

Complexes of 2-Guanidinobenzimidazole with Copper(II)

P. D. SINGH and L. K. MISHRA*

Department of Chemistry, Science College, Patna University, Patna-800 005

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Some complexes of 2-guanidinobenzimidazole with copper(II) have been prepared and characterised by elemental analysis, magnetic moment measurement, ir spectral and electronic reflectance spectral studies.

THE complexes of 2-guanidinobenzimidazole(GB) and several benzimidazole derivatives have been reported¹⁻⁶. Ghosh and Banerjee have reported¹ that magnetic moment values of $\text{Cu}(\text{GB})_2\text{X}_2 \cdot n\text{H}_2\text{O}$ ($\text{X}=\text{Cl}, \text{Br}, \text{NO}_3$ and $\frac{1}{2}\text{SO}_4$; $n=3$ to 7) fall in the range of 1.76 to 1.86 BM. All *et al*⁷ latter on prepared anhydrous $\text{Cu}(\text{GB})_2\text{X}_2$ ($\text{X}=\text{Cl}, \text{Br}, \text{NO}_3$ and $\frac{1}{2}\text{SO}_4$) and claimed that magnetic moment values of these copper(II) complexes fall in the range of 1.50-1.55 BM. Besides reexamining these results, we are reporting the preparation and characterisation of a number of copper(II) complexes with 2-guanidinobenzimidazole of formulae $[\text{Cu}(\text{GB})_2(\text{RCOO})_2]n\text{H}_2\text{O}$ ($\text{RCOO}=\text{formate, acetate, propionate, butyrate, lactate and chloroacetate}$; $n=0$ or 2), $[\text{Cu}(\text{GB})_2\text{X}_2]$ [$\text{X}=\text{Cl}$ or Br] and neutral chelate $[\text{Cu}(\text{GB}-\text{H})_2]$.

Experimental

The ligand was prepared as described earlier¹. In general, the complexes were collected on a filter, washed with ethanol and dried in air.

$[\text{Cu}(\text{GB})_2(\text{RCOO})_2]n\text{H}_2\text{O}$, $[\text{Cu}(\text{GB})_2\text{X}_2]$ ($\text{X}=\text{Cl}$ and Br) and $[\text{Cu}(\text{GB})_2\text{X}_2]$ ($\text{X}=\text{Cl}, \text{Br}$ and NO_3): The complexes were obtained when appropriate copper(II) salts dissolved in dry ethanol were refluxed with the hot ethanolic solution of the ligand in stoichiometric proportion.

The *bis* chelated complex sulphate $(\text{Cu}(\text{GB})_2\text{SO}_4) \cdot n\text{H}_2\text{O}$ was obtained by adding a saturated aqueous solution of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ to a hot ethanolic solution of the ligand (in 1 : 2.5 molar ratio).

$[\text{Cu}(\text{GB}-\text{H})_2]$: It was obtained as a dull brown product on refluxing an aqueous suspension of $[\text{Cu}(\text{GB})_2\text{Cl}_2]$ at pH 10-11 on a water bath.

The magnetic susceptibility, electrical conductance, infrared and visible reflectance spectra of the complexes were recorded as reported earlier⁸.

The analytical results, colour, molar conductance data in DMF at 28°, μ_{eff} at 300°K and

electronic reflectance data of the complexes are given in Table 1.

Results and Discussion

2-Guanidinobenzimidazole forms two types of complexes with copper(II) salts in methanol or ethanol: (a) $[\text{Cu}(\text{GB})_2\text{X}_2]n\text{H}_2\text{O}$ (where $\text{X}=\text{Cl}, \text{Br}, \text{NO}_3, \frac{1}{2}\text{SO}_4, \text{HCOO}, \text{CH}_3\text{COO}, \text{CH}_3\text{CH}_2\text{COO}, \text{CH}_3\text{CH}_2\text{CH}_2\text{COO}, \text{CH}_3\text{CH}(\text{OH})\text{COO}$ and ClCH_2COO and $n=0, 1$ and 2). (b) $[\text{Cu}(\text{GB})\text{X}_2]$ (where $\text{X}=\text{Cl}$ and Br only).

At higher pH the ligand is deprotonated and a neutral *bis* chelate $[\text{Cu}(\text{GB}-\text{H})_2]$ is formed. The hydrated complexes lose water molecules below 120°, indicating them to be uncoordinated. The complexes $[\text{Cu}(\text{GB})_2\text{X}_2]n\text{H}_2\text{O}$ and $[\text{Cu}(\text{GB})\text{X}_2]$ are slightly soluble in ethanol, dioxane and acetone but dissolve appreciably in DMF. At room temperature the DMF solution of the complexes show electrical conductances in the range 8-22 $\text{ohm}^{-1} \text{mole}^{-1} \text{cm}^2$, indicative of non-ionic nature of the complexes. The slight conductance values of the complexes are attributed to some solvation of coordinated anions. At room temperature, the magnetic moment values (Table 1) of the complexes $[\text{Cu}(\text{GB})_2\text{X}_2]n\text{H}_2\text{O}$ ($\text{X}=\text{Cl}, \text{Br}, \text{NO}_3$ and $\frac{1}{2}\text{SO}_4$ and $n=0$ or 1) are in the range of 1.84-1.88 BM which are almost similar to the reported values of Ghosh and Banerjee¹. The values reported by Ali *et al*⁷ are in the range of 1.50-1.55 BM (at 295°K) which are decidedly different. The magnetic moment values of carboxylate complexes $[\text{Cu}(\text{GB})_2(\text{RCOO})_2]n\text{H}_2\text{O}$ are also found in the range of 1.90-2.03 BM. The μ_{eff} values of the complexes suggest an octahedral or distorted octahedral stereochemistry⁹. The magnetic moment values of $[\text{Cu}(\text{GB})\text{Cl}_2]$ ca. 1.90 BM, $[\text{Cu}(\text{GB})\text{Br}_2]$ ca. 1.81 BM and neutral *bis* chelate $[\text{Cu}(\text{GB}-\text{H})_2]$ ca. 1.96 BM also fall in the range of magnetically dilute copper(II) complexes.

The electronic reflectance spectra of complexes $[\text{Cu}(\text{GB})_2\text{X}_2]n\text{H}_2\text{O}$ exhibit a d-d transition in the

TABLE 1

Complexes	Colour	Analytical data, Found (Calc.)			μ_{eff} at 300°K BM	λ_m (Ohm ⁻¹ mole ⁻¹ cm ²)	Electronic bands' position (cm ⁻¹)
		N(%)	Metal(%)	Anions(%)			
[Cu(GB) ₂ (HCOO) ₂]	Ash grey	27.61 (27.80)	12.81 (12.61)	—	1.94	—	17241, 22780
[Cu(GB) ₂ (OH ₂ COO) ₂]	Greenish-blue	26.18 (26.33)	12.01 (11.95)	—	2.03	8	16950, 25000
[Cu(GB) ₂ (CH ₂ CH ₂ COO) ₂]	Greenish-brown	24.89 (25.02)	11.46 (11.35)	—	1.90	10	17241, 23809
[Cu(GB) ₂ (CH ₂ CH ₂ OH ₂ COO) ₂].2H ₂ O	Greenish-brown	22.31 (22.45)	10.21 (10.18)	—	2.00	11	17544, 22780
[Cu(GB) ₂ (ClOH ₂ COO) ₂]	Greenish-brown	23.21 (23.31)	10.61 (10.57)	—	1.94	9	17544, 23809
[Cu(GB) ₂ (CH ₂ CHCOO) ₂].2H ₂ O OH	Bluish-green	22.24 (22.31)	10.25 (10.12)	—	1.94	8	16950, 22780
[Cu(GB)Cl ₂]	Light-brown	22.51 (22.61)	20.61 (20.51)	23.01 (22.94)	1.90	13	11900, 19608sh 25000
[Cu(GB)Br ₂]	Deep-brown	17.61 (17.57)	16.01 (15.94)	40.41 (40.14)	1.81	16	19510, 20000sh 25000
[Cu(GB-H) ₂]	Brown	33.99 (34.05)	15.31 (15.43)	—	1.96	6	17544, 23809sh
[Cu(GB) ₂ Cl ₂]	Bluish-grey	28.63 (28.89)	13.15 (13.10)	14.71 (14.65)	1.84	15	17860, 12820sh
[Cu(GB) ₂ Br ₂]	Ash grey	24.51 (24.41)	11.12 (11.08)	27.91 (27.87)	1.84	21	17544, 26315
[Cu(GB) ₂ (NO ₂) ₂]	Bluish-green	31.12 (31.25)	11.65 (11.82)	—	1.88	22	18020, 25641
[Cu(GB) ₂ SO ₄].H ₂ O	Bluish-green	26.44 (26.53)	11.90 (12.04)	18.01 (18.19)	1.88	—	17241, 24390

range 18020-16950 cm⁻¹ assignable to E_g→T_{2g} transition in approximately octahedral field⁹⁻¹¹. The complexes also display strong absorption near 26315-22730 cm⁻¹ due to the charge transfer transition. It has been found that the energy of the d-d band slightly differs from one anion to another indicating that anions are involved in coordination. The reflectance spectra of [Cu(GB)X₂] (where X=Cl and Br) display very broad and asymmetric band at 13510-11900 cm⁻¹ assignable to the combination of ³B_{1g}→³B_{2g}, ³B_{1g}→³E_g and ³B_{1g}→³A_{1g} transitions in distorted octahedral field. Besides the broad d-d transition, the complexes also exhibit a charge transfer band at 25000 cm⁻¹ and a shoulder near 20000-19608 cm⁻¹. The shoulder is attributed to some contribution from d-d transition. The complex [Cu(GB-H)₂] displays a weak d-d band at 17544 cm⁻¹ and a charge transfer band at 23809 cm⁻¹. The d-d band at 17543 cm⁻¹ is assigned to ³E_g→³T_{2g} transition in distorted octahedral field. From the energy of d-d transition it is found that tetragonal distortion in complexes [Cu(GB)X₂] is larger than *bis* chelated complexes [Cu(GB)₂X₂].nH₂O.

The ir spectra of carboxylate complexes display greater separation of $\nu_s(\text{COO})$ and $\nu_{\text{as}}(\text{COO})$ vibrations than free acid¹². It is also observed that $\nu_s(\text{COO})$ vibrations shift to lower frequency from the ionic carboxylate group indicating that carboxylate ions are bonded to central copper(II) atom as monodentate anions (Table 2)¹².

TABLE 2—INFRARED VIBRATION OF COORDINATED CARBOXYLATE ANIONS IN cm⁻¹

Complexes	$\nu_{\text{as}}(\text{COO})$	$\nu_s(\text{COO})$	Diff
[Cu(GB) ₂ (HCOO) ₂]	1560	1940	220
HCOONa ¹³	1567	1368	201
[Cu(GB) ₂ (CH ₂ COO) ₂]	1570	1400	170
CH ₂ COONa ¹³	1576	1414	162
[Cu(GB) ₂ (CH ₂ CH ₂ COO) ₂]	1568	1408	160
[Cu(GB) ₂ (CH ₂ CH ₂ OH ₂ COO) ₂].2H ₂ O	1570	1405	165
[Cu(GB) ₂ (ClOH ₂ COO) ₂]	1568	1390	178
[Cu(GB) ₂ (CH ₂ CHCOO) ₂].2H ₂ O	1570	1415	155
OH	1105(OH)	Out of plane bending	

The ir spectra of dinitrate complex [Cu(GB)₂(NO₂)₂] exhibits nitrate group vibrations at 1460, 1350 and 820 cm⁻¹ which according to Curtis and Curtis¹⁴ are characteristics of coordinated nitrate group. The ir spectra of the complex, Cu(GB)₂SO₄.H₂O, exhibit broad SO₄²⁻ vibrations at 1140 and 1090 (ν_2 split) and 940 cm⁻¹ (ν_1) indicating that SO₄²⁻ group is coordinated to copper(II) ion as a unidentate sulphate¹⁴. It is found that GB displays imidazole ring NH vibration at 3335 cm⁻¹ and several weak and broad guanidine =NH and -NH₂ vibrations between 3250-2850 cm⁻¹. The imidazole ring C=N stretch, N-H bending vibration, guanidine part -NH₂ and -NH- bending bands are observed between 1550 and 1650 cm⁻¹. The =NH bending band of the guanidine is observed at 1690 cm⁻¹. In almost all the complexes, benzimidazole NH stretching band is not

affected indicating that benzimidazole ring N-H is not involved in coordination. The (=NH) bending band (guanidine part) shifts to lower frequency and is observed at $1670 \pm 10 \text{ cm}^{-1}$. Thus, it is concluded that the ligand is bonded to copper(II) through tertiary nitrogen of benzimidazole ring and C=NH nitrogen of guanidine part. In neutral *bis* chelate, the absence of =NH bending band at 1690 cm^{-1} of the ligand indicates the chelation of the ligand by the deprotonation of =NH hydrogen.

References

1. S. P. GHOSH and A. K. BANERJEE, *Indian J. Chem.*, 1964, **2**, 292; *J. Indian Chem. Soc.*, 1961, **38**, 227.
2. S. P. GHOSH and A. K. BANERJEE, *J. Inorg. Nuclear Chem.*, 1968, **28**, 167.
3. S. P. GHOSH and A. I. P. SINHA, *Indian J. Chem.*, 1964, **2**, 312.
4. S. P. GHOSH and A. K. BANERJEE, *J. Indian Chem. Soc.*, 1967, **44**, 589; 1969, **46**, 811.
5. S. P. GHOSH and L. K. MISHRA, *Inorg. Chim. Acta*, 1973, **7**, 545.
6. S. P. GHOSH, L. DUBBY, P. BHATTACHARJEE and L. K. MISHRA, *J. Indian Chem. Soc.*, 1977, **54**, 230.
7. S. M. ALI, N. AHMED and M. S. HUSSAIN, *Pakistan J. Sci. Res.*, 1963, **18**, 33; *Chem. Abs.*, 1968, **68**, 8882p.
8. R. S. NYHOLM and J. LEWIS, *Progress of Inorganic Chemistry*, Edited by F. A. COTTON, Vol. 6, p. 41.
9. L. SACCONI and M. CIAMPOLINI, *J. Chem. Soc.*, 1964, 278.
10. J. FERGUSON and B. O. WEST, *J. Chem. Soc.*, 1966A, 1959.
11. J. L. FUNK and T. R. ORTOLOANO, *Inorg. Chem.*, 1968, **7**, 567.
12. K. NAKAMOTO, "Infrared Spectra of Inorganic and Coordination Compounds", John Wiley & Sons, Inc., 1967, p. 198.
13. N. F. CURTIS and Y. M. CURTIS, *Inorg. Chem.*, 1965, **4**, 804; A. B. P. LEVYER, *Inorg. Chem.*, 1965, **4**, 1042.
14. K. NAKAMOTO, "Infrared Spectra of Inorganic and Coordination Compounds", John Wiley & Sons, Inc., 1967, p. 176.