

TRANSITION METAL COMPLEXES OF 2-GUANIDINOBENZIMIDAZOLE

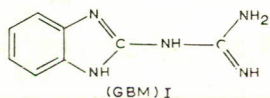
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Metal complexes of the type $[M(\text{GBM})_2\text{X}_2]$ and $[M(\text{GBM})_3\text{X}_{2-3}\cdot y\text{H}_2\text{O}]$, where $M=\text{Fe(III)}$ and Co(II) , $\text{X}=\text{anions}$ such as chloride, nitrate, acetate, perchlorate and sulphate, $\text{GBM}=\text{2-guanidinobenzimidazole (I)}$, have been prepared from nonaqueous solvents. These complexes are found high spin with magnetic moments in the range 5.8-5.85 B.M. (for Fe(III) complexes) and 4.45-5.12 B.M. (for Co(II) complexes). The electronic spectra of Co(II) complexes show bands at $18,380\text{-}20,000\text{ cm}^{-1}$ (d-d transition bands) and $32,900\text{-}34,120\text{ cm}^{-1}$ (charge transfer bands). IR spectra made it possible to assign the metal-nitrogen bond sites.

2-Guanidinobenzimidazole (I) forms complexes with nickel and copper.^{1,2,3} The empirical formulae for these complexes are found to be $M(\text{GBM})_2\text{X}_2\cdot y\text{H}_2\text{O}$ where $M=\text{Ni(II)}$ and Cu(II) , $\text{X}=\text{anions}$ such as chloride, bromide, sulphate etc., and $y=0\text{-}3$.



Bannerjee and Ghosh² assigned a square planar structure to diamagnetic Ni(II) and paramagnetic Cu(II) complexes while Ali *et al.*³ assigned an octahedral structure to these complexes when prepared from nonaqueous solvents, considering anions in the coordination sphere. To date there is no evidence reported for the existence of complexes of this ligand which conform to a 1:3 metal to ligand stoichiometry, thus providing a conclusive proof for a perfect octahedral symmetry around the metal ion.

This ligand is of particular interest because it contains a number of potentially available donor nitrogen atoms. Bannerjee and Ghosh² assigned the metal-nitrogen bonding through cyclic secondary amine and terminal imide nitrogen, thus forming a six-membered ring. This assignment was made purely by comparison with biguanide complexes and no practical evidence was presented.

The present investigation was undertaken with an object to prepare new metal complexes of this ligand which conform to a 1:3 metal to ligand ratio and ascertain their metal-nitrogen bond sites through the IR spectral studies. This is achieved by preparing a number of Fe(III) and Co(II) complexes from nonaqueous solvents (such as alcohols). In general iron(III) complexes

conform to a 1:3 metal to ligand ratio while only one compound of cobalt(II) could be isolated with this composition. In the case of Co(II) complexes, common anions have the tendency to enter the coordination sphere and compounds of the type $[\text{Co}(\text{GMB})_2\text{X}_2]$ are formed. Perchlorate anion is a poor coordinating agent and so cobalt(II) perchlorate form a complex of the former type. Magnetic properties and absorption spectra have been used to determine the structure of these complexes.

Experimental

Reagents and Synthesis of the Ligand

All the reagents used were of reagent grade and used without further purification. Elemental analyses were done by Midwest microlabs, Inc. 6000 East 46th Street, Indianapolis, Indiana, U.S.A.

2-Guanidinobenzimidazole was prepared by the method reported by Bannerjee and Ghosh.² Satisfactory chemical analysis was obtained.

Found: C, 55.13; H, 5.18; N 39.97%. Calc. for $\text{C}_8\text{H}_9\text{N}_5$: C, 54.85; H, 5.45; N, 40.26%.

Preparation of Coordination Compounds

1. *Tris(2-guanidinobenzimidazole) Iron (III) Nitrate Trihydrate.* $[\text{Fe}(\text{GBM})_3](\text{NO}_3)_3\cdot 3\text{H}_2\text{O}$.—2.626 g ligand was dissolved in 60 ml boiling isopropyl alcohol (IPA) and filtered to remove undissolved material. 2.0 g ferric nitrate 9-hydrate was dissolved in 15 ml methanol and poured in the boiling solution of ligand. The mixture was kept boiling for 15 min on the steam bath, when a fine precipitate formed. It was removed, washed with acetone and dried in air.

Found: C, 35.11; H, 4.07; N, 30.56; O, 23.01%. $[\text{Fe}(\text{C}_8\text{H}_9\text{N}_5)_3](\text{NO}_3)_3\cdot 3\text{H}_2\text{O}$ requires; C, 35.05; H, 4.04; N, 30.65; O, 23.34%.

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2. *Tris(2-guanidinobenzimidazole) Iron (III) Perchlorate Trihydrate*. $[\text{Fe}(\text{GBM})_3](\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}$.—The same procedure was followed as for the ferric nitrate complex. The brown precipitate was removed, washed several times with acetone and dried in air. Found: C, 30.73; H, 3.67; N, 22.45; O, 25.30; Cl, 11.48%. $[\text{Fe}(\text{C}_8\text{H}_9\text{N}_5)_3](\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}$ requires: C, 30.87; H, 3.56; N, 22.49; O, 27.70; Cl, 11.39%.

3. *Chloro-aquo-bis(2-guanidinobenzimidazole) Iron (III) Chloride*. $[\text{Fe}(\text{GBM})_2(\text{H}_2\text{O})\text{Cl}]\text{Cl}_2$.—0.005 moles ferric chloride 6-hydrate was dissolved in 15 ml methanol and poured into a boiling solution of 0.015 moles ligand in the same solvent. A brown precipitate (0.5 g) was formed and discarded. The filtrate was evaporated under vacuum to a small volume, when an orange-brown precipitate formed. The solution was filtered and the filtrate (IA) reserved. The precipitate was washed with acetone and dried. Found: C, 35.10; H, 3.98; N, 25.50; Cl(ionic), 12.92%. $[\text{Fe}(\text{C}_8\text{H}_9\text{N}_5)_2(\text{H}_2\text{O})\text{Cl}]\text{Cl}_2$ requires: C, 35.07; H, 4.01; N, 25.54; Cl(ionic), 12.86%.

4. *Tris(2-guanidinobenzimidazole) Iron (III) Chloride Hydrate*. $[\text{Fe}(\text{GBM})_3]\text{Cl}_3 \cdot \text{H}_2\text{O}$.—25 ml acetone was added to the filtrate IA, when a yellow precipitate was formed. The precipitate was washed with acetone and dried *in vacuo* at 50°C. Found: C, 40.72; H, 4.15; N, 29.68; Cl, 15.00%. $[\text{Fe}(\text{C}_8\text{H}_9\text{N}_5)_3]\text{Cl}_3 \cdot \text{H}_2\text{O}$ requires: C, 40.85; H, 4.14; N, 29.76; Cl, 15.07%.

5. *Sulphato-aquo-bis(2-guanidinobenzimidazole) Cobalt (II)*. $[\text{Co}(\text{GBM})_2(\text{H}_2\text{O})\text{SO}_4]$.—When a hot methanol solution of cobaltous sulphate was poured in a boiling solution of the ligand in isopropyl alcohol in a molar ratio 1:3, a dirty pink, bulky precipitate separated immediately. The precipitate was washed with IPA and then several times with acetone, and dried in air. Found: C, 36.53; H, 4.09; N, 26.80; S, 5.86; O, 15.1%. $[\text{Co}(\text{C}_8\text{H}_9\text{N}_5)_2(\text{H}_2\text{O})\text{SO}_4]$ requires: C 36.72; H 3.85; N 26.75; S 6.12; O 15.29%.

6. *Dichloro-bis(2-guanidinobenzimidazole) Cobalt (II)*. $[\text{Co}(\text{GBM})_2\text{Cl}_2]$.—2.63 g (0.015 moles) of ligand were dissolved in 65 ml boiling IPA and filtered to remove undissolved matter. To this boiling filtrate was added a hot solution of 0.005 moles of metal chloride in 15 ml methanol. The colour of the solution turned red. The volume of the solution was reduced to 40 ml on a steam bath when a light pink compound separated. This was filtered, washed with acetone and dried in vacuum at 50°C. Found: C, 39.94; H, 3.99; N, 28.81; Cl, 14.55%. $[\text{Co}(\text{C}_8\text{H}_9\text{N}_5)_2\text{Cl}_2]$ requires: C, 40.02; H, 3.78; N, 29.17; Cl, 14.76%.

7. *Dinitrato-bis(2-guanidinobenzimidazole) Cobalt (II)*. $[\text{Co}(\text{GBM})_2(\text{NO}_3)_2]$.—To a boiling IPA solution of 0.015 moles of ligand was added a hot methanol solution of metal nitrate (0.005 moles). The resultant deep red solution was evaporated on the steam bath to a volume of 50 ml when a coral-coloured complex separated, which was washed with a small volume of acetone and dried. Found: C, 36.20; H, 3.67; N, 31.52; O, 18.12%. $[\text{Co}(\text{C}_8\text{H}_9\text{N}_5)_2(\text{NO}_3)_2]$ requires: C, 36.04; H, 3.40; N, 31.53; O, 18.01%.

8. *Diacetato-bis(2-guanidinobenzimidazole) Cobalt (II) Hydrate*. $[\text{Co}(\text{GBM})_2(\text{CH}_3\text{COO})_2]\text{H}_2\text{O}$.—Boiling solutions of metal salt and ligand (1:3 molar ratio) in IPA were mixed and the mixture was kept hot for 15 min when a powder separated. The complex was washed with acetone and dried *in vacuo* at 50°C. Found: C, 44.22; H, 4.97; N, 25.47; O, 14.63%. $[\text{Co}(\text{C}_8\text{H}_9\text{N}_5)_2(\text{CH}_3\text{COO})_2]\text{H}_2\text{O}$; requires C, 44.02; H, 4.81; N, 25.69; O, 14.67%.

9. *Tris(2-guanidinobenzimidazole) Cobalt (II) Perchlorate Monoisopropanolate*. $[\text{Co}(\text{GBM})_3](\text{ClO}_4)_2 \cdot \text{C}_3\text{H}_7\text{OH}$.—0.015 moles of the ligand were dissolved in boiling IPA. To this solution were added 5 millimoles of cobaltous perchlorate 6-hydrate dissolved in 15 ml methanol. The volume of the resulting deep red solution was reduced to 25 ml on a steam bath and left overnight, when a red-coloured complex was crystallized. The crystals were washed with a small volume of acetone, dried in air and then at 50°C under vacuum. Found: C, 38.69; H, 4.43; N, 24.80; O, 16.81; Cl, 8.20%. $[\text{Co}(\text{C}_8\text{H}_9\text{N}_5)_3](\text{ClO}_4)_2 \cdot \text{C}_3\text{H}_7\text{OH}$ requires: C, 38.40; H, 4.18; N, 24.87; O, 17.06; Cl, 8.39%.

Physical Properties and Magnetic Susceptibility Measurements

Iron(III) complexes and $[\text{Co}(\text{GBM})_2(\text{H}_2\text{O})\text{SO}_4]$ were found insoluble in most of the polar and nonpolar solvents. Other Co(II) complexes are soluble in methanol and give pink solutions. Cobaltous perchlorate complex is soluble in acetone and isopropyl alcohol and gives a red solution.

The magnetic measurements were done on solid compounds on a Gouy magnetic balance. Crystalline $\text{Hg}[\text{Co}(\text{SCN})_4]$ was used as a standard. The gram susceptibility of this compound has been reported as 16.44×10^{-6} c.g.s. units at 20°C.⁴ The colours of the solid complexes, decomposition temperatures and their magnetic data are presented in Table 1.

Absorption Spectra

The absorption spectra of iron(III) complexes and $[\text{Co}(\text{GBM})_2(\text{H}_2\text{O})\text{SO}_4]$ could not be studied due to the insolubility of these complexes. The electronic spectra of cobalt(II) complexes were studied with Cary model 14

spectrophotometer using glass cells of 1 cm thickness. Methanol was used as a solvent for these complexes and the concentrations of the solutions were in the range 1.5–4.8 millimolar. The results are given in Table 2. The plot of extinction coefficient vs wavelength is shown in Fig. 1.

TABLE I.—COLOUR, DECOMPOSITION TEMPERATURES, MOLAR SUSCEPTIBILITY AND MAGNETIC MOMENTS OF METAL-GBM COMPLEXES.

Complex	Colour	Decomposition temp. °C	Molar susceptibility $\chi_M \times 10^6$	Magnetic moment μ_{eff} B.M.]
$[\text{Fe}(\text{GBM})_3](\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$	Deep yellow	235	14420	5.85
$[\text{Fe}(\text{GBM})_3](\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}$	Brown	241	14230	5.81
$[\text{Fe}(\text{GBM})_2(\text{H}_2\text{O})\text{Cl}]\text{Cl}_2$	Yellow	275	14230	5.81
$[\text{Fe}(\text{GBM})_3]\text{Cl}_3 \cdot \text{H}_2\text{O}$	Orange brown	240	14210	5.80
$[\text{Co}(\text{GBM})_2(\text{H}_2\text{O})\text{SO}_4]$	Dirty pink	292	8479	4.48
$[\text{Co}(\text{GBM})_2\text{Cl}_2]$	Pink	282	8546	4.50
$[\text{Co}(\text{GBM})_2(\text{NO}_3)_2]$	Coral	276	9454	4.73
$[\text{Co}(\text{GBM})_2(\text{CH}_3\text{COO})_2] \cdot \text{H}_2\text{O}$	Light pink	227	8379	4.45
$[\text{Co}(\text{GBM})_3](\text{ClO}_4)_2 \cdot \text{C}_3\text{H}_7\text{OH}$	Red	247	11230	5.15

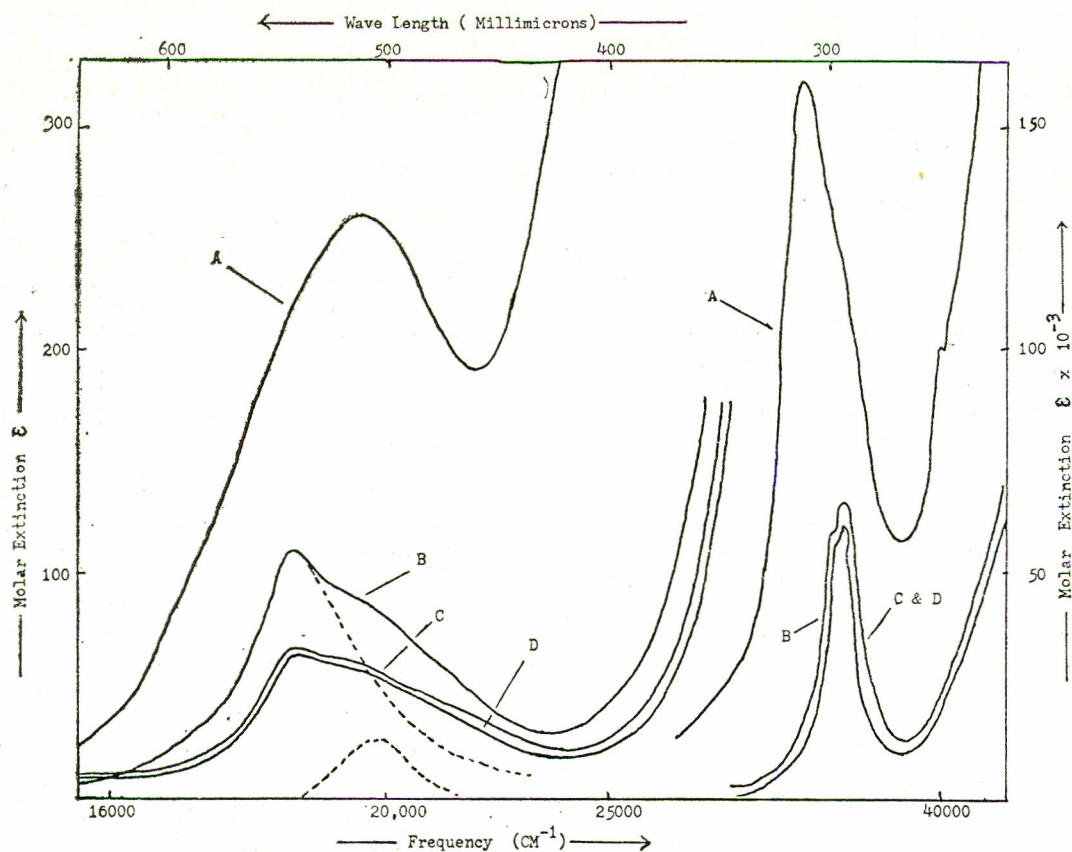


Fig. 1.—Absorption spectra in visible and UV region of A, $[\text{Co}(\text{GBM})_3](\text{ClO}_4)_2 \cdot \text{C}_3\text{H}_7\text{OH}$. B, $[\text{Co}(\text{GBM})_2(\text{CH}_3\text{COO})_2] \cdot \text{H}_2\text{O}$. C, $[\text{Co}(\text{GBM})_2\text{Cl}_2]$. D, $[\text{Co}(\text{GBM})_2(\text{NO}_3)_2]$ in methanol solutions.

TABLE 2.—ABSORPTION SPECTRA IN VISIBLE AND UV REGION.

Complex	Max. absorption		Molar extinction coefficient ^a litre/mole-cm
	Frequency (cm ⁻¹)	Wave length (m μ)	
[Co(GBM) ₂ Cl ₂]	18,520	540	66.8
	20,000	500 (sh)*	14.0
	32,900	304 (sh)	2.77 × 10 ⁴
	34,120	293	3.08 × 10 ⁴
[Co(GBM) ₂ (NO ₃) ₂]	18,380	544	66.65
	19,840	504 (sh)	13.8
	32,900	304 (sh)	2.77 × 10 ⁴
	34,120	293	3.1 × 10 ⁴
[Co(GBM) ₂ (CH ₃ COO) ₂] · H ₂ O	18,350	545	110.5
	20,000	500 (sh)	24.0
	33,010	303 (sh)	3.05 × 10 ⁴
	34,350	292	3.05 × 10 ⁴
[Co(GBM) ₃](ClO ₄) ₂ · C ₃ H ₇ OH	19,605	510	261.2
	32,050	312	16.1 × 10 ⁴

*sh=shoulder

Infrared Spectra

The IR spectra were recorded for solid compounds using KBr disc technique. Perkin Elmer model 621 grating spectrophotometer was used to record the spectra in the range 4000–200 cm⁻¹. Each spectrum was calibrated at 906.7 and 1028.0 cm⁻¹ with standard polystyrene film. Characteristic IR frequencies and band assignments are given in Table 3 and the spectra are reproduced in Fig. 2-4.

Discussion

2-Guanidinobenzimidazole contains many electron-rich nitrogen atoms which could act as donor sites to form coordinate bond with metals. The geometry of the molecule is such that it can act only as a bidentate ligand thus forming a stable six-membered ring.

The stoichiometry of the iron(III) complexes is radically different from those of the cobalt(II) complexes. Three GBM molecules are found to coordinate with Fe(III) while only two coordinate with Co(II). At least one example of the reverse stoichiometry is achieved for each metal ion. Physical properties of the iron(III) complexes are likewise different from those of the cobalt(II) complexes. In particular iron(III) complexes are found insoluble in most of the polar and non-polar solvents, while cobalt(II) complexes dissolve easily in methanol (except [Co(GBM)₂(H₂O)SO₄] which could not be dissolved in any solvent). The two classes of compounds also differ in their decomposition temperatures. Com-

plexes with the structure [M(GBM)₂XY]X₀₋₁ (X anion, Y anion or water, M metal) in general are thermally more stable and decompose at 35–50°C higher than the complex compounds with formula [M(GBM)₃]X₂₋₃ (an exception is [Co(GBM)₂(CH₃COO)₂]H₂O which decomposes at the lowest temperature, probably due to the coordinated acetate).

Magnetic moments of the iron(III) complexes listed in Table 1 agree well with the values predicted for the spin-free complexes, thus showing the presence of five unpaired electrons. Cobalt(II) complexes have moments in the range 4.45–5.15 B.M. In an octahedral field, the magnetic moment for a high spin Co(II) complex ion is expected to be 5.12 B.M. This higher value of the magnetic moment than the spin only value is due to the orbital angular momentum contribution.⁵ [Co(GBM)₃](ClO₄)₂ · C₃H₇OH being surrounded by a uniform octahedral field, has its magnetic moment in this range while rest of the cobalt(II) complexes have considerably lower magnetic moments. These data seem to indicate that these molecules are in a distorted octahedral environment.

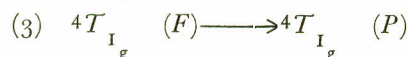
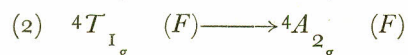
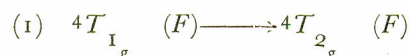
Since the iron(III) complexes and [Co(GBM)₂(H₂O)SO₄] could not be dissolved in any solvent, it was not possible to study their electronic spectra in solution. Absorption spectra of cobalt(II) complexes were studied in methanol solution and the observed bands are listed in Table 2. Generally two spectral bands are observed at 18,350 and 20,000 cm⁻¹ in the visible region. The second

TABLE 3.—IR BAND ASSIGNMENTS IN METAL-2-GUANIDINOBENZIMIDAZOLE COMPLEXES.

(Frequency in CM ⁻¹)										
GBM	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	Band assignments
3445	3400	3440	3430	3440s	3437	3380	3400	3440	3420sh	C=N stretch
3423						3355		3325		
3200-3100 (b,d)	3340-3140	3340-3120	3400-3180	3350	3350	3300	3300	3140	3300	N—H stretch
				3280	3200	3185	3200		3200sh	
					3180					
								1685		COO' asymmetric stretch
1655			1660	1660						
1648 t	1660		1655	1655	1670	1670	1655m	1660b	1650	C=N stretch
1640										
	1630	1630	1630	1635sh	1745			1645		HOH bending
1595	1610	1600	1595sh	1598m	1580sh	1618	1580w		1595	o-substituted ring stretch
							1583s			
1560	1560		1559			1557	1560sh	1555	1560	—NH—
1545	1545	1541	1545	1544	1555	1555	1550	1550s	1545	bending
1472sh			1478				1475			C—H multiple bond stretch
1460m	1455	1468s		1475s	1465	1462s		1473	1472w	
	1380		1460				1465			
							1380s			NO ₃ stretch
								1335		COO' symmetric
		1140s								CIO ₄ stretch
		1110s							1140	
		1080s							1107	
1010	1005	1005	1012	1010	1007s	1007	1010	1010	1015	C—H (arom) in plane bending
			1000	1002	995	995		1000		NO ₃ stretch
	983									H ₂ O stretch
760 t	910	898		900	913					C—H bending
	755s	755	750sh	757	750	750	752	756		
	690m	717	695	712						
					612			645		COO' bending
										M—O—S stretch
						595				M—Cl stretch
	527	510	510							Fe—N stretch
					512	505	505sh	515	535sh	Co—N stretch
					465					O—S—O deformation
					425	427	425	427	427	Co—N stretch
					360	355		355		N—Co—N bending

b broad; m medium; s sharp; sh shoulder; t triplet; w weak, d doublet.

band is very weak and appear as a shoulder. This weak band is lost in very intense charge transfer bands in the complex $[\text{Co}(\text{GBM})_3](\text{C}_{10}\text{H}_4)_2\text{-C}_3\text{H}_2\text{OH}$, and only one strong band at $19,650\text{ cm}^{-1}$ is observed. The examination of the energy level diagram of a cobalt(II) complex (*a d⁷ ion*) in an octahedral environment, reveals that three spin allowed transitions are possible for this ion.⁶ These three transitions are



Assignment of the band at $18,350\text{ cm}^{-1}$ to transition 2 and that at $20,000\text{ cm}^{-1}$ to transition 3 leads to a crystal field splitting parameter value ($10 Dq$) of $10,440\text{ cm}^{-1}$. On this basis transition 1 should be observed at about 8352 cm^{-1} . This portion of the spectrum could not be studied due to the experimental difficulties. Jorgensen⁷ studied the spectra of octahedral cobalt(II) complexes and observed bands at $21,550$, $19,440$, $16,000$, and $8,000\text{ cm}^{-1}$, and made similar assignments to these bands. Our assignments of absorption bands are in good agreement with those of Jorgenson. In the UV region very intense bands at $32,900$ and $34,120\text{ cm}^{-1}$ are observed. These are charge transfer bands and can be assigned to $n \rightarrow \pi^*$ (nonbonding \rightarrow antibonding) transitions.

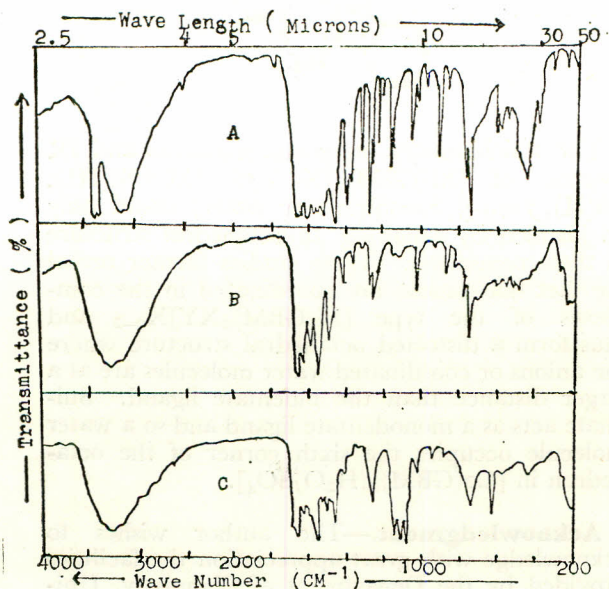


Fig. 2.—The IR spectrum of A, 2-guanidinobenzimidazole; B, $[\text{Fe}(\text{GBM})_2(\text{H}_2\text{O})\text{Cl}]\text{Cl}_2$; C, $[\text{Co}(\text{GBM})_3(\text{ClO}_4)_2 \cdot \text{C}_3\text{H}_7\text{OH}]$.

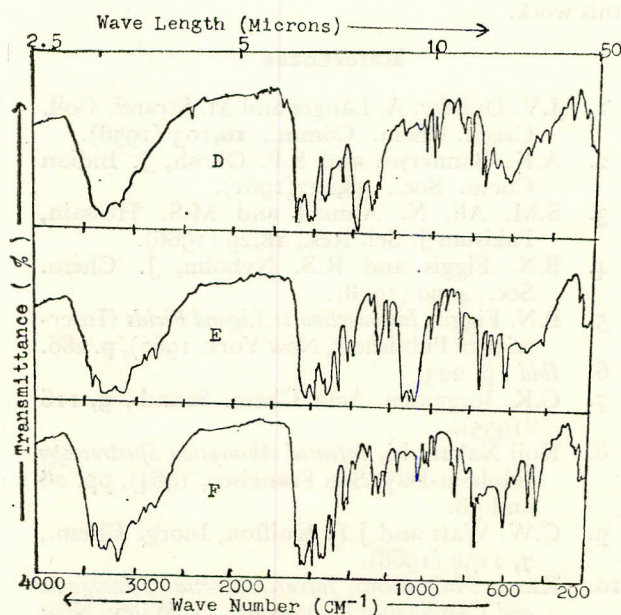


Fig. 3.—The IR spectrum of D, $[\text{Fe}(\text{GBM})_3(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}]$; E, $[\text{Fe}(\text{GBM})_3(\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}]$; F, $[\text{Fe}(\text{GBM})_3]\text{Cl}_3 \cdot \text{H}_2\text{O}$.

A comparison of the IR spectra of 2-guanidinobenzimidazole with that of its metal complexes is necessary to decide the metal-nitrogen bonding in these complexes. A strong doublet at 3445 and 3423 cm^{-1} assigned to the stretching vibration of $-\text{C}=\text{N}-$ groups is either completely lost in the broad band of $-\text{NH}_2$ stretch or appears as a

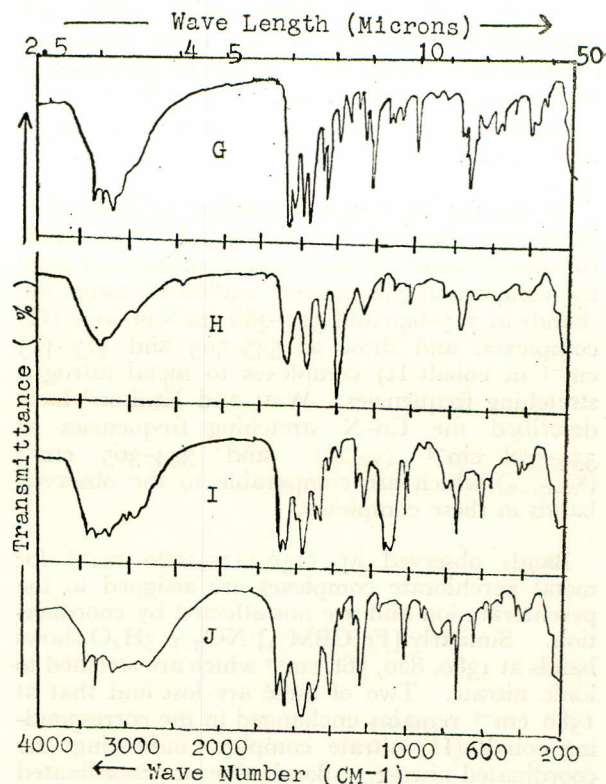


Fig. 4.—The IR spectrum of G, $[\text{Co}(\text{GBM})_2\text{Cl}_2]$; H, $[\text{Co}(\text{GBM})_2(\text{NO}_3)_2]$; I, $[\text{Co}(\text{GBM})_2(\text{H}_2\text{O})\text{SO}_4]$; J, $[\text{Co}(\text{GBM})_2(\text{CH}_3\text{COO})_2] \cdot \text{H}_2\text{O}$.

sharp singlet displaced slightly, upon coordination. This indicates that one of the two $\text{C}=\text{N}$ groups present in the ligand is no longer free to vibrate. Since the terminal $\text{C}=\text{N}$ has a small group (i.e. proton) attached to it, it should be greatly affected upon coordination as compared to the other $\text{C}=\text{N}$ group which is a member of a big diffused ring. Similarly a poorly defined triplet at 1655–1640 cm^{-1} (also assigned to $-\text{C}=\text{N}-$) in the ligand is shifted to lower wave number and appears as a doublet or singlet in the complexes. This also indicates the bonding through one $\text{C}=\text{N}$ group nitrogen.

The bands assigned to inplane bending of $-\text{NH}_2$ group in the region 1640–1595 cm^{-1} and $-\text{NH}-$ bending vibrations⁸ at 1545–1530 cm^{-1} remain unchanged in these complexes, thus pointing to the fact that these groups do not take part in the coordinate bond formation. The triplet observed at 765, 760 and 737 cm^{-1} for $-\text{NH}$ group out of plane bending in the ligand is displaced in the spectra of complexes and in certain cases appear as a doublet. This shift and decrease in the number of bands signifies the second coordination site.

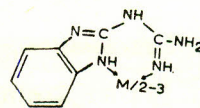
On the basis of these observations it is justified to assume that one secondary amine (cyclic) and terminal imide nitrogen take part in the coordinate bond formation with metal ion thereby forming an unsaturated six-membered ring. This is in agreement with the structure assumed by Bannerjee and Ghosh.

In the far IR region a number of absorption bands are observed for the ligand which made the interpretation of spectra more difficult. Purely by comparison one can very tentatively assign the bands at 717-690 and 527-486 cm^{-1} in iron(III) complexes, and those at 535-505 and 427-425 cm^{-1} in cobalt(II) complexes to metal-nitrogen stretching frequencies. Watt and Knifton⁹ have described the Co-N stretching frequencies at 534-538 cm^{-1} ($\nu_{\text{Co-N}}$) and 344-365 cm^{-1} ($\delta_{\text{N-Co-N}}$) which are comparable to the observed bands in these complexes.

Bands observed at 1140, 1110, 1080 cm^{-1} for metal perchlorate complexes are assigned to the perchlorate ion and are not affected by coordination. Similarly $[\text{Fe}(\text{GBM})_3](\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$ shows bands at 1380, 820, 568 cm^{-1} which are assigned to ionic nitrate. Two of these are lost and that at 1380 cm^{-1} remains unchanged in the corresponding cobalt (II) nitrate complex, indicating the coordinated nitrate. Bands due to coordinated water are observed at 798 cm^{-1} for Co-OH₂ and at 805 and 682 cm^{-1} for Fe-OH₂. Coordinated acetate bands are observed at 1400 cm^{-1} (ν_{S}) and 625 cm^{-1} ($\pi_{\text{COO}'}$) which are displaced from those of free anion. Sulphate shows its vibrations at 612 and 390 cm^{-1} which are probably due to the monodentate sulphate. These bands are in good agreement with those reported in literature.¹⁰

Conclusions

These studies indicate that metal complexes of the type $[\text{M}(\text{GBM})_3]\text{X}_{2-3} \cdot \gamma\text{S}$ ($\gamma=0-3$ and S=solvent or water) could be prepared. The IR studies are found helpful in deciding the metal-nitrogen bonding sites in these complexes. These studies strongly favor the metal-nitrogen bonding through the cyclic secondary amine and terminal imide groups thereby forming a six-membered ring of the type shown.



The stoichiometry, magnetic moments and IR spectra of $[\text{M}(\text{GBM})_3]\text{X}_{2-3} \cdot \gamma\text{S}$ ($\text{M}=\text{Fe}(\text{III})$, $\text{Co}(\text{II})$, $\gamma=0-3$, S=solvent or water) could only be justified by assigning an octahedral structure to these complexes. These studies further reveal the fact that anions are coordinated in the complexes of the type $[\text{M}(\text{GBM})_2\text{XY}]\text{X}_{0-2}$ and thus form a distorted octahedral structure where the anions or coordinated water molecules are at a larger distance than the bidentate ligand. Sulphate acts as a monodentate ligand and so a water molecule occupies the sixth corner of the octahedron in $[\text{Co}(\text{GBM})_2(\text{H}_2\text{O})\text{SO}_4]$.

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