc., **381**, 61 (1984).
30. V.D. Kumari, M. Khare and K.N. Munshi, Indian J. Chem., **72**, 24A (1985).
31. K.C. Satpathy, B.B. Laland R. Mishra, Indian J. Chem.,**147**, 24A (1985).
32. R. Neiman and D. Kinelson, J. Chem. Phys., **149**, 35 (1961).
33. A.C. Fabretti, C.G. Franchini, C.P. Preti and G. Tosi, Canadian J. Chem.,. **137**, 19A (1980).
34. N.S. Biradar and S.D. Angadi, J. Inorg. Nucl. Chem., **1405**, 38 (1976).
35. C.R. Panda, S.C. Nayak, V. Chakravortty and K.C. Dash, Indian J. Chem., **141**, 24A (1985).