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Magneto-chemistry and Infrared Spectra of Ammonia and Primary Aliphatic Amine Complexes of Copper(II) Chromate

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Synopsis. Complexes of divalent copper of the type $CuCrO_4 \cdot 4Am$ and $CuCrO_4 \cdot 2Am \cdot 2H_2O$ with Am=ammonia or primary aliphatic amine, have been prepared and characterized. All the compounds reported are paramagnetic and values of μ_{eff} in the range 1.77—1.86 B.M. The assignment of the vibrational bands of the ligands and their shifts in frequency on co-ordination with copper(II) ion are discussed.

Many complexes of copper(II) have been described in literature and in particular complexes with ammonia and primary aliphatic amines. Relatively, very little work has been done on copper(II)chromate.[1] So far, most studies have been concerned with synthesis of copper(II) chromate–ammonia complexes and apart from few isolated examples, there have been no reports of magnetic data or absorption spectra. In the present communication, we report the results of an investigation into preparation, characterization, magnetic properties and infrared spectra of several complexes of copper(II)chromate with ammonia and primary aliphatic amines.

Experimental

The complexes were prepared by the following two methods:

(a) Shaking Method. About 5 g of copper(II) chromate was suspended in 40 ml of acetone with calculated quantity of liquor ammonia in a 250 ml conical flask. The contents were shaken for about two days. The complex formed was filtered, washed with acetone and dried over P_4O_{10}.

(b) Vapor Method. About 5 g of copper(II) chromate was placed in a calcium chloride tube fitted with a glass wool plug at the bottom. This tube was fitted in a conical flask containing the anhydrous primary aliphatic amine, thereby exposing the solid to vapors for about thirty hours. The complex formed was dried over P_4O_{10}.

1. Tetraaminecopper(II) Chromate. Prepared by Method a. The complex is green in color. Found: Cu, 25.59; N, 22.58; H, 6.88%. Calcd for $H_{16}O_4CrN_4Cu$: Cu, 25.23; N, 22.25; H, 6.40%.

2. Tetramethylaminecopper(II) Chromate. Prepared by Method b. Green. Found: Cu, 21.00; N, 18.42; C, 16.10; H, 6.14%. Calcd for $C_4H_{20}O_4CrN_4Cu$: Cu, 20.92; N, 18.44; C, 15.82; H, 6.58%.

3. Tetraethylaminecopper(II) Chromate. Prepared by Method b. Green. Found: Cu, 17.62; N, 15.40; C, 26.68; H, 7.49%. Calcd for $C_8H_{28}O_4CrN_4Cu$: Cu, 17.67; N, 15.58; C, 26.70; H, 7.78%.

4. Diaquodi-n-propylaminecopper(II) Chromate. Prepared by Method b. Green. Found: Cu, 18.98; N, 8.35; C, 21.86; H, 6.19%. Calcd for $C_6H_{22}O_6CrN_2Cu$: Cu, 19.06; N, 8.39; C, 21.59; H, 6.59%.

5. Diaquodi-n-butylaminecopper(II) Chromate. Prepared by Method b. Green. Found: Cu, 17.52; N, 7.61; C,

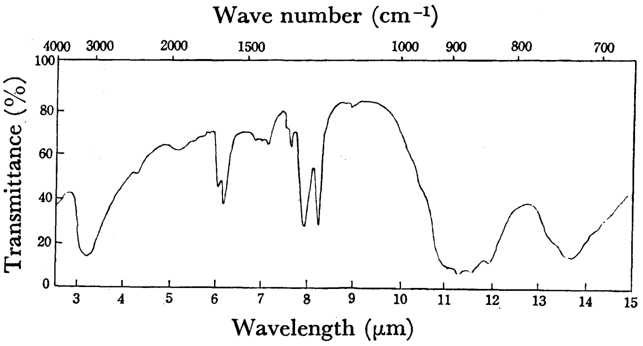

Fig. 1. Infrared spectrum of tetraamminecopper(II) chromate.

TABLE 1. MAGNETIC MOMENTS AND INFRARED BADNS (cm^{-1})

Compound	μ_{eff} (B.M.)	ν(NH)	NH_2 deform.	ν(CN)	Symm. C–N–H bend.	Asymm. C–N–H bend.	ν(OH)	$\nu\delta$ (Cr–O)
1. Tetraamminecopper(II) chromate	1.86	3205br	1646m	—	—	—	—	880br
2. Tetramethylaminecopper(II)-chromate	1.77	3325m	—	1075s 1037w	750m	837w	—	885s
3. Tetraethylaminecopper(II)-chromate	1.82	3230m	—	1078m 1042w	745m	839w	—	886s
4. Diaquodi-*n*-propylaminecopper(II)chromate	1.81	3240m	—	1085m 1051w	745m	851w	3480m	889s
5. Diaquodi-*n*-butylaminecopper(II) chromate	1.84	3365sh 3250m	1586s	1100w 1073vw	743s	845s	3490m	888s
6. Diaquodi-*n*-amylaminecopper(II) chromate	1.81	3368sh 3252m	1586s	1095w 1075vw	741s	845m	3485w	889s
7. Free aliphatic amine	—	3400	1620±30	1079±11	778±15	825±15	—	—

s, strong; m, medium; w, weak; vw, very weak; sh, shoulder; br, broad.

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26.33; H, 6.88%. Calcd for $C_8H_{26}O_6CrN_2Cu$: Cu, 17.58; N, 7.74; C, 26.56; H, 7.19%.

6. *Diaquodi-*n*-amylaminecopper(II) Chromate.* Prepared by Method b. Green. Found: Cu, 16.27; N, 7.16; C, 31.20; H, 7.32%. Calcd for $C_{10}H_{30}O_6CrN_2Cu$: Cu, 16.31; N, 7.19; C, 30.81; H, 7.70%.

Magnetic Measurements. The absolute values of magnetic moments of the compounds were measured at room temperature (304 K) using Gouy's method. (Table 1). The infrared spectra were obtained on a Infracord Model 137 spectrophotometer with the samples mounted as KBr disks. (Table 1, Fig. 1.)

Results and Discussion

The copper(II) chromate complexes possess general molecular formulae $[Cu(Am)_4]CrO_4$ and $[Cu(Am)_2(H_2O)]CrO_4$, where Am in the former represents either ammonia, methylamine or ethylamine and in the latter either *n*-propylamine, *n*-butylamine or *n*-amylamine.

All the complexes have been found to be paramagnetic and the value of effective magnetic moment is between 1.77—1.86 B.M. The four co-ordinate planar copper(II) complexes should have a value close to spin-only value of 1.73 B.M.²⁾ The magnetic moments of tetrahedral copper(II) complexes are expected to be around 2.2 B.M.³⁾ The tetrahedral arrangement of ligands has been found to be extremely rare for all copper(II) complexes, as a perfectly tetrahedral complex is orbitally triply degenerate and hence unstable.⁴⁾

The ν(NH) in all complexes is observed in the range 3205—3368 cm^{-1}, whereas in ammonia and free aliphatic amines the band is observed at 3414 and 3400 cm^{-1}, respectively. The ν(NH) shifts to a lower value on co-ordination due to drainage of electrons from the nitrogen atom, thereby weakening N–H bond and resulting in a highly covalent metal–nitrogen bond.⁵⁾ The magnitude of the negative shift decreases as the molecular weight of the amine increases, which indicates that covalency of metal–nitrogen bond and stability of complexes decrease in the above order.⁶⁾ The position of all other bands are affected by co-ordination when compared with free amines.⁷⁻⁹⁾

The O–H stretching band near 3485 cm^{-1} has been observed in all aquo complexes. There is a decrease in O–H stretching frequency due to co-ordination of water molecule with metal atom.¹⁰⁻¹²⁾ In addition to ν(OH), a characteristic band of co-ordinated water at 795 cm^{-1} in all aquo complexes has been observed.¹³⁻¹⁵⁾

The $\nu\delta$(Cr–O) band in all complexes has been observed near 884 cm^{-1} indicating the presence of ionic chromate.¹⁶⁾

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