

Synthesis & Characterization of Halogeno N,N'-Bis(dithiocarboxy)- piperazine Complexes of Cr(III), Fe(III) & Cu(II)

K K ARAVINDAKSHAN

Department of Chemistry, University of Calicut, Kerala, 673 635

Received 2 December 1985; revised 2 May 1986; accepted
27 May 1986

Halogeno N,N'-bis(dithiocarboxy)piperazine complexes of Cr(III), Fe(III) and Cu(II) have been prepared by interacting the respective metal halides with bis(benzoyldithiocarboxy)piperazine. The complexes have the compositions $[\text{CrXL}].2\text{H}_2\text{O}$, $[\text{FeXL}]$ and $[\text{Cu}_2\text{X}_2\text{L}].2\text{H}_2\text{O}$ [where $\text{X}=\text{Cl}$ or Br and $\text{L}=\text{N,N}'\text{-bis(dithiocarboxy)piperazine}$] and have been characterized by molar conductance and magnetic susceptibility measurements and UV IR and thermal data.

Sodium salts of dithiocarbamates react with metal halides to give instead of the expected halogeno derivatives, only simple dithiocarbamate complexes. Martin and White¹ prepared a series of monohalogeno bis(N,N'-dialkyldithiocarbamato)iron(III) by vigorously shaking a benzene solution of tris(N,N'-dialkyldithiocarbamato)iron(III) with minimum quantity of conc. hydrochloric acid. In view of the susceptibility of the complexes to hydrolysis in hydrolytic media such as water or alcohol, the preparation of the complexes by this procedure required extra care. Nair and Yusuff^{2,3} prepared these halogeno complexes by a simple procedure involving treatment of metal halides with mixed benzoic

dithiocarbamic anhydride in acetone medium. This prompted us to undertake the title investigation.

The ligand, bis(benzoyldithiocarboxy)piperazine (I) was prepared following the procedure described in the literature⁴.

The complexes were prepared as follows: An acetone solution of the respective metal halide [0.01 mol for Cr(III) and Fe(III) and 0.02 mol for Cu(II)] was slowly added to a hot dioxane solution of the ligand (slightly greater than 0.01 mol). The complexes that separated out on slow evaporation of the reaction mixture were filtered, washed with dioxane followed by acetone and dried *in vacuo* over P_4O_{10} .

The analytical data of the complexes are presented in Table I. Molar conductances of 10^{-3} M solutions of the complexes in methanol and nitrobenzene, determined at $28 \pm 2^\circ\text{C}$ using an Elico's direct reading conductivity bridge type M 82T, indicate that the complexes behave as non-electrolytes. However, the complexes are observed to undergo slight dissociation in methanol.

The magnetic susceptibilities were determined at room temperature by Gouy method using $\text{Hg}[\text{Co}(\text{NCS})_4]$ as calibrant. The complexes, $[\text{CrXL}].2\text{H}_2\text{O}$, where $\text{X}=\text{Cl}$ or Br and $\text{L}=\text{N,N}'\text{-bis(dithiocarboxy)piperazine}$, have magnetic moments of 3.68 and 3.65 B.M. respectively, which are slightly lower than the spin-only value (3.81 B.M.)⁶ expected for octahedral Cr(III) complexes.

The chloro and bromo complexes of Fe(III) have μ_{eff} values of 4.20 and 3.95 B.M., respectively, corresponding to three unpaired electrons (3.87 B.M.).

Table I—Analytical Data of Halogeno N,N'-Bis(dithiocarboxy)piperazine Complexes of Cr(III), Fe(III) and Cu(II)

Complexes	Found (Calc), (%)				
	M*	C	N	S*	Halogen*
$[\text{CrClL}].2\text{H}_2\text{O}$	14.40	20.51	7.62	35.20	9.92
	(14.45)	(20.03)	(7.78)	(35.64)	(9.85)
$[\text{CrBrL}].2\text{H}_2\text{O}$	12.75	17.81	6.75	31.80	19.84
	(12.86)	(17.83)	(6.93)	(31.72)	(19.76)
$[\text{FeClL}]$	16.93	22.05	8.52	39.08	10.83
	(17.04)	(21.99)	(8.55)	(39.13)	(10.82)
$[\text{FeBrL}]$	14.98	19.56	7.60	34.55	21.25
	(15.01)	(19.36)	(7.53)	(34.46)	(21.47)
$[\text{Cu}_2\text{Cl}_2\text{L}].2\text{H}_2\text{O}$	27.00	15.11	5.89	27.38	15.00
	(27.02)	(15.32)	(5.96)	(27.26)	(15.07)
$[\text{Cu}_2\text{Br}_2\text{L}].2\text{H}_2\text{O}$	22.78	12.63	5.11	23.02	28.47
	(22.72)	(12.88)	(5.01)	(22.93)	(28.57)

[L = N,N'-Bis(dithiocarboxy)piperazine]

*Determined by standard procedures (see reference 5)

These complexes may have square-pyramidal geometry in analogy with other halogeno dithiocarbamatoiron(III) complexes of known structure^{1,2}. The Cu(II) complexes, $[\text{Cu}_2\text{Cl}_2\text{L}]\cdot 2\text{H}_2\text{O}$ and $[\text{Cu}_2\text{Br}_2\text{L}]\cdot 2\text{H}_2\text{O}$ show magnetic moments of 1.73 and 1.63 B.M. respectively, but exact prediction of geometries of the complexes could not be made on these data alone.

The reflectance spectra of Cr(III) complexes, recorded on a Shimadzu model SP 200, exhibit two bands at 435 and 565 nm, which are assigned to the transitions ${}^4A_{2g}(\text{F}) \rightarrow {}^4T_{1g}(\text{F})$ and ${}^4A_{2g}(\text{F}) \rightarrow {}^4T_{2g}(\text{F})$ respectively. These are characteristic of octahedral Cr(III) complexes⁷. The reflectance spectra of Fe(III) complexes do not show any distinct band in the visible region. The Cu(II) complexes show two broad bands, one around 670 nm due to ${}^2B_{1g} \rightarrow {}^2A_{1g}$ transition and another one around 540 nm due to ${}^2B_{1g} \rightarrow {}^2B_{2g}$ transition, which may be indicative of square-planar geometry⁸ for Cu(II) complexes.

The IR spectra of the complexes were recorded in KBr in the region 4000–400 cm^{-1} and far IR spectra in nujol employing Perkin-Elmer model 397 and Beckman IR 12 instrument. The IR spectra of the Cr(III) and Cu(II) complexes exhibit bands of medium intensity in the region 3600–3300 cm^{-1} assignable to νOH of water. Though the appearance of δOH around 1620 cm^{-1} suggests the presence of coordinated water, bands due to wagging, twisting and rocking modes of coordinated water are not present⁹. Further the thermogravimetric analysis indicates that water is present as purely lattice-held water (loss of water molecules near 100°C).

The $\nu\text{C}-\text{N}$ band appears at a higher wavenumber (1475 cm^{-1}) in bis(benzoyldithiocarboxy)piperazine, as compared to that (1450 cm^{-1})¹⁰ in N,N'-bis(dithiocarboxy)piperazine. This difference in $\nu\text{C}-\text{N}$ is reflected in the IR spectra of the complexes also—it occurs at $\sim 1500 \text{ cm}^{-1}$ in the present halogeno dithiocarbamate complexes in comparison to that at $\sim 1470 \text{ cm}^{-1}$ in N,N'-bis(dithiocarboxy)piperazine complexes. Similar observations have been recorded by other workers also^{10,12}. The free ligand band at 1000 cm^{-1} , assignable to $\nu\text{C}=\text{S}$ undergoes shift to lower wavenumber (990 cm^{-1}) in the complexes.

In the far IR region the appearance of intense band near 370 cm^{-1} in the complexes is attributed to $\nu\text{M}-\text{S}$ mode¹³. In the spectra of the chloro and bromo complexes of Cr(III) and Fe(III) the bands near 330 and 240 cm^{-1} are attributed to terminal $\nu\text{M}-\text{Cl}$ and $\nu\text{M}-\text{Br}$ respectively¹. In the Cu(II) complexes $\nu\text{Cu}-\text{Cl}$ and $\nu\text{Cu}-\text{Br}$ appear at 270 and 200 cm^{-1}

respectively. The presence of these bands in lower wavenumber region, in comparison to the normal $\nu\text{M}-\text{Cl}$ and $\nu\text{M}-\text{Br}$ regions indicates the bridged nature of halogens in these Cu(II) complexes^{9,14}.

Thermal decomposition studies were carried out at a heating rate of 10°/min using a Du Pont 990 analyser. The decomposition of Cr(III) and Cu(II) complexes starts between 90 and 100°C. The DTG peaks and the corresponding endothermic DTA peaks around 110°C indicate the elimination of lattice-held water molecules. The Fe(III) complexes are stable up to $\sim 155^\circ\text{C}$. The final decomposition products were analysed to be Cr_2O_3 , Fe_2O_3 and CuO. The mass loss data obtained in independent pyrolysis experiments agree favourably with the TG data.

Considering the analytical data [metal: ligand:halogen, 1:1:1 for Cr(III) and Fe(III) and 1:0.5:1 for Cu(II) complexes] and the fact that a ligand molecule can coordinate to two metal ions, linear polymeric structures can be assigned to the halogeno bis(dithiocarboxy)piperazine complexes under investigation. The physicochemical studies suggest a penta-coordinated square-pyramidal structure (II) for Fe(III) complexes and halogen bridged planar structure (III) for Cu(II) complexes. The Cr(III) complexes have octahedral geometry, where the sixth coordination position in structure (II) may be satisfied by the interaction with an electron-rich centre in the neighbouring molecule.

The author thanks Prof C G R Nair, Department of Chemistry, University of Kerala for his guidance. Thanks are also due to Prof C P Savariar, for encouragement.

References

- Martin R L & White A N, *Inorg Chem*, **6** (1967) 712.
- Nair C G R & Yusuff K K M, *Inorg nucl chem Lett*, **11** (1975) 753.
- Nair C G R & Yusuff K K M, *J inorg nucl Chem*, **39** (1977) 281.
- Nair P G & Joshua C P, *Tetrahedron Lett*, **47** (1972) 4785.
- Vogel A I, *A textbook of quantitative inorganic analysis* (ELBS and Longman, London), 1978.
- Figgis B N & Lewis J, *Progress in inorganic chemistry*, Vol. 6, edited by F A Cotton (Interscience, New York), 1964.
- Figgis B N, *Introduction to ligand fields* (Interscience, New York) 1964.
- Weeks M J & Fackler J P, *Inorg Chem*, **7** (1968) 2548.
- Nakamoto K, *Infrared spectra of inorganic and coordination compounds* (John Wiley, New York), 1963.
- Aravindakshan K K, *Indian J Chem*, **25A** (1986) 592.
- Chatt J, Duncanson L A & Venanzi L M, *Suomen Kemi*, **29B** (1956) 75.
- Nakamoto K, Jujita J, Condrate R A & Morimoto Y, *J chem Phys*, **39** (1963) 423.
- Ojima T, Onishi T, Iwamoto T, Inamoto N & Tamaru K, *Inorg nucl chem Lett*, **6** (1970) 65.
- Adams D M & Lock P J, *J chem Soc (A)* (1967) 620.