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Preparation and Spectral Properties of Copper(II), Iron(II) and Iron(III) Complexes of 1-(2′-Hydroxybenzyl)-2-(2′-hydroxyphenyl)benzimidazole

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Abstract

A series of binuclear square planar complexes of copper(II) with hydroxy bridges and iron(II) and iron(III) binuclear octahedral complexes have been synthesized and studied by IR, electronic, vibrational spectral techniques and also by physicochemical techniques such as magnetic, thermal and conductance studies. The absorption bands appearing in the region greater than 16 000 were attributed to $n \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$ and $\sigma \rightarrow \sigma^*$ transitions within the ligand molecule, and metal to ligand charge transfer transitions. The ligand field bands were not assigned for the present complexes, because all the ligand fields bands were obscured by $\pi \rightarrow \pi^*$ transitions and charge transfer bands of high intensity. The copper(II) complexes were assumed to be square-planar complexes since a significant absorption band was detected in the range below 17 000 cm^{-1}. A strong IR band appearing around 1480 cm^{-1} was assigned to the C=N stretching mode, and it is observed that this band was shifted to lower frequencies upon coordination. A magnetic moment lower than 1.9 BM for all copper(II) complexes is consistent with a square-planar geometry. The values for iron(II) and iron(III) are somewhat less than the reported values, which may be due to metal–metal interaction. Conductance studies show the existence of both ionic and non-ionic complexes.

Introduction

In general, metal ions bind to proteins through functional groups that are substituents on the macropolypeptide backbone [1]. For example metal ions can interact with the imidazole nitrogen of the histidine, the phenolic oxygen of tyrosine, the carboxylic oxygen of the glutamic acid, the amine nitrogen of lysine or the imine nitrogen of argenine. Metal–protein binding also involves multidentate coordination to two, three or more of the coordination positions of the metal ion. Good models for protein bound metals would then be complexes with multidentate ligands with phenolic oxygen and imine-like nitrogen donars e.g. tetradentate Schiff's base complexes. Complex compounds of transition metal ions with imidazole, benzimidazole and their substituted ligands have been studied extensively [2–6].

The benzimidazole nucleus and its derivatives are known to play an extremely important part in the structures and functioning of a number of biologically important molecules, generally by virtue of their being coordinated to a metal ion. Thus dimethylbenzimidazole supplies one of the five nitrogen atoms coordinated to Co(III) in vitamin B_{12} and several of its derivatives. There is a strong evidence that in protein containing heme as a prosthatic group, for example haemoglobin, myoglobin, cytochrome *c*, imidazole N atom, and probably in histidine, residues of the protein are coordinated to the iron atom.

Current interest in the study of Cu(II) complexes with imidazole ligands has emphasized the importance of the bond between copper and imidazole from histidine residues of blue copper proteins and non-blue proteins [7–9]. The X-ray structural studies of popular plastocyanine [10] and pseudomones of *Aerdginos azurin* [11] have revealed that imidazoles from histidine residues of these proteins are involved in the bonding of copper(II) at the active site. It is also known that the imidazole acts as a bridging ligand at the active site of the bovine erythrocyte superoxide dismutase which catalyses the conversion of superoxide to peroxide [12, 13]. The study of a series of model Cu(II) complexes has suggested a distorted square-pyramidal configuration at the copper site in galactose oxidase in oxyhemocyanine and magnetically coupled ion pairs behind to constitute type III copper [14]. Recently, many low molecular weight complexes of Cu(II) containing imidazole ligand(s) have been proposed as models of active site of copper proteins [15–17]. The synthesis and characterization of complexes of uranium(VI) and cerium(IV) with 1-(2′-hydroxybenzyl)-2-(2′-hydroxyphenyl)benzimidazole (HBHPB)

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have been reported earlier [18]. In continuation of our earlier work, herein we report our investigations on the synthesis, spectral, magnetic, thermal and conductance studies of some of the complexes of copper(II), iron(II) and iron(III) with HBHPB.

Experimental

Copper(II) Complexes

Copper(II) complexes with various anion combinations (acetate, chloride, nitrate, sulphate) were prepared by refluxing the respective metal salts (0.003 mol) with hot methanolic solution containing 0.002 mol of ligand. After refluxing for 3 h the contents were concentrated under vacuum and cooled until the solid separated out. The separated solid was collected by filtration and washed with aqueous methanol and water to remove excess ligand and excess metal respectively. The product was dried under vacuum for 24 h.

Iron(II) Complexes

These complexes were prepared by treating 0.003 mol of metal solution (methanol) with 0.002 mol of ligand solution. After refluxing for 6 h the resulting brown solution was concentrated and cooled. The solid that separated was washed with aqueous methanol and water and dried under vacuum for 24 h.

Iron(III) Complexes

These complexes are prepared as described above using iron(III) salts.

Spectral Measurements

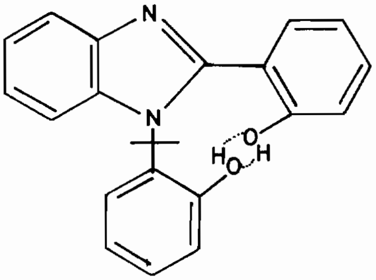
Ultra violet and visible spectra were recorded on a Pye Unicam SP-100 UV–Vis double beam spectrophotometer at room temperature. Infrared spectra covering the 200–4000 cm^{-1} range were measured on a Perkin-Elmer 983 G grating spectrophotometer at room temperature. The magnetic susceptibilities of all complexes were determined by the Guoy method using $Hg[Co(SCN)_4]$ as calibrant at room temperature. The thermal stabilities of the complexes were determined by recording TG and DTA curves of the complexes on a Nlvac-Sinku-Rikuta 1500 Thermal Analyser simultaneously in one operation. A Systronics direct reading conductivity bridge provided with a conventional dip-type platinum blacked electrodes was used to examine the behaviour of the complexes in solution.

Physical Properties

All complexes are crystalline, coloured substances except iron(II) and iron(III) chloride complexes which are colourless. The copper(II) acetate and nitrate complexes are green in colour while sulphate and chloride complexes are red and black coloured solids respectively. The remaining iron(II) and iron(III) complexes are brown coloured compounds. All the complexes are insoluble in water but soluble in organic solvents.

Synthesis and Spectral Characteristics of the Ligand

1-(2′-hydroxybenzyl)-2-(2′-hydroxyphenyl)benzimidazole was prepared according to Subba Rao and Ratnam [19] with slight modifications. The IR spectra measured in KBr pellets showed a peak at 1480 cm^{-1} which can be assigned to (C=N) stretching frequency. A broad peak at 3500–3700 cm^{-1} corresponding to the free phenolic –OH is not observed, instead a peak at 3400 cm^{-1} confirms the intramolecular hydrogen bonding of the two OH groups [20–22]. Based on the above observations the structure of the ligand can be represented as



Anal. Calc.: C, 75.94; H, 5.61; N, 8.86. Found: C, 75.80; H, 5.76; N, 8.72%.

Results and Discussion

Physicochemical and Spectral Characters of Complexes

Analytical data of all complexes are presented in Table I. The ligand has two potential sites for coordination, the pyridine nitrogen and the phenolic oxygen atom. Since no change was observed in the pH of the free ligand solution and its solution after complexation, it can be inferred that the ligand has not deprotonated. This fact is further supported by the IR spectra where the shift corresponding to the –OH stretching vibration is not observed.

Infrared Spectra

The band at 1480 cm^{-1} in the free ligand assigned to the ν(C=N) stretching vibration is lowered to 1470 cm^{-1} in the case of all copper complexes. A broad absorption band centred around 3300 cm^{-1} attributed to the intramolecular hydrogen bonded –OH [20–22] groups is not shifted on complexation. The ν(C–O) frequency vibration observed at 1240 cm^{-1} in the free ligand, remains at the same position indicating that phenolic oxygen [23] is not participating in coordination. Moreover, in all complexes, and in the free ligand, a sharp band due to the bend-

TABLE I. Analytical, Conductance and Magnetic Susceptibility Data

Complex	Carbon(%)		Hydrogen(%)		Nitrogen(%)		Metal(%)		Molecular conductance		Magnetic moment μ_{eff} (BM)
	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Solvent	*m*	
$[Cu(OH)LH_2O]_2SO_4 \cdot H_2O$	49.80	50.90	4.14	4.24			13.50	13.45	DMF	80.00	1.62
									DMSO	69.00	
									MeOH		
$[Cu(OH)LCl]_2 \cdot 2H_2O$	54.59	53.33	4.00	4.20	6.00	6.20	14.09	14.11	DMF	55.00	1.71
									DMSO	45.00	
									MeOH		
$[Cu(OH)LOAc]_2 \cdot 2H_2O$	50.94	50.68	3.90	4.00	6.00	5.91	13.50	13.41	DMF	0.00	1.66
									DMSO	0.00	
									MeOH	0.00	
$[(Cu(OH)L)_2NO_3]NO_3 \cdot 4H_2O$	48.43	48.53	3.80	3.84	8.31	8.49	12.81	12.84	DMF	108.00	1.73
									DMSO	70.00	
									MeOH	90.00	
$[Fe(OH)L_3SO_4]_2 \cdot 6H_2O$	60.99	61.53	4.58	4.78	7.72	7.51	4.93	4.91	DMF	242.00	5.10
									DMSO	170.00	
									MeOH	30.00	
$[Fe(SO_4)(H_2O)_2]_2$	58.50	58.60	4.79	4.88	6.55	6.83	6.75	6.80	DMF	162.00	5.12
									DMSO	70.00	
									MeOH	40.00	
$[Fe(OH)L_2(NO_3)_2]_2 \cdot 4H_2O$	57.56	55.00	4.15	4.20	10.08	9.70	6.43	6.45	DMF	21.73	4.95
									DMSO	7.60	
									MeOH	20.00	
$[FeL_4Cl_2]Cl$	66.92	67.32	4.58	4.48	7.92	7.85	3.89	3.92	DMF	133.00	4.34
									DMSO	210.00	
									MeOH	90.00	
$[Fe(OH)L_2OAc]_2 \cdot 4H_2O$	54.99	55.91	4.31	4.30	6.49	6.52	6.48	6.49	DMF	35.00	5.32
									DMSO	25.00	
									MeOH	40.00	
$[FeL_4(OAc)_2] \cdot 2H_2O$	65.20	65.17	4.59	4.61	7.59	7.60	3.75	3.78	DMF	29.00	5.21
									DMSO	17.00	
									MeOH	35.00	
$[FeL_4Cl_2] \cdot 2H_2O$	66.99	67.32	4.52	4.76	6.59	6.73	3.89	3.91	DMF	54.35	5.41
									DMSO	49.20	
									MeOH	45.00	
$[FeL_4(NO_3)_2] \cdot 2H_2O$	64.86	64.90	4.56	4.59	9.50	9.46	3.59	3.77	DMF	43.59	5.19
									DMSO	35.43	
									MeOH	30.00	

ing mode of the phenolic –OH group is observed at 1390 cm^{-1} confirming the non-participation of the –OH group in coordination.

Sharp bands at 1130 and 970 cm^{-1} which are due to ionic sulphate groups [24, 25] are recognized in the case of copper(II) sulphate complexes. The iron(III) sulphate complex shows a peak at 1125 that could be attributed to the monodentate sulphato groups [24–26], whereas in the iron(II) sulphate complex peaks at 1070 and 1170 cm^{-1} are attributed to the bridged sulphato groups. This assignment is in accordance with that of earlier workers [27, 28].

A peak at 1380 cm^{-1} is attributed to the ionic nitrate group in the case of copper(II) nitrate. However other peaks at 1500, 1290, 810 and 740 cm^{-1} were also observed which may be due to the coordinated nitrate group. Thus it can be concluded that one of the two nitrate groups is coordinated, while the other is free from coordination. This fact is also supported by the conductance study where the complex behaves as a 1:1 electrolyte. In the case of Fe(II) and Fe(III) nitrate complexes, the peaks at 1500, 1280, 800 and 740 cm^{-1} are attributed to the modes of coordinated nitrate groups. The coordina-

TABLE II. Selected IR Spectral Data (cm^{-1})

Complex	ν(OH) stretch	ν(C=N)	ν(C–O)	ν(OH) bend	NO_3^-	SO_4^{2-}	CH_3COO^-	M–N	M–Cl
Ligand	3300(br)	1480(sh)	1240(sh)	1390(sh)					
$(CuOHLH_2O)_2SO_4 \cdot H_2O$	3280(br)	1470(sh)	1240(sh)	1385(sh)		1130(sh) 970(sh)		390 360	
$(CuOHLCl)_2 \cdot 2H_2O$	3280(sh)	1470(sh)	1240(sh)	1400(sh)				390 360	320
$[Cu(OH)L(OAc)]_2 \cdot 2H_2O$	3300(br)	1470(sh)	1240(sh)	1400(br)			1550(sh) 1430(sh)	390 360	
$[(Cu(OH)L)_2NO_3]NO_3 \cdot 4H_2O$	3300(br)	1470(sh)	1240(br)	1400(sh)	1380(sh) 1500(sh) 1290(m) 810(w) 740(sh)			390 360 350	
$[Fe(OH)L_3SO_4]_2 \cdot 6H_2O$	3280(br)	1470(sh)	1240(br)	1390(sh)		1125(sh)		460(sh)	
$[FeL_2SO_4(H_2O)_2]_2$	3320(br)	1470(sh)	1240(br)	1390(sh)		1070(sh) 1170(sh)		450(br)	
$[FeOHL_2(NO_3)_2]_2 \cdot 4H_2O$	3300(br)	1470(sh)	1240(br)	1390(sh)	1500(sh) 1280(sh) 800(m) 740(w)			460(br)	
$[FeL_4Cl_2]Cl \cdot$	3300(br)	1470(sh)	1240(br)	1390(sh)				450(sh) 460(sh)	390 370
$[FeOHL_2OAc]_2 \cdot 4H_2O$	3300(br)	1470(sh)	1240(br)	1390(sh)			1550(sh) 1430(sh)	450(sh) 460(sh) 430(sh)	
$[FeL_4(OAc)_2] \cdot 2H_2O$	3300(br)	1470(sh)	1240(sh)	1390(sh)			1550(sh) 1430(sh)	450(sh) 444(sh) 430(m)	
$[FeL_4Cl_2] \cdot 2H_2O$	3300(br)	1470(sh)	1240(sh)	1390(sh)				450(sh) 440(sh) 420(m)	360 340
$[FeL_4(NO_3)_2] \cdot 2H_2O$	3300(br)	1470(sh)	1240(br)	1400(br)	1500(sh) 1280(sh) 800(m) 740(w)			450(sh) 440(sh) 415(m)	

tion of nitrate groups is further confirmed by the non-ionic nature of the complexes in both DMF and DMSO.

Sharp peaks at 1550 and 1430 cm^{-1} in the case of copper(II), iron(II) and iron(III) acetate complexes [29, 30] are due to the coordination of the acetate group to the metal ion.

A broad and strong band observed in all four complexes of copper around 1100 cm^{-1} which is not present in the ligand is assigned to the binuclear nature. This assignment agrees with that given by Nakamoto [31].

New bands observed in copper(II) complexes around 450–500 cm^{-1} are attributed to M–O bands and bands in the range 350–390 cm^{-1} which are absent in the free ligand are attributed to M–N stretching vibrations [32, 33]. In the case of iron(II) and iron(III) complexes, the M–O stretching modes and M–N stretching bands are observed in the range 500–550 and 450–500 cm^{-1} respectively [34].

Sharp peaks at 970 and 700 cm^{-1} that were observed in copper(II) sulphate and iron(II) sulphate complexes indicate the coordination of water in both of these complexes [35, 36].

Electronic Spectra

The ligand exhibits three electronic transitions at 42000, 34000 and 32000 cm^{-1} due to $n \rightarrow \sigma^*$ or $\sigma \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions respectively [37–42]. In all complexes the transitional band due to $n \rightarrow \sigma^*$ disappears and the $\pi \rightarrow \pi^*$ transitional band moves towards lower energy and the $n \rightarrow \pi^*$ transition moves towards the higher energy side. This is due to the increase in energy of 'π' levels relative to the 'n' levels and is indicative of the involvement of the Schiff's base in coordination.

In addition to the above transitions the copper(II) complexes show absorptions around 14000–15000 cm^{-1} (sulphate, 14800; chloride, 14200; acetate, 14800; nitrate, 14200 cm^{-1}) characteristic of square-planar geometry. These transitions may be assigned to the combination of $^2B_{1g} \rightarrow {}^2A_{1g}$; $^2B_{1g} \rightarrow {}^2B_{2h}$ and $^2B_{1g} \rightarrow E_{1g}$ transitions in D_{4h} symmetry suggesting the square-planar arrangement around the copper(II) ion. The bands around 22000 cm^{-1} may be due to a charge transfer type of transition [43]. Furthermore all copper(II) complexes show bands around 2500 cm^{-1} which is characteristic of a binuclear nature [44, 45].

All iron(II) and iron(III) complexes show bands around 40000 and 35000 cm^{-1} in the UV range indicating interaction of the ligand with the metal ion. Here also it is assumed that the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions overlapped and appeared at 35000, in complexes, whereas the $n \rightarrow \pi^*$ moves towards the low energy side. In addition to the above transitions, iron(III), irion(II) sulphate and nitrate complexes show bands around 13700, 21000 and 12000, 21000 in the visible region respectively. The band at 12000 cm^{-1} in iron(II) complexes assigned to the transition $5E_g \rightarrow {}^5T_{2g}$ and corresponding to iron in a +2 oxidation state [46] is characteristic of high spin octahedral iron(II) complexes [24]. The bands in iron(III) complexes are assigned to $^6A_{1g} \rightarrow {}^4T_{1g}$ (13600), $^6A_{1g} \rightarrow {}^4A_{1g}$, ^4E_g (21000) transitions. These transitions are characteristic of high spin iron(III) octahedral complexes [47].

Conductance Studies

The molar conductance values of the binuclear Cu(II) sulphate (Table I) and Cu(II) nitrate complexes are in the range 30–90, while the molar conductance of copper acetate and chloride complexes is zero, which shows that the former two complexes are 1:1 electrolytes in DMF, DMSO. These values are far below the molar conductance values for 1:2 electrolytes in this solvent (DMF) which are about 130–170 ohm^{-1} cm^2 mol^{-1}. The sulphate, chloride and acetate complexes of iron(II) and (III) behave as 1:3 and 1:2 electrolytes in DMF respectively, whereas the remaining iron(II) and iron(III) nitrate complexes are non-electrolytes. The reason for some complexes behaving as electrolytes may be due to cleavage of the hydroxy bridges between the two metal ions.

Magnetic susceptibility Data

The magnetic moments in Bohr magnetons are presented in Table I. All copper(II) complexes are paramagnetic and have magnetic moments corresponding to one unpaired electron. Magnetic moment values of the binuclear copper(II) complexes at room temperature, are lower than the expected spin only value for one unpaired electron on each copper(II) ions. This may be due to the antiferromagnetic interaction between two copper ions [48]. The low μ_{eff} (1.65) values of the $Cu(L\text{-}H)_2(H_2O)$ binuclear complex was attributed earlier to the metal–metal or super exchange interactions by Yamada *et al.* [49]. The iron(II) and iron(III) complexes have somewhat lower μ_{eff} values than the expected values for high spin complexes, but are in the range reported in the literature.

Thermal Analysis

Extrapolation of the farily linear portions of the pyrolysis curves at high and low temperatures, and taking the intersection point as decomposition temperature, leads to the following thermal stability in the case of iron(II) and iron(III) complexes; acetate > nitrate > chloride > sulphate.

Conclusions

Based on the above investigations it can be concluded that copper(II) complexes are square-planar, while iron(II) and iron(III) complexes are high spin octahedral.

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References

1 B. L. Vallee and W. E. C. Wacker, in H. Neurth (ed.), 'The Proteins', Vol. 5, Academic Press, New York, 1970.
2 S. P. Gosh, *J. Indian Chem. Soc.*, *28*, 710 (1951).
3 S. P. Gosh, H. M. Gosh, *J. Indian Chem. Soc.*, *33*, 894 (1956).
4 G. Goodgame and F. A. Cotton, *J. Am. Chem. Soc.*, *84*, 1543 (1962).
5 D. M. L. Goodgame and M. Goodgame, *Inorg. Chem.*, *4*, 139 (1965).
6 J. Reedijk, *J. Inorg. Nucl. Chem.*, *35*, 239 (1973).
7 A. R. Amud Sen and J. Whelan, *J. Am. Chem. Soc.*, *99*, 6730 (1979).

8 R. Osterberg, *Coord. Chem. Rev., 12*, 309 (1974).

9 Y. Nokao, W. Mori, T. Sakurai and A. Nakahara, *Inorg. Chim. Acta, 55*, 103 (1981).

10 S. J. Lippard, C. L. O'Young, J. C. Devan and R. Lilienthal, *J. Am. Chem. Soc., 100*, 7291 (1978).

11 A. R. Manyk, C. B. S. Murphy and A. E. Martell, *Arch. Biochem. Biophys., 39*, 373 (1955).

12 J. Dehand, J. Jordanoo and F. Keck, *Inorg. Chim. Acta, 21*, 33 (1977).

13 R. Driver and W. R. Walker, *Aust. J. Chem., 21*, 671 (1968).

14 B. N. Figgis and J. Levis, in J. Lewis and R. G. Wilkins (eds.), 'Modern Coordination Chemistry', Interscience, New York, 1960, p. 400.

15 K. Nakamota, 'Infrared and Raman Spectra of Inorganic and Coordination Compounds', 3rd edn., Wiley, New York, 1978, p. 314.

16 J. R. Dyer, 'Applications of Absorption Spectroscopy of Organic Compounds', Prentice Hall, New Jersey, 1965, p. 33.

17 B. J. Hathaway, *J. Chem. Soc., Dalton Trans.*, 1196 (1972).

18 K. M. M. S. Prakash, L. D. Prabhakar and M. C. Chowdary, *Polyhedron*, in press.

19 N. S. Subba Rao and C. V. Ratnam, *Curr. Sci., 24*, 299 (1955).

20 A. Palm and H. Werbin, *Can. J. Chem., 31*, 1004 (1953).

21 R. Bline and D. Hadzi, *J. Chem. Soc., 36*, 45 (1958).

22 L. E. Khoo and E. Frank Smith, *Polyhedron, 1*, 213 (1982).

23 S. S. Satapathy and B. Sahoo, *J. Inorg. Nucl. Chem., 32*, 2223 (1970).

24 K. Nakamoto, 'Infrared and Raman Spectra of Inorganic and Coordination Compounds', 3rd edn., Wiley, New York, 1978, p. 239.

25 B. Singh, B. P. Yamada and R. C. Aggarwal, *Indian J. Chem., 23A*, 441 (1984).

26 B. Singh, R. N. Singh and R. C. Aggarwal, *Indian J. Chem., 23A*, 480 (1984).

27 M. Goodgame and L. I. B. Hains, *J. Chem. Soc.*, 174 (1966).

28 K. Nakamoto, 'Infrared Spectra of Inorganic and Coordination Compounds', Wiley, New York, 1963, p. 164.

29 S. S. Satapathy and B. Sahoo, *J. Inorg. Nucl. Chem., 33*, 1971 (1971).

30 K. S. Bose and C. C. Patel, *J. Inorg. Nucl. Chem., 32*, 1141 (1970).

31 K. Nakamoto, 'Infrared and Raman Spectra of Inorganic and Coordination Compounds', 3rd edn., Wiley, New York, 1978.

32 L. Nakagana and Shimanocchi, *Spectrochim. Acta, 20*, 429 (1964).

33 G. Venkata Reddy, D. Suryarao and M. C. Ganorkar, *Indian J. Chem., 20A*, 194 (1981).

34 C. R. Saha and N. K. Ray, *J. Coord. Chem., 12*, 163 (1983).

35 I. Gamo, *Bull. Chem. Soc. Jpn., 24*, 760 (1961).

36 N. Saha and K. M. Datta, *Indian J. Chem., 20A*, 506 (1981).

37 K. K. Chattergee and B. E. Druglas, *Spectrochim. Acta, 21*, 1625 (1965).

38 D. Heinerj and A. E. Martell, *J. Am. Chem. Soc., 85*, 188 (1963).

39 G. M. Bryant and J. E. Fergusson, *Aust. J. Chem., 24*, 275 (1971).

40 A. Syamala, O. P. Singhal and S. Banergee, *Synth. React. Inorg. Met.,-Org. Chem., 10*, 243 (1980).

41 A. Syamala, O. P. Singhal, *Transition Met.- Chem., 4* (1979); *J. Inorg. Nucl. Chem., 43*, 2821 (1981).

42 A. Syamal and B. K. Gupta, *Indian J. Chem., 23A*, 260 (1984).

43 R. S. Srivatsava, L. D. S. Yadava, R. K. Khare and A. K. Sreevatsava, *Indian J. Chem., 20A*, 516 (1981).

44 M. Kato, H. B. Jonassen and Fanning, *Chem. Rev., 64*, 99 (1964).

45 C. M. Harries and R. L. Martin, *Proc. Chem. Soc.*, 259 (1958).

46 K. S. Siddiqi, M. A. Neyazi and A. A. Zaidi, *Synth. Inorg. Met.- Org. Chem., 11*, 253 (1981).

47 A. K. Rana and J. R. Saha, *Indian J. Chem., 20A*, 929 (1982).

48 K. V. Patel and P. K. Bhattacharya, *J. Chem. Soc., Dalton Trans.*, 359 (1982).

49 S. Yamada, H. Nishikava and T. Tsuchida, *Bull. Chem. Soc., Jpn., 33*, 1278 (1960).