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Synthesis and Spectral Properties of 1-(2′-Methoxybenzyl)-2-(2′-Methoxyphenyl)-Benzimidazole Complexes with Cu(II), Co(II), Mn(II), U(VI) and Ce(IV)

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A series of square planar complexes, copper(II) and interesting binuclear octahedral low spin complexes of cobalt(II), manganese(II) with corresponding anion bridges and octahedral complexes of cerium(IV) sulfate and polynuclear complexes of uranium(VI) phosphate of 1-(2'-methoxybenzyl)-2-(2′-methoxyphenyl)–benzimidazole were synthesized and studied by spectral, magnetic, thermal and conductance studies. 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 1,490 cm^{-1} was assigned to the C=N stretching mode, and it is observed that this band was shifted to lower frequencies upon coordination. The measured magnetic moments support square planar copper(II) and low spin ocatahedral cobalt(II), manganese(II) geometry. As expected the uranium(VI) and Ce(IV) complexes yield diamagnetic susceptibilities. Conductance studies show the existence of both ionic and non-ionic species present in all cases.

INTRODUCTION

Survey of the literature shows existence of low spin octahedral cobalt(II) complexes is rare. With many class of compounds as ligands cobalt(II) is coordinated in high spin octahedral geometry. Very rare instances are observed in the literature where low spin octahedral cobalt(II) complexes are reported by Chakrabarti *et al.*[1] and Prabhakar *et al.*[2]. Benzimidazole class of compounds are reported to form low spin Co(II) complexes as ligands. In continuation of our work with substituted benzimidazoles, we found that in 1-(2′-hydroxybenzyl)-2-(2′-hydroxyphenyl)-benzimidazole the two hydroxyl groups are binded through hydrogen bonding and there by not available for coordination. In the same direction now we undertake the present work to examine the behaviour and availability of $-OCH_3$ groups for coordination with several metal ions. Herein we report the synthesis and spectral properties of 1-(2′-methoxybenzyl)-2-(2′-methoxyphenyl)-benzimidazole (MBMPB) ligand and its complexes with diverse metal ions (Cu(II), Co(II), Mn(II), U(VI) and Ce(IV)).

EXPERIMENTAL

Copper(II) complexes with various anion combinations (acetate, chloride, nitrate) were prepared by refluxing the respective metal salts (0.004 mol) with hot methanolic solution containing (0.003 mol) of ligand. After refluxing for 3 hrs. 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 hrs.

Cobalt(II) complexes from various anion combinations (acetate, chloride, nitrate) were prepared by refluxing the respective metal salts (0.004 mol) with a hot 50 ml methanolic solution containing (0.003 mol) of the ligand. After refluxing for 3 hrs., 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 of ligand and metal, respectively. The product was dried under vacuum for 24 hrs.

The maganese(II), uranium(VI) and cerium(IV) complexes were prepared by treating 0.004 mol of corresponing metal salt solution in 50 ml methanol with 0.003 mol of ligand in 50 ml methanol solution. After refluxing for 4 hrs, the resulting solution was concentrated and cooled. The solid that separted was washed with aqueous methanol and water and dried under vacuum for 24 hrs.

Ultraviolet and visible spectra were recorded on a UVIDEC–340 double beam spectrophotometer at room temperature. Infrared spectra were recorded on a Perkin Elmer–781 spectrophotometer at room temperature. The magnetic susceptibilities of all complexes were determined by a model 155 vibrating sample magnetometer. The thermal stabilities of the complexes were determined by recording TG and DTA curves of the complexes on a ULVAC SINK-RIKUTA 1500 thermal analyser. A systronics direct reading conductivity bridge type CM 82T provided with a conventional di-type platinum blacked electrode was used to examine the behaviour of the complexes in solution.

All complexes are crystalline, coloured, non-hygroscopic substances. The acetate, nitrate and chloride complexes of Cu(II) is black, green and brown in colour respectively. Cobalt(II) complexes were green in colour and manganese(II) complexes were light brown, while those of cerium(IV) and uranium(VI) complexes were yellow. All the complexes are insoluble in water but soluble in organic solvents.

RESULTS AND DISCUSSION

1-(2′-Methoxybenzyl)-2-(2′-methoxyphenyl)-benzimidazole was prepared according to Subbarao *et al.*[3] with slight modification. The IR spectra measured in KBr pellets showed a peak at 1,490 cm^{-1} which can be assigned to (C=N) stretching frequency. Based on the above observations, the structure of the ligand can be represented as

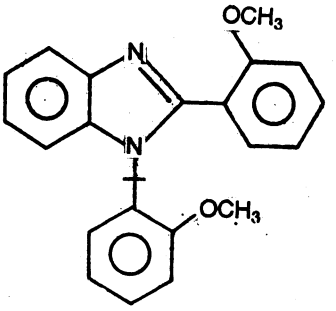

Fig. 1

Anal: Found (Calc)% C 75.2 (76.0); H 5.4 (58); N 7.75 (8.1) (yield 50–60%, m.pt. 149°C)

Complexes of the title ligand with respective metals were formed in MeOH solvent after refluxing for 3 to 4 hrs. and distillation of the excess of the solvent under vacuum. The representative scheme of the formation of complexes is shown below:

$$MX \cdot xH_2O + mL \xrightarrow[\text{2. Reflux 3 hrs}]{\text{1. MeOH}} ML_nX_n(H_2O)_y \cdot xH_2O$$

M = Co(II), Cu(II) Mn(II), Ce(IV)

$X = NO_3^-, Cl^-, OAc^-, PO_4^{3-}$

n = x = y = 0, 1, 3, . . .

Analytical data of all complexes are presented in Table-1. The ligand has two potential sites for coordination, the pyridine nitrogen and methoxyl oxygen.

The band at 1,490 cm^{-1} in the free ligand that can be assigned to the (C=N) stretching vibration is lowered to 1,480–1,470 cm^{-1} in all the complexes. The ν(C–O) vibrtion observed at 1,240 cm^{-1} in the free ligand remains at the same position in all complexes indicating that the methoxyl oxygen[4] is not participating in coordination. This fact is further supported by the characteristic absorption bands observed at 2,830 cm^{-1} and 2,960 cm^{-1} which are assignable for stretching modes of $-OCH_3$ group were remains unchanged in all the complexes studies. Hence it is concluded that the two $-OCH_3$ groups were not participated in coordination. The fall in stretching frequencies from 1,490 to 1,480 cm^{-1} corresponding to the (C=N) of pyridine nitrogen suggest that the pyridine nitrogen is involved in the coordination (Table-2).

A prominent sharp band observed at 1,290 cm^{-1} and 1,390 cm^{-1} in the nitrate omplexes of Cu(II), Co(II) and Mn(II) can be assigned to the coordinated

TABLE 1
ANALYTICAL, CONDUCTANCE AND MAGNETIC SUSCEPTIBILITY DATA

Complex	% Carbon Found (Cal.)	% Hydrogen Found (Cal.)	% Nitrogen Found (Cal.)	% Metal Found (Cal.)	Solvent molar conductance		Magnetic moment μ_{eff} (BM)
$[Cu(NO_3)_2L_2(H_2O)_2]H_2O$	55.00 (56.80)	4.54 (4.94)	8.82 (9.00)	10.5 (10.1)	DMSO Acetonitrile Dioxane *n*–butanol	184.3 119.0 3.96 1.72	1.6
$[CuCl_2L_2(H_2O)_2]H_2O$	60.00 (60.00)	5.40 (5.21)	5.05 (6.30)	14.2 (13.8)	Acetonitrile Dioxane DMSO *n*–butanol	256.4 65.2 58.2 15.2	1.63
$[Cu(OAc)_2L(H_2O)_3]$	57.50 (54.00)	4.23 (5.30)	4.23 (4.80)	11.9 (12.3)	Dioxane Acetonitrile *n*-butanol	— — —	1.66
$[Co(NO_3)L(H_2O)(OH)]_2$	54.10 (52.80)	4.20 (4.60)	8.67 (8.40)	10.6 (11.0)	DMSO Acetonitrile Dioxane *n*–butanol	141.0 601.0 37.8 17.1	2.40
$[Co_2L_3(H_2O)_3(OAc)_2(OH)_2]$	62.50 (61.90)	5.00 (5.40)	5.50 (6.10)	7.2 (8.1)	DMSO Acetonitrile Dioxane *n*–butabol	11.13 214.20 126.00 —	2.40
$[CoCl_2L(H_2O)_2]_2H_2O$	51.00 (50.80)	4.48 (4.80)	4.80 (5.30)	9.3 (9.0)	DMSO Acetonitrile Dioxane *n*–butanol	162.3 — 78.75 —	—

Complex	% Carbon Found (Cal.)	% Hydrogen Found (Cal.)	% Nitrogen Found (Cal.)	% Metal Found (Cal.)	Solvent molar conductance		Magnetic moment μ_{eff} (BM)
$[Mn(OAc)_2(H_2O)_2L]_2$	57.00 (56.40)	5.90 (5.40)	5.17 (5.00)	12.6 (12.8)	Acetonitrile Dioxane *n*–butanol	200.00 256.00 —	1.50
$[Mn(NO_3)_2(H_2O)_2L]_2$	47.80 (47.20)	3.80 (4.20)	9.50 (10.0)	8.3 (9.0)	Acetonitrile Dioxane *n*–butanol	20.00 — 30.00	1.40
$[UO_2(OAc)_2L]_2$	42.00 (42.60)	3.90 (3.50)	3.00 (3.80)	15.1 (14.8)	Acetonitrile Dioxane *n*–butanol	— 76.00 17.00	—
$[(UO_2)_3(PO_4)_2(H_2O)_2L_4]$	44.20 (43.80)	3.70 (3.30)	4.67 (4.60)	13.2 (12.8)	Acetonitrile Dioxane *n*–butanol	— — —	—
$[Ce(OH)_4(H_2O)L]$	46.70 (46.30)	4.80 (4.50)	5.22 (4.90)	6.4 (6.7)	Acetonitrile Dioxane *n*–butanol	— — —	—

TABLE 2
SELECTED IR SPECTRAL (cm^{-1}) BANDS.

Complex	ν(OH)	ν(C=N)	ν(C–O)	ν(C–O)	NO_3^-	CH_3COO	PO_4^{3-}	ν(M–N)	ν(M–O)	ν(M–Cl)
$[Cu(NO_3)_2L_2(H_2O)]H_2O$	3480 (br)	1470 (sh)	1020 (sh)	1240 (sh)	1290 (sh)	—	—	450–400	550–500	—
$[CuCl_2L_2(H_2O)_2]H_2O$	3480 (br)	1480 (sh)	1020 (sh)	1240 (sh)	—	—	—	450–400	550–500	330 (sh)
$[Cu(OAc_2)L(H_2O)_3]$	3480 (br)	1480 (sh)	1020 (sh)	1240 (sh)	—	1450 (sh)	—	450–400	550–500	—
$[Co(NO_3)L(H_2O)(OH)]_2$	3480 (br)	1480 (sh)	1020 (sh)	1240 (sh)	1390 (sh) 1290 (sh)	—	—	450–400	550–500	—
$[Co_2L_3(H_2O)_3(OAC)_2(OH)_2]$	3480 (br)	1480 (sh)	1020 (sh)	1240 (sh)	—	1430 (sh)	—	450–400	550–500	—
$[CoCl_2L(H_2O)_2]_2H_2O$	3480 (br)	1480 (sh)	1020 (sh)	1240 (sh)	—	—	—	450–400	550–500	330 (sh)
$[Mn(OAc)_2(H_2O)_2L_2]$	3480 (br)	1480 (sh)	1020 (sh)	1250 (sh)	—	1430 (sh)	—	450–400	550–500	—
$[Mn(NO_3)_2(H_2O)_2L]_2$	3480 (br)	1480 (sh)	1020 (sh)	1250 (sh)	1390 (sh) 1290 (sh)	—	—	450–400	550–500	—
$[UO_2(OAc)_2L]_2$	3480 (br)	1480 (sh)	1020 (sh)	1250 (sh)	—	1430 (sh)	—	450–400	550–500	—
$[(UO)_3(PO_4)_2(H_2O)_2L_4]$	3480 (br)	1480 (sh)	1020 (sh)	1250 (sh)	—	—	2400–2300 1620–1600	450–400	550–500	—
$[Ce(OH)_4(H_2O)L]$	3480 (br)	1480 (sh)	1020 (sh)	1250 (sh)	—	—	—	450–400	550–500	—

nitrate group[5]. A sharp peak observed at 1,450 cm^{-1} and 1,430 cm^{-1} in all the acetate complexes is assigned to the coordinated acetate group[6]. The uranium(VI) phosphate complex exhibited a broad peaks at 2,400–2,300 cm^{-1} and 1,620–1,600 cm^{-1} indicates the coordinated phosphate group[7]. The sharp bands observed at 330 cm^{-1} and cobalt (II) and copper (II) chloride complexes indicates the presence of M–Cl bond[8].

The M–N stretching frequency were observed in all the complexes in the range 450–400 cm^{-1}. Multiple absorption bands were observed in the range of 550–500 cm^{-1} in all the complexes are assigned to M–O bond vibrations. The sharp bands were observed around 740–710 cm^{-1} in all the complexes (except uranium (VI) acetate) are assigned to the coordinated water. In uranium complexes the UO_2^{2+} moiety is confirmed[9] after recognising a sharp peak in the range of 920–900 cm^{-1}.

The absorption bands around 46,500 cm^{-1}, 45,450 cm^{-1} observed in the UV spectrum of the free ligand are assigned $\sigma \rightarrow \sigma^*$ transition and a shoulder around 37,000 cm^{-1} to $\pi \rightarrow \pi^*$ transitions. The $n \rightarrow \pi^*$ transitions is observed at 31,250 cm^{-1} which is expected to move towards downside frequency upon coordination. Coordination of the ligand is further supported by the fact that the $\pi \rightarrow \pi^*$ transition is moved towards higher frequency side. The ligand under investigation contains two methoxyl groups and one pyridine nitrogen, and the above assignments are consistant with Syamal *et al*[10]

The absorption bands around 14,000 cm^{-1} to 14,600 cm^{-1} in the visible region of all the copper (II) complexes may be due to the combination of $2B_{1g} \rightarrow 2A_{1g}$, $2B_{1g} \rightarrow 2B_{eg}$ (or) $2B_{1g} \rightarrow 2E_g$ and $2E_g \rightarrow 2T_{2g}$ transitions, suggesting the distorted octrahedral or square planar[11] geometry. The absorption band appeared around 24,000 cm^{-1} in all cooper (II) complexes are assigned to the charge transfer transitions.

An intense absorption band around 18,000 cm^{-1} and 18,800 cm^{-1}, two weak absorption bands at 22,700 cm^{-1} and 25,000 cm^{-1} on the higher energy side were observed in the visible spectra of cobalt (II) complexes. Chakrabarti *et al.*[1]. reported a weak band around 8500 cm^{-1} and a more intense band around 18,000 cm^{-1} for low spin cobalt (II) complexes. They further suggested that under an octahedral field the 2G term for the free ion splits into $2E_g$, $2T_{2g}$, $2T_{1g}$ components in the increasing order of energy. Hence the four bands observed at 25,000, 20,400, 18,800–18,000 and 16,300–16,100 cm^{-1} may be assigned to $2A_{2g} \rightarrow 2T_{2g}$, $2T_{1g}(F) \rightarrow 2T_{1g}(P)$, $2A_2 \rightarrow 2T_1(P)$ and $2T_{1g}(F) \rightarrow 2A_{2g}(F)$ transitions respectively. Hence, it may be concluded that the above complexes were belongs to low spin octahedral complexes.

High spin manganese (II) complexes are expected to give many absorption

bonds in the range of 18,000–27,500 cm^{-1} are assignable to $6A_{1g} \rightarrow 4T_{1g}(G)$, $4T_{2g}(G) \rightarrow 4E_g$ and $4T_{2g}(D)$ transitions. But the manganese (II) complexes under investigation exhibited only one absorption band at 25,000 cm^{-1}. Hence the manganese (II) complexes were assumed to have low spin octahedral compounds.

The visible spectra of cerium (IV) and uranium (VI) complexes exhibited a strong absorption band around 18,400–18,200 cm^{-1} and a weak absorption band around 24,000 cm^{-1}. The weak broad absorption band in the visible spectra of unanium (VI) complexes was attributed to the $E_g \rightarrow 3u$ transition of the UO_2^{2+} moiety[12,13]. The absorption bands exhibited by these complexes in the visible region may be of charge transfer type.

The conductance values of copper (II) nitrate and copper (II) chloride shows that these complexes are 1 : 1 electrolytes in DMSO, dioxane and *n*-butanol solvents. While copper(II) acetate is neutral in nature. The complexes of cobalt(II), uranium(VI) and cerium(IV) records low molar conductance values show the non ionic nature in various solvents. Verification of the Table-1 shows the molar conductances of all complexes were depends upon the nature of the solvents. The reason may be the displacement of the anions by the solvent molecules from the inner sphere to the outer. This ionization of the complex in a solvent is represented as:

$$[ML_NX_M]^{n+}yH_2O + ZX \rightleftarrows [ML_NX_{M-Z}X_Z]^{(n-Z)} + yH_2O + ZX^-$$

X = DMSO, acetonitrile, dioxane or *n*–butanol.

The magnetic moments in B.M. are presented in Table 1. All copper (II) complexes are para magnetic and have magnetic moments corresponding to one unpaired electrons and consistent of square planar geometric requirements.

The calculated spin only value of a spin free cobalt (II) complex is 3.89 B.M. and for spin paired complex it is 1.73 B.M. The observed moments for spin free octahedral and tetragonally distorted octahedral complexes were in excess of the spin only value by 0.8–1.3 B.M and are attributed to unquenched orbital contribution of both the ground state and first excited state[14]. The observed moments for the spin-paired octahedral complexes were much closer to the calculated spin only value, since the ground state configuration allows no orbital contribution. The magnetic moments (μ_{eff}) of the complexes in the present study is nearly 2.4 and these higher values may be due to a contribution from some unquenched orbital momentum in the first excited level. Hence it may be concluded that the cobalt (II) complexes presented here may be spin-paired octahedral ones.

The value of 5.92 B.M is expected for the magnetic moment (μ_{eff}) for d^5 managanese (II) complexes. The observed value for the managanese (II) complexes is very low than expected and corresponds for one electron B.M. This is similar sub-normal values were reported by Ray *et al.*[15] for manganese (II) complex with 1–amino–2–thiourea and proposed a dimeric structure. The lowering

of the magnetic moments may therefore be attributed to the dimeric octahedral complex formation. The observed μ_{eff} value shows cerium (IV) and uranium (VI) complexes is diamagnetic.

Extrapolation of the fairly 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 copper (II) and cobalt (II) complexes

acetate = nitrate > chloride

In manganese (II), uranium (VI) and cerium (IV) complexes

acetate > sulphate

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