Asian Journal of Chemistry Vol. 9, No. 3 (1997), 541–543

NOTE

Synthesis, Spectral and Thermal Studies of Some Divalent Metal Complexes with 8-Acetyl-7-Hydroxy-4-Methyl Coumarin Oxime/Hydrazone†

G.P. POKHARIYAL*, BABU LAL‡ and V.K. RASTOGI‡
Department of Chemistry
M.M. College, Khekra-201 101, India

In the present work some divalent transition metal complexes of biologically active ligands are synthesised and characterised.

The present paper describes the synthesis and characterisation of the Co(II), Cu(II), Pd(II), Zn(II) and Cd(II) complexes of 8-acetyl-7-hydroxy-4-methyl coumarin oxime/hydrazone. The empirical composition of the complexes has been confirmed on the basis of analytical data (Table-1). The molar conductance values of 10^{-3} M solutions of the complexes (5.6–11.2 $\text{ohm}^{-1}\ \text{cm}^2\ \text{mol}^{-1}$) in DMF showed them to be non- electrolytic in nature. The compounds were found to be soluble only in methanol, ethanol, dimethyl sulphoxide and dimethyl formamide.

The infrared spectra of 1 : 2 complexes exhibited a broad band in the region 3400–3200 cm^{-1} indicating the presence of coordinated water[1] excepting Pd(II) complexes. The strong band at (1025–1018 cm^{-1}) in the spectra of ligand is assigned to ν(C—O) vibration of the phenolic OH group, which is shifted to higher frequencies in the range (1060–1025 cm^{-1}) in the spectra of metal complexes. In addition to this the spectra of ligands show a band in the region (1320–1300 cm^{-1}) due to OH vibration of the phenolic OH group[2]. These bands shift to lower frequences in the spectra of corresponding metal complexes, which suggests that the metal binds with the *ortho* hydroxy phenolic oxygen. The sharp bands due to ν(C═N) in the region 1635–1620 cm^{-1} are located at slightly lower frequencies in the corresponding metal complexes, indicating bonding through the azomethine nitrogen. Similar small lowering of ν(C═N) also reported in literature[3-5]. In the far infared spectra of the complexes, the bands at 450–410 and 525–500 cm^{-1} can be assigned to ν(M—O) and ν(M—N) vibrations[6] respectively.

The electronic spectra of Co(II) complexes show three bands around *ca.* 8,300,

---

*For correspondence : Sulbha Niwas, Jain College Road, Khekra-201101 (U.P.)

†Presented in the 31st Annual Convention of Chemists held at Banaras Hindu University, Varanasi during 21–24 Dec. 1994.

‡Department of Physics, Lajpat Rai Post-Graduate College, Sahibabad-201005, India.

17,000, 20,000 and 34,000 cm^{-1} which may be assigned to the spin-allowed transitions $^4T_{1g}$ (F)→$^4T_{2g}(\nu_1)$, →$^4A_{2g}$ (F)(ν_2)→$^4T_{1g}$ (P)(ν_3) and charge transfer respectively characteristic of octahedral geometry[7, 8]. Magnetic moment of Co(II) complexes was found to be 4.52–4.54 BM which is characteristic of high spin octahedral Co(II) species.

TABLE-1

ANALYTICAL AND PHYSICAL DATA OF METAL COMPLEXES

Compound	Analysis %, Found/(Calcd.)				Mol. Wt.
(Colour, Decomp. Temp (°C))	M	C	H	N	Found/(Calcd.)
$[Co(C_{12}H_{10}NO_4)_2{\cdot}2H_2O]$	10.46	51.40	4.25	4.94	524.00
(Brown, 281)	(10.54)	(51.53)	(4.29)	(5.00)	(558.90)
$[Cu(C_{12}H_{10}NO_4)_2{\cdot}2H_2O]$	11.09	51.00	4.21	4.94	533.00
(Green, 274)	(11.27)	(51.10)	(4.25)	(4.97)	(563.54)
$[Pd(C_{12}H_{10}NO_4)_2]$	18.50	50.40	3.44	4.81	535.00
(Yellow, 290)	(18.65)	(50.49)	(3.50)	(4.90)	(570.40)
$[Zn(C_{12}H_{10}NO_4){\cdot}2H_2O]$	11.45	50.45	4.16	4.81	533.00
(White, 263)	(11.56)	(50.94)	(4.24)	(4.95)	(565.37)
$[Cd(C_{12}H_{10}NO_4)_2{\cdot}2H_2O]$	18.22	47.00	3.82	4.45	580.00
(White, 265)	(18.36)	(47.05)	(3.92)	(4.57)	(612.40)
$[Co(C_{12}H_{11}N_2O_3)_2{\cdot}2H_2O]$	10.46	51.59	4.56	10.01	524.00
(Brown, 283)	(10.58)	(51.71)	(4.67)	(10.05)	(556.90)
$[Cu(C_{12}H_{11}N_2O_3)_2{\cdot}2H_2O]$	11.20	51.16	4.54	9.83	542.00
(Green, 272)	(11.31)	(51.28)	(4.63)	(9.93)	(561.54)
$[Pd(C_{12}H_{11}N_2O_3)_2]$	18.22	50.53	3.80	9.74	544.00
(Yellow, 292)	(18.72)	(50.67)	(3.87)	(9.85)	(568.40)
$[Zn(C_{12}H_{11}N_2O_3)_2{\cdot}2H_2O]$	11.40	51.05	4.52	9.84	546.00
(White, 256)	(11.60)	(51.12)	(4.61)	(9.94)	(563.37)
$[Cd(C_{12}H_{11}N_2O_3)_2{\cdot}2H_2O]$	18.20	47.02	4.18	9.04	580.00
(White, 263)	(18.41)	(47.18)	(4.26)	(9.17)	(610.40)

The electronic spectra of Cu(II) complexes show a broad unsymmetrical absorption in the visible region having maxima in the region of 17850–16000 cm^{-1}. This absorption corresponds to the transition ^2E_g→$^2T_{2g}$ and characteristic of tetragonally distorted octahedral Cu(II) complexes[9, 10].

The electronic spectra of Pd(II) complexes exhibit two bands in the regions of 17800–17200 and 26000–24800 cm^{-1} corresponding to the transitions $^1A_{1g}$→$^1A_{2g}$ and →$^1B_{1g}$ respectively. These two bands are characteristic of square-planar geometry in palladium complexes[11].

The zinc(II) and cadmium(II) complexes are diamagnetic as expected for d^{10} configuration.

The thermal behaviour of all the complexes is almost identical except of the palladium(II) complexes, hence only that of $[Co(C_{12}H_{10}NO_4)_2{\cdot}2H_2O]$ complex is being given. The DTG curve indicates the decomposition in three steps, 45–70°C, 110–135°C and 140–240°C. The loss of first water molecule occurred at

56°C with a mass of about 3.00% (theoretical 3.22%). The second water molecule was lost at 128°C (mass loss 6.33%; theoretical 6.44%). The organic moiety starts decomposing after 140°C. The formation of cobalt oxide and carbon dioxide was indicated at 236°C with loss in mass 86.00% (theoretical 86.58%). Cobalt oxide was found to be the end product at 290°C and above.

All the chemicals and solvents used were of AnalaR and GR grade. 8-Acetyl-7-hydroxy-4-methyl coumarin (AHC) was prepared by the reported procedure[12, 13]. The Schiff bases of AHC have been obtained by the standard procedures[14].

Preparation of metal complexes

A general method involving the metal ion template reaction has been applied for the synthesis of metal derivatives with AHC Schiff bases. A solution of metal chloride (1 mmol) and the ligand (2 mmol) in minimum amount of ethanol was shaken, crystals of the complexes separated were filtered, washed with ethanol, ether and dried *in vacuo* over P_2O_5

REFERENCES

1. I. Gamo, *Bull. Chem. Soc.*, **34,** 760 (1961).
2. S.J. Gruber, C.M. Harris and E. Sinn, *J. Inorg. Nucl. Chem.*, **30,** 1805 (1968).
3. D.K. Rastogi and P.C. Pachauri, *Indian J. Chem.*, **15A**, 748 (1977).
4. L.W. Lano and C.T. Taylor, *J. Coord. Chem.*, **2,** 195 (1973).
5. L.T. Spencer and C.T. Taylor, *Inorg. Chem.*, **10,** 240 (1971).
6. J.R. Ferraro, Low Frequency Vibrations of Inorganic and Coordination Compounds, Plenum Press, New York.
7. Mathews and R.A. Walton, *Inorg. Chem.*, **10,** 1443 (1971).
8. B.N. Figgis and J. Lewis, *Prog. Inorg. Chem.*, **6,** 97 (1964).
9. A.B.P. Lever, Inorganic Spectroscopy, Elsevier Amsterdam (1968).
10. Nishiday and S. Kida, *Coord. Chem. Rev.*, **27,** 275 (1979).
11. B.J. Hathaway and D.E. Billing, *Coord. Chem. Rev.*, **5,** 1734 (1971).
12. A. Russel and J.P. Frye, *Org. Synth.*, **3,** 281 (1955).
13. P. Singh, G.P. Pokhariyal, V. Singh, C. Singh and G.K. Agarwal, *Acta Chem. Acad. Sci.*, **104,** 63 (1980).
14. A.I. Vogel, A Text Book of Practical Organic Chemistry, ELBS, London, p. 341 (1972).

(*Received:* 4 November 1996; *Accepted:* 3 February 1997) AJC-1245