J. Indian Chem. Soc.,
Vol. LVI, March 1979, pp. 244-247

Magnetic and Spectral Properties of Fe(II), Fe(III), Co(II), Ni(II), Cu(II) and Pd(II) Chelates of 2'-Hydroxy-4-Methoxy-5'-Methylchalkone Oxime (HMMCO)

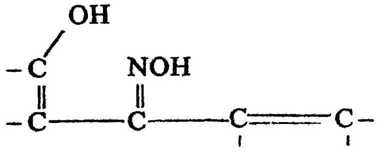
NARAYAN S. BHAVE and R. B. KHARAT

Chemistry Department, Nagpur University Campus, Nagpur-440 010

Manuscript received 23 May 1978, revised 9 November 1978, accepted 22 December 1978

Studies on the complexes of transition metals with bidentate oxime ligand 2'-hydroxy-4-methoxy-5'-methylchalkone oxime (HMMCO) has been carried out. On the basis of elemental analysis, molar conductance and thermal analysis the complexes have been assigned the formulæ Fe(II)(HMMCO)$_2$5H$_2$O, Fe(III)(HMMCO)$_3$6H$_2$O, Co(HMMCO)$_2$3H$_2$O, Ni(HMMCO)$_2$2H$_2$O, Cu(HMMCO)$_2$3H$_2$O and Pd(HMMCO)$_2$. The attempts have been made to assign their probable structures with the aid of magnetic data, electronic and i.r. spectral data.

SEVERAL transition metal complexes of different oximes[1-5] have been reported and characterised. Recently 2'-hydroxy-4-methoxy-5'-methylchalkone oxime (HMMCO) having system,



has been used in this laboratory by Kharat et. al[6-8] as an analytical reagent. However the structural studies on the complexes of transition metal ion with HMMCO have not been undertaken so far. The present paper describes the isolation and characterization of tenative structures for the complexes of Fe(II), Fe(III), Co(II), Ni(II), Cu(II) and Pd(II) on the basis of conductance, spectral and magnetic measurement data, and the results of chemical analysis and thermal analysis[9].

Experimental

Chemicals : The chemicals used were all of analar or chemically pure grade. The ligand 2'-hydroxy-4-methoxy-5'-methylchalkone oxime (HMMCO) was prepared by known method[10].

Preparation of Metal Complexes :

Fe(II)(HMMCO)$_2$5H$_2$O : 25 ml aqueous solution of ferrous ammonium sulfate (0.3 g) was gradually added to 70 ml of alcoholic solution of HMMCO (0.70 g) with constant stirring. It was then diluted to 200 ml with distilled water with constant stirring and digested on water bath for about half an hour. Dark violet precipitate obtained was filtered, washed with hot water and aqueous alcohol (1 : 1) and dried in an desicator over calcium chloride.

Fe(III)(HMMCO)$_3$6H$_2$O : In the preparation of Fe(III) complex with HMMCO, ferric nitrate (0.5 g) was gradually added to 100 ml alcoholic solution of HMMCO (1.0 g). The above procedure (i. e., for Fe(II) complex) was repeated to obtain dark violet precipitate, it was filtered, washed with hot water and aqueous alcohol (1 : 1) and dried in desiccator over calcium chloride.

Co(II), Ni(II) and Cu(II) : For the preparation of Co(II), Ni(II) and Cu(II) complexes with HMMCO, aqueous solution of their metal acetate (0.2 g) was gradually added to 60 ml alcoholic solution of HMMCO (0.6 g) ; remaining procedure was repeated as above.

Pd(II)(HMMCO)$_2$: Orange yellow precipitate of Pd(II) complex with HMMCO was obtained by adding 25 ml aqueous solution of Pd(II) chloride (0.2 g) to 60 ml alcoholic solution of HMMCO (0.6 g) ; remaining procedure was repeated as above.

Physical Measurement :

Magnetic measurements were made on the solid samples at room temperature for all the complexes and Co(II), Ni(II), and Cu(II) complexes were studied from room temperature to liquid-nitrogen temperature with Gouy balance using mercury tetrathiocyanato cobalt(II) as magnetic susceptibility standard at Bhabha Atomic Research Centre, Bombay. Diamagnetic corrections were calculated by the method given in the literature[11], visible and ultraviolet spectra of the ligand and the complexes were recorded on Beckman DU-2 spectrophotometer in specpure chloroform in 1000-250 nm range. Karlzeiss USU-2-p spectrophotometer was used for measurements of reflectance spectra. Infrared spectra of the ligand and the complexes were obtained from Central Drug Research Institute, Lucknow (India). The conductance measurements were made using Toshniwal Conductivity meter in nitrobenzene solution at 25°±1° with a conventional closed type cell.

Results and Discussion

Analytical data and some properties of prepared complexes are reported in Table 1. All complexes are quite soluble in chloroform, nitrobenzene, benzene, DMF and sparingly soluble in ethanol and acetone. Molar conductance values in nitrobenzene in the range between 2-13 ohm^{-1}cm^{2}mole^{-1} are very close to those reported for nonelectrolyte in nitrobenzene solution[12] are reported in Table 1.

Infrared Spectra :

IR spectra (4000-400 cm^{-1}) of the complexes are practically identical. The frequency of some significant band of the free ligand and of the metal complexes are reported in Table 2. The assignments for the frequencies of different groups in the metal complexes corresponding to those considered for ligands have been proposed tentatively and have been arrived at on the basis of literature data[13-16].

Examination of the IR spectrum of the complex shows that phenolic hydrogen is replaced by metal because the band at 2900 cm^{-1} due to hydroxyl group of oximinate moiety appears more or less at the same position in the ligand at the complexes and 3100 cm^{-1} peak of the phenolic OH disappear in the complexes.

Magnetic Measurements :

Variable temperature data (Table 3) suggest that the Cu(II) complex may be slightly antiferromagnetic, the high-spin Ni(II) species feebly ferromagnetic. The behaviour of Co(II), Fe(II), Fe(III) are consistent with pseudooctahedral geometries with $^{4}T_{1g}$, $^{5}T_{2g}$ and $^{6}A_{1g}$ ground states respectively.

The diamagnetism of Pd(II)(HMMCO)$_2$ indicates that it is square planar.

TABLE 1—ANALYTICAL DATA, COLOURS, MOLAR CONDUCTANCE IN NITROBENZENE AND μ_{eff} AT ROOM TEMPERATURE

No.	Complex	M% found (reqd)	C% found (reqd)	H% found (reqd)	N% found (reqd)	Colour	M*	μ_{eff}B.M. (295°K)
1.	Cu(HMMCO)$_2$3H$_2$O	10.23 (9.32)	62.15 (59.87)	5.21 (5.57)	4.18 (4.10)	Buff (Brown)	2.35	1.92
2.	Ni(HMMCO)$_2$2H$_2$O	8.29 (8.91)	55.70 (61.94)	5.17 (5.46)	3.82 (4.25)	Light green	3.6	3.03
3.	Co(HMMCO)$_2$3H$_2$O	9.35 (8 70)	60.60 (60.27)	5.84 (5.61)	4.54 (4.15)	Cream	13.5	4.96,
4.	Fe(III)(HMMCO)$_2$6H$_2$O	6.04 (5.52)	62.90 (60.60)	5.52 (5.94)	3.96 (4.15)	Dark violet	—	6.01
5.	Fe(II)(HMMCO)$_2$5H$_2$O	8.01 (7.86)	59.82 (57.48)	5.32 (5.91)	4.47 (3.94)	Dark violet	—	5.70
6.	Pd(II)(HMMCO)$_2$	15.47 (15.70)	60.72 (60.89)	5.33 (5.32)	4.20 (4.17)	Orange yellow	12.9	Diamagnetic

* Molar conductance M(ohm^{-1}, cm^{2}.mol.$^{-2}$) in $1\times10^{-2}M$ solution of Nitrobenzene at 25°.

TABLE 2—INFRARED SPECTRAL DATA (4000-400 cm^{-1}) OF LIGAND AND CHELATES

HMMCO	Cu(II)	Ni(II)	Co(II)	Fe(III)	Fe II)	Pd(II)	Assignment
$2900_{m,Bd}$	$2900_{m,Bd}$	$2900_{m,Bd}$	$2870_{m,Bd}$	$2900_{m,Bd}$	$2880_{m,Bd}$	2900	OH of NO—H stretching
1620_{s}	1600_{s}	1600_{s}	1590_{s}	1600_{s}	1600_{s}	1600	C=N Stretch
940_{s}	935_{s}	930_{s}	920_{s}	925_{s}	925_{s}	950_{Bd}	N—O Stretch
1250_{s}	1250_{s}	1250_{s}	1250_{s}	1250_{s}	1250_{s}	1250_{s}	
1300_{s}	1330_{s}	1325_{s}	1320_{s}	1320_{s}	1310_{s}	1320_{s}	C—O Stretch
3100	—	—	—	—	—	—	OH Phenolic
—	$3390_{m,Bd}$	$3400_{m,Bd}$	$3420_{m,Bd}$	$3400_{m,Bd}$	$3380_{m,Bd}$	—	Lattice water
—	$500_{m,s}$	$495_{m,s}$	490_{m}	$510_{m,s}$	$505_{m,s}$	$580_{m,Bd}$	M—N
—	$550_{m,s}$	545_{m}	540_{m}	$540_{m,s}$	$545_{m,s}$	$515_{m,Bd}$	M—O

m = medium ; s = sharp ; Bd = Broad

Electronic Spectra :

The electronic spectral data for ligand field transition are summarised in Table 4. The spectra of complexes show a group of three or more bands in the 28-33 kK range (not included in Table 4) which can be assigned as $\pi \rightarrow \pi^*$ or ligand-metal transition. The electronic absorption spectra of these complexes in chloroform solution are not similar to the diffused reflectance spectra in many cases, and indicate a shift to lower energy, this probably due to solvolitic effect of chloroform on the ligand molecule bonded to the metal ion.

A broad band for $Cu(HMMCO)_2 3H_2O$ at 13 kK (Table 4) suggests distorted octahedral geometry[17]. Distorted octahedral species of Cu(II) complexes are also characterized by the presence of two main absorption bands near 10.50 kK and 14.00 kK[18].

The electronic spectra of the Ni(II) complex (Table 4) resemble those of other polymeric octahedral nickel(II) complexes[20,21] and are different from those of tetrahedral[19,20,27] or planar[22] nickel(II) complexes. Therefore, octahedral geometry may be assigned to the $Ni(HMMCO)_2 2H_2O$.

The electronic spectrum of Co(II) complex (Table 4) is consistent with a very broad low intensity band in the 10.5 kK region and two bands in the 16-19 kK range. A shoulder also appears in the 21.3 kK region, this region is screened by the intense charge-transfer band exhibited in the 25 kK region, and probably the shoulder is due to transition essentially d-d in character. The spectrum resembles those of Co(II) complexes in octahedral environment.

TABLE 3—MAGNETIC DATA AT DIFFERENT TEMPERATURES

$Cu(HMMCO)_2 3H_2O$ $\theta = +15°K$			$Ni(HMMCO)_2 H_2O$ $\theta = -25°K$			$Co(HMMCO)_2 3H_2O$ $\theta \doteq 20°K$		
Temp. (K)	$\chi_{Cu} \times 10^6$ (erg $G^2 mole^{-1}$)	μ_{eff} (BM)	Temp. (K)	$\chi_{Ni} \times 10^6$ (erg $G^2 mole^{-1}$)	μ_{eff} (BM)	Temp. (K)	$\chi_{Co} \times 10^6$ (erg $G^2 mole^{-1}$)	μ_{eff} (BM)
294.5	1,571	1.92	295.0	3,913	3.03	294.5	10,291	4.96
238.0	1,891	1.90	270.0	4,435	3.09	280.8	10,089	4.95
195.5	2,244	1.87	240.3	4,962	3.10	246.2	12,079	4.88
185.4	2,268	1.83	217.0	5,535	3.09	217.0	13,369	4.82
153.2	2,631	1.80	183.0	6,512	3.13	185.4	15,389	4.7
120.0	3,340	1.79	147.0	8,652	3.19	150.4	18,683	4.75
92.0	4,350	1.79	108.0	12,236	3.25	104.2	26,925	4.74

$\mu_{eff} = 2.83\sqrt{\chi_A T}$ BM.

χ_A = susceptibility correction for the presence of dimagnetic component.

TABLE 4—ELECTRONIC SPECTRAL DATA OF COMPLEXES

Complex	Absorption spectra in chloroform (nm)	Reflectance spectra (nm)	Assignments
$Cu(HMMCO)_2 3H_2O$	870	900	$^2B_{1g} \rightarrow {}^2A_{1g}$
	750	800	
	650		$^2B_{1g} \rightarrow {}^2B_{2g}$
	560	550	$^2B_{1g} \rightarrow {}^2E_g$
	420	450	C→T
$Ni(HMMCO)_2 2H_2O$	905	910	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$
	560	570	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$
	480	480	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$
	400	400	
$Co(HMMCO)_2 3H_2O$	950	920	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$
	640	625	$^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$
	540	530	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$
	470	450	
$Fe(III)(HMMCO)_2 6H_2O$		500	$^6A_{1g} \rightarrow {}^4T_{1g}$
$Fe(II)(HMMCO)_2 5H_2O$		830	$^5T_{2g} \rightarrow {}^5E_g$
		520	C→T.
		400	
$Pd(II)(HMMCO)_2$	400		d—d
	370		
	355		
	325		

Fe(II) complex shows a strong charge transfer band at 19 kK-25 kK region and a broad d-d band near 12 kK (Table 4) which suggest high spin octahedral geometry[23].

Fe(III) complex shows very broad band at about 20 kK and shoulder appears at about 23 kK (Table 4). This favours an octahedral symmetry for the complex[24].

The planar configuration of Pd(II)(HMMCO)$_2$ is supported by electronic spectra[8] (Table 4.)

Acknowledgements

Thanks are due to Prof. K. N. Munshi, Head, Department of Chemistry, Nagpur University, Nagpur for the requisite facilities. One of the authors (N. S. B.) is grateful to the U. G. C. for award of a Junior Research Fellowship.

References

1. M. Boftelsky and E. Jungries, *J. Inorg. Nuclear Chem.*, 1956, 3, 38.
2. C. F. Liu and C. H. Liu, *J. Amer. Chem. Soc.*, 1969, **83**, 2515.
3. B. C. Haldar, *J. Indian Chem. Soc.*, 1974, **51**, 224.
4. Asha Kapahi, K. B. Pandeya and R. P. Singh, *Indian J. Chem.*, 1976, **14A**, 444.
5. A. Chakrovorty, *Annual Convention of Chemists*, 1973, Dec. 20-30, Calcutta.
6. B. K. Deshmukh and R. B. Kharat, *J. Indian Chem. Soc.*, 1976, **53**, 1067.
7. B. K. Deshmukh and R. B. Kharat, *Indian J. Chem.*, 1976, **14A**, 214.
8. B. K. Deshmukh and R. B. Kharat, *J. Inorg. Nuclear Chem.*, 1977, **39**, 165.
9. Narayan S. Bhave and R. B. Kharat, Communicated to *Thermochemica Acta*
10. B. K. Deshmukh, C. N. Vyas and R. B. Kharat, *J. Indian Chem. Soc.*, 1975, **52**, 385.
11. B. N. Figgis and D. J. Martin, *Inorg. Chem.* (Washington), 1966, **5**, 100.
12. Sutton, *Aust. J. Chem.*, 1959, **12**, 122.
13. J. Charalanbons and M. J. Frazer, *J. Chem. Soc.*, 1968, **10A**, 2361.
14. G. C. Percy and D. A. Thornton, *J. Inorg. Nuclear Chem.*, 1972, **34**, 3357, 3369.
15. K. K. Ramaswamy, C. I. Bose and D. N. Sen, *Indian J. Chem.*, 1967, **5**, 156.
16. Miss P. C. Trivedi and B. C. Haldar, *J. Indian Chem. Soc.*, 1973, **50**, 81.
17. M. Kelton, A. B. P. Lever and B. S. Ramaswamy *Can. J. Chem.*, 1970, **48**, 3185.
18. J. I. Bullock and S. L. Jones, *J. Chem. Soc. (A)*, 1971, 2351.
19. N. S. Gill and R. S. Nyholm, *J. Chem. Soc.*, 1959, 3997.
20. D. M. L. Goodgame, M. Goodgame, M. A. Hitchman and M. J. Weeks, *J. Chem. Soc. (A)*, 1966, 1769.
21. K. C. Patel, *J. Coord. Chem.*, 1975, **5**, 13.
22. J. H. Nelson and R. O. Ragsdale, *Inorg. Nuclear Chem. Letters*, 1967, **3**, 585.
23. C. J. Ballhausen in "Introduction to Ligand Field Theory", McGraw Hill, New York, 1962 p. 257.
24. P. Singh, V. Singh, B. P. Singh, S. P. Pokharyal and R. P. Mahesh, *J. Indian Chem. Soc.*, 1976, **53**, 355.