METAL COMPLEXES OF 2-GUANIDINOBENZIMIDAZOLE

M. Sakhawat Hussain, Taj Ali and S. Marghoob Ali

Department of Chemistry, University of Peshawar, Peshawar

(Received January 30, 1973; revised April 11, 1973)

Abstract. GBM forms complexes not only with the first row transition metals, but it also coordinates with metals like Au(I), Pt(IV), Th(IV) and Cd(II). Some of these metals form only mono complexes whereas bis- and tris-complexes are formed with other metals. The physical measurements on these complexes indicate that in bis-complexes two GBM molecules coordinate with the central metal atom in the *xy*-plane and the anions occupy the apical *z*-positions, resulting in a distorted octahedral configuration around the metal atom.

Previous work[1-3] has demonstrated the use of 2-guanidinobenzimidazole (GBM) as a ligand. Stable complexes of GBM with Ni(II), Cu(II), Co(II) and Fe(III) have been isolated. On the basis of elemental analysis, spectral, magnetic and conductance measurements, Cu(II) and Ni(II) were assigned square-planar or octahedral structures, depending on the solvents from which the complexes were prepared. Fe(III) and Co(II) form complexes, having $M(GBM)_3X_{2-3}YS$ [M = Fe(III), Co(II), Y = 0–3, X = anions and S solvent] stoichiometry and octahedral structure. In all of these complexes GBM acts as a bidentate ligand with the cyclic secondary amine and terminal imide groups engaged in metal–nitrogen bonding.
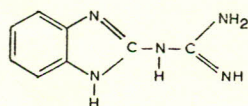
2-Guanidinobenzimidazole

In the present study a few more complexes of Co(II) and some new complexes of Mn(II) are reported. We have also extended our studies of the complexes of GBM to metals other than first row transition series, to demonstrate the versatility of GBM. Thus, we prepared the complexes of Cd(II), Pt(IV), Th(IV) and Au(I). Magnetic properties, conductance measurements, absorption spectra and elemental analysis have been used to explain the possible structure of these compounds.

Experimental

Reagents and Preparation of the Ligand. The ligand 2-guanidinobenzimidazole, was prepared according to the procedure given by Banerjee and Ghosh.[1] The product was isolated and purified using 20% NaOH (Found: C, 54.60; H, 5.07; N, 39.78; m.p. 245°C. Calc. for $C_8H_9N_5$:C, 54.85; H, 5.45; N, 40.26%.

Metal salts were used without further purification. The partial dehydration of the salts was done by drying the hydrated salts in a vacuum-oven for several hours at room temperature. All the solvents were obtained from E. Merck, and were distilled at least once before using. In some cases the solvent was distilled off twice or thrice to remove last traces of moisture.

Analyses. Carbon, hydrogen and nitrogen analyses of a few crystalline complexes were performed using F and M microanalytical analyser model 180. Usual volumetric, gravimetric and instrumental methods were used for the analyses of metal ions and anions.[4] Elemental analyses were further verified by getting the metal complexes analyzed from the University of California, Chemical Analytical Services, Berkeley, California. The analytical data are given in Table 1.

General Method of Preparation of Solid Complexes. All the complexes were prepared using similar general procedure. The required amount of partially dehydrated salts was dissolved in minimum amount of dry

TABLE 1. ANALYTICAL DATA FOR GBM COMPLEXES.

Complex	Dec.pt. (°C)	Colour	Metal (%)		Anion (%)		C(%)		H(%)		N(%)	
			Found	Calc	Found	Calc	Found	Calc	Found	Calc	Found	Calc
$Mn(GBM)_2Cl_2$	285	Green	11·40	11·53	14·54	14·89	43·37	40·35	4·35	3·81	30·18	29·41
$Co(GBM)_2Br_2$	273	Blue	9·52	10·37	20·86	28·01	33·60	33·76	4·31	4·18	24·50	24·61
$Co(GBM)_2I_2$	286	Maroon	8·51	8·89	37·21	38·29	28·81	28·97	2·82	2·73	21·21	21·12
$Cd(GBM)I_2$	229	Brown	20·35	20·76	46·42	46·88	17·75	17·75	1·81	1·68	12·94	12·80
$Cd(GBM)(NO_3)_2$	220	Red	27·06	27·31	30·47	30·13	32 61	32·74	3·15	3·09	28·72	28·66
$Au(GBM)Cl$	290	Brown	48·02	48·32	8·81	8·69	25·55	23·57	2·33	2·23	18·55	17·18
$Th(GBM)_2(NO_3)_43H_2O$	249	Brown	25·90	26·25	28·36	28·05	21·08	21·71	2·71	2·71	38·44	39·59
$Pt(GBM)_2Cl_6$	330	Rusty	25·42	25·73	28·11	28·05	25·01	24·75	2·47	2·59	17·99	18·05

TABLE 2. ELECTRONIC SPECTRAL DATA FOR GBM COMPLEXES.

Compound	Medium	λ(nm)	ν(cm^{-1})	ε_{max}^2 1 lm^{-1} cm^{-1}	Comments[b]
Mn(GBM)$_2$Cl$_2$	n-Butanol	320	31250	3600	L — M
		350	28550	2280	L — M
		400(sh)	25000	1100	
		540(sh)	18500	320	d — d
		600(sh)	16650	240	d — d
Co(GBM)$_2$Br$_2$	Methanol or	490	20400	314	d — d
	morpholine	530	18850	270	d — d
		790(sh)	12500	180	d — d
Co(GBM)$_2$I$_2$	Morpholine	595	16750	360	
Cd(GBM)I$_2$	Morpholine	430	23200	25	
		500(sh)	20000	9	
		520(sh)	18250	8	
		550(sh)	18500	6	
		600(sh)	16650	5	
Cd(GBM)(NO$_3$)$_2$	Methanol or morpholine	430	23200	30	
		572	17850	22	
		660	15150	10	
		730	13700	9	
Au(GBM)Cl	Morpholine	300	33350	12750	L — M
		340	29400	1250	L — M
		400(sh)	25300	760	d — d
		425	23950	580	d — d
		500(sh)	20000	260	d — d
Th(GBM)$_2$(NO$_3$)$_4$3H$_2$O	Morpholine	300	33350	13900	L — M
		370(sh)	27050	1050	L — M
		420	23800	97	d — d
		540(sh)	18500	34	d — d
Pt(GBM)$_2$Cl$_6$	Morpholine	320	31250	18850	L — M

(a) The values of the extinction coefficients for the high intensity bands in the UV region are to be considered accurate to the order of magnitude.   (b) Abbreviation d—d; d—d transitions; L–M, ligand to metal transitions.

methanol. Excess of the ligand was dissolved in the same solvent in a separate container. The ligand solution was slowly added to the salt solution with constant stirring. On reducing the volume of the resulting solution under vacuum the solid complex was obtained which was filtered through a sintered-glass crucible, washed several times with methanol and dried under vacuum. In the case of thorium, the complex was obtained immediately on mixing the salt and ligand solutions. The complexes are insoluble in benzene, carbon tetrachloride, dioxane, nitrobenzene, chloroform, moderately soluble in methanol, nitromethane, ethanol and were completely soluble in morpholine. The complexes are also soluble in water but the colour changes. None of the complexes is hygroscopic.

Conductance Measurements. A conductivity bridge (Mullard Equipment Limited, London) was used to measure conductivities of the complexes in methanol, butanol and morpholine. For comparison of the conductivities of the pure metal salts with that of their complexes, the conductivities of the pure salts were also measured in the same solvent and under similar conditions. The cell constant (1.44) was calculated using a 0.1N solution of Analar potassium chloride.[5] All measurements were made at room temperature. Conductivity data are given in Table 4.

Spectral Measurements. IR spectra were obtained as nujol mulls with Beckman spectrophotometer model IR-4. The electronic spectra in the region 350–1000 nm were measured with Beckman model DU spectrophotometer using 0.5 or 0.1 cm quartz cells.

Solutions of the complexes were prepared in butanol or methanol. The spectrum of each complex was taken at least three times using solutions of different concentrations. The spectrophotometer was standardized each time with blank solvent assuming it to be 100% transmittant. Spectral data are summarized in Tables 2 and 3.

Magnetic Susceptibility Measurements. The magnetic moments of the solid complexes were determined by the Gouy method at room temperature and are listed in Table 4. A double ended Gouy-tube was calibrated using Hg[Co(NCS)$_4$] as the standard. The magnetic moments were calculated by using the procedure described by Figgis and Lewis.[6]

Discussion

Molecular models (Fig. 1) indicate that a nearly square and perfectly planar arrangement of four nitrogen atoms (local symmetry D_{4h}) would be present when two GBM molecules are chelated to a metal ion through the cyclic secondary amine and a terminal imide group. The chain conformation of both the six-membered chelate rings will be preferred in order to minimize all intramolecular non-bonded interactions. In this conformation, the axial position of the metal ion are open for additional coordination with a monodentate ligand, an anion or a solvent molecule. Three GBM molecules can also coordinate to the contral metal ion resulting in an octahedral arrangement around the metal atom. In fact, tris-complexes of Fe(III) have already been reported[3] in which Fe(III) is six-coordinated. The tetrahedral arrangement around the metal atom is the third possibility. However, both tetrahedral and octahedral arrangements have to be extremely strained and full of non-bonded interactions. The comparison of these three arrangement shows that planar disposition of the two ligand molecules around the central metal atom is most suitable. The physical measurements on these complexes are also indicative of the planar arrangement in most of the complexes.

Analytical Data. Elemental analyses of the complexes indicate the presence of two GBM molecules for each metal atom when Mn(II), Co(II), Th(IV) and Pt(IV) were used as the central metal atoms. When Au(I) and Cd(II) are used as the metal, only 1:1 metal–ligand adducts could be prepared.

Conductance and Magnetic Measurements. In Table 4 are listed molar conductance values for these complexes in various solvents. When morpholine is used as solvent, molar conductance values range from about 1 to 5 cm^2 ohm^{-1} $mole^{-1}$. In the light of elemental analyses and other results to be discussed subsequently, we take these data to indicate that each of these complexes is non-electrolyte in morpholine. In solvents other than morpholine, the conductance data indicate that Mn(II) and Co(II) complexes are 1:2 electrolytes. The molar conductance values are within the range reported by Holt and Carlin[7] for 1:2 electrolytes.

The magnetic data of GBM complexes in the solid state at room temperature are given in Table 4. The magnetic moments of Mn(II) and Co(II) complexes are within the ranges commonly observed for maximum spin octahedral complexes. The complexes of Cd(II), Au(II), Th(II) and Pt(IV) are diamagnetic.

Electronic Spectra. The data on electronic transitions of the complexes are given in Table 2. From the intensity, which is rather high, the bands observed in the case of Mn(II), Au(I), Th(IV) and Pt(IV) at 31250 and 28500 cm^{-1}, could be considered as if resulting from the ligand itself. In fact, pure ligand also exhibits transitions in this region except that their energies are slightly different. The slight energy shifts could be the result of the metal–ligand interactions when the ligand is bonded to the metal atom.

The spectrum of Mn(II) complex in n-butanol consists of three low-intensity peaks at 400 nm ($\varepsilon = 1100$), 540 nm($\varepsilon = 320$) and 600 nm($\varepsilon = 240$). The

TABLE 3. IR BAND ASSIGNMENT OF COBALT COMPLEXES OF GBM.

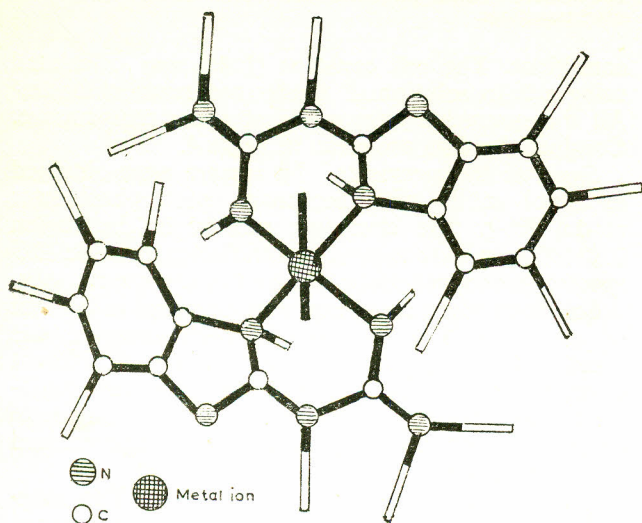| Ligand	Cobalt bromide complexes	Cobalt iodide complexes	Band assignment
3423	3400(sh)	3380	C=N stretch
3445			
3200-3100 b,d	3300	3185	N=H stretch
1655			
1648-1640	1670	2670	C=N band
1595	1608	1600	o-substituted ring stretch
1010	1011	1015	C–H(aromatic) inplane bending
760	750	750	C–H bonding

N
Metal ion
C

Fig. 1. Molecular model showing idealized conformation of distorted octahedral complexes of GBM. In bis-complexes two GBM molecules coordinate with the metal atom in xy-plane leaving apical z-positions open for coordinating anions or solvent molecules.

TABLE 4. MAGNETIC AND CONDUCTANCE DATA OF SOLID COMPLEXES OF GBM AT ROOM TEMPERATURE.

Compound	Molar conductance[a] cm^2/ohm/mole	Corrected[b] $10^{-6}X_m$ c.g.s. unit	μ_{eff} (B.M.)[c]
$Mn(GBM)_2Cl_2$	4	8154	5·1
$Co(GBM)_2Br_2$	0·4	8681	4·60
$Co(GBM)_2I_2$	0·4	8164	4·46
$Cd(GBM)I_2$	0·3	—2641	Diamagnetic
$Cd(GBM)(NO_3)_2$	0·4	—2991	Diamagnetic
$Au(GBM)Cl$	1·0	—	—
$Th(GBM)_2(NO_3)_43H_2O$	2·0	—	—
$Pt(GBM)_2Cl_6$	0 2	—	Diamagnetic

(a) Molar conductance values of about 10^{-2}M solutions of the complexes in morpholine.

(b) Diamagnetic correction values were approximated from values given in ref. 6(c). $\mu_{eff} = 2.84\sqrt{X_mT}$ B.M. average of two determinations.

spectrum is typical of six-coordinated Mn(II) and the peaks can be assigned to the electronic transitions, $^6A_{1g} \rightarrow {}^4E_g$ (G), $^6A_{1g} \rightarrow {}^6T_{2g}$ (G) and $^6A_{1g} \rightarrow {}^4T_{1g}$ (G) respectively.[8,9]

The spectrum of Co(II) complexes in morpholine and methanol indicates the presence of Co(II) in distorted octahedral configuration. Two absorption bands were observed in about 490 and 530 nm regions. Walmsley and Tyree[9] observed a peak at 538 nm with a shoulder at 480 nm for an octahedral Co(II) complex. The peak at 538 nm was attributed to the transition $^4T_{1g} \rightarrow {}^4A_{2g}$ (F) and the shoulder at 480 nm to the transition $^4T_{1g} \rightarrow {}^4T_{1g}$ (P). The peaks for Co(GBM)$_2$Br$_2$ which correspond to these transitions are at 530 and 490 nm.

When Cd(II) and Au(II) were used as central metal atoms only mono·GBM complexes could be prepared. Even a large excess of the ligand resulted in the same 1:1 adducts. The spectra of Cd(GBM)I$_2$ and Au(GBM)Cl were not conclusive so far as the stereochemistry of the metal atoms are concerned.

IR Spectra of the Complexes. A comparison of the IR spectra of the ligand with that of its Mn(II) and Co(II) complexes indicates that one secondary amine (cyclic) and terminal imide nitrogen coordinate with the metal atom forming an unsaturated six-membered chelate ring. This conclusion is in agreement with the structure assumed by previous workers.[1-3]

References

1. A.K. Bannerjee and S.P. Ghosh, J. Indian Chem. Soc., **38,** 237 (1961).
2. S.M. Ali, N. Ahmad and M.S. Hussain, Pakistan J. Sci. Res., **18,** 29 (1966).
3. N. Ahmad, Pakistan J. Sci. Ind. Res., **12,** 342(1969).
4. A. I. Vogel, *A Textbook of Quantitative Inorganic Analysis* (Longman Green, London, 1962), pp. 266, 375, 460, 513, 583 and 787.
5. F. Danials, J.W. Williams, P. Bender, P.A. Alberty and C.D. Cornwell, *Experimental Physical Chemistry* (McGraw, New York, 1962), pp. 158, 473.
6. B.N. Figgis and J. Lewis, *Modern Coordination Chemistry* (Interscience, New York, 1960), p. 412.
7. S.L. Holt Jr. and R.L. Carlin, J. Am. Chem. Soc., **86,** 3017 (1964).
8. L.J. Heidt, G.F. Koster and A.N. Johnson, J. Am. Chem. Soc., **80,** 6471 (1959).
9. J. Lewis and R.G. Wilkins, *Modern Coordination Chemistry* (Interscience, New York, 1960), p. 291.