

## Preparation, Characterization and Thermal Studies of Cu(II) and Ni(II)-ammine Paramolybdate Complexes

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Copper and nickel ammine paramolybdate complexes were prepared and characterized via their nitrogen content and i.r. study. The complexes were also subjected to TG and DTA. The i.r. study suggests that the compounds prepared are of the ion-pair type. Heat treatment of both complexes gave the mixed oxides  $3\text{NiO} \cdot 7\text{MoO}_3$  and  $3\text{CuO} \cdot 7\text{MoO}_3$  respectively.

### INTRODUCTION

Dji and Gabriel<sup>1</sup> synthesised a series of complexes such as Mo-Cu, Cr-Ni, Cr-Cu with ammonium triammine tetranickel (II) pentamolybdate and find that their lattice parameters are very similar. Also, in a recent study<sup>2</sup> the paramolybdates of five cobaltammine complexes were subjected to IR, TG, DTA and elemental analysis. Their magnetic properties were also studied. The present work is devoted to study on copper and nickel-ammine paramolybdate complexes.

### EXPERIMENTAL

#### Synthesis of Molybdate Complexes

Nickelhexammine sulphate and coppertetrammine chloride were prepared as described in the literature<sup>3</sup>, ammonium paramolybdate solution was added with constant stirring to the solution of each complex in the molar ratio 1 : 3. The mixtures were left overnight and the precipitated products filtered, washed with distilled water and dried for few hours at 110°C. The pH of the reaction mixture was close to 6.5. Such relatively low pH value is responsible for the conversion of the cationic part of the precipitated salts from  $[\text{Cu}(\text{NH}_3)_4]^{++}$  into  $[\text{Cu}(\text{NH}_3)_3\text{H}_2\text{O}]^{++}$  and  $[\text{Ni}(\text{NH}_3)_6]^{++}$  into  $[\text{Ni}(\text{NH}_3)(\text{H}_2\text{O})_5]^{++}$ .

All the physical measurements were performed as reported earlier.<sup>2</sup>

### RESULTS AND DISCUSSION

From the elemental analysis and magnetic properties (Table 1) it is clear that the value of  $\mu_{\text{eff}}$  for the copper (II) complex is lower than the expected value for a  $d^9$  system. A similar low value was observed with the Co(II) complex<sup>1</sup>, which was attributed to the effect of  $\text{NH}_3$  and  $\text{H}_2\text{O}$  as

ligands. The high value in case of the nickel complex is most probably due to some sort of octahedral-tetrahedral distortion which is a phenomenon generally encountered in nickel complexes<sup>4</sup>. This assumption may explain the observed rapid and explosive loss of water on heating. If such an assumption is true, two of the five coordinated water molecules from the octahedral  $[\text{Ni}(\text{NH}_3)(\text{H}_2\text{O})_5]^{++}$  cation will turn into water of crystallisation in the tetrahedral cation  $[\text{Ni}(\text{NH}_3)(\text{H}_2\text{O}_3)]^{++}$ . It is well known that water of crystallization is much more easily lost than coordinated water.

TABLE I  
NITROGEN PERCENTAGE AND MAGNETIC SUSCEPTIBILITY OF  
THE PRESENT COMPLEXES

Complexs	Colour	% N		
		Calcd.	Found	$\mu_{\text{eff}}$
$[\text{Cu}(\text{NH}_3)_3(\text{H}_2\text{O})_3]\text{Mo}_7\text{O}_{24}$	Pale green	8.4	8.4	1.69
$[\text{Ni}(\text{NH}_3)(\text{H}_2\text{O})_5]\text{Mo}_7\text{O}_{24}$	Pale blue	2.7	2.7	3.42
$[\text{Co}(\text{HN}_3)_4(\text{H}_2\text{O})_3]\text{Mo}_7\text{O}_{24}$	Lilac	10.9	11.4	1.64

The vibrational spectra of copper- and nickelammine complexes have been studied by Schmidt and Muller<sup>5</sup>. It is observed that the antisymmetric and symmetric  $\text{NH}_3$  stretching, the  $\text{NH}_2$  degenerate deformation, the  $\text{NH}_2$  symmetric deformation and  $\text{NH}_2$  rocking vibrations appear in the regions of 3330–3310, 1625–1605, 1285–1245 and 740  $\text{cm}^{-1}$  respectively. The metal-ammine stretches and deformation ( $\nu_{\text{M-N}}$  and  $\delta_{\text{N-M-N}}$ ) are also observed at *ca* 400  $\text{cm}^{-1}$  and 260  $\text{cm}^{-1}$  respectively<sup>6</sup>. The shift in vibration bands of the cationic ammine complexes and of the paramolybdate anion due to ion-pair formation are given in Table 2. In all the thermally treated compounds, the originally broad  $\text{Mo}=\text{O}$ ,  $\text{Mo}-\text{O}-\text{Mo}$  bands at about 830 and 890  $\text{cm}^{-1}$  have been resolved while those at 1400  $\text{cm}^{-1}$  and 1100  $\text{cm}^{-1}$  remained unchanged. The resolution of the former bands may be attributed to the removal of the  $\rho_r(\text{NH}_2)$  vibration in the resulting mixed oxide.

### Thermal Studies

The weight-loss curves of the copper and nickel complexes are given in Fig 1, Table 3. These complexes dissociate thermally in two steps. For copper a plateau is observed in the region 450°–750°C as observed before with the cobalt (II) complex<sup>1</sup>. Slow weight loss took place at first followed by rapid decomposition. The slow weight loss began in the temperature range of 100°–180°C. For nickel a rapid weight loss of water of crystallisation is observed in the range 100°–150°C followed by a sharp loss in the range 280°–540°C. The endothermic peak below 290°C is very

TABLE 2  
VIBRATIONAL SPECTRA OF DIVALENT METAL AMMINE PARAMOLYBDATE COMPLEXES

	$\nu_a(\text{NH}_3)$	$\delta_a(\text{NH}_3)$	$\delta_s(\text{HNH})$	$\rho_r(\text{NH}_2)$	$\nu_{\text{M}-\text{N}}$	$\delta(\text{N}-\text{M}-\text{N})$	$\nu_1 + \nu_3$	$\nu_{\text{M}=\text{O}}$	$\nu_{\text{M}=\text{O}-\text{O}}$	$\nu_{\text{M}=\text{O}-\text{M}=\text{O}}$	$\nu_{\text{M}=\text{O}}$	$\nu_{\text{Ni}-\text{OH}}$
$[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2 \cdot 7$	3345 3190	1607	1176	685	335							
$[\text{Ni}(\text{NH}_3)(\text{H}_2\text{O})_5]_2\text{Mo}_7\text{O}_{24}$	3330	1625	1245	—	385	217	850	1630	1400	890	830	450
$\text{Cu}(\text{NH}_3)_6\text{SO}_4 \cdot \text{H}_2\text{O}^a$	3327 3253 3169	1669 1639	1300	735	426	256						
$[\text{Cu}(\text{NH}_3)(\text{H}_2\text{O})_5]_2\text{Mo}_7\text{O}_{24}$	3310 3150	1605	1285	740	440	260	870	1605	1410	130	$\nu_{\text{Cu-Cl}}$ 325	$\nu_{\text{CH-O-NO}_2}$ 620
$[\text{Co}(\text{NH}_3)_6]\text{Cl}_2^b$	3330 3250	1602	1163	654	325	292						
$[\text{Co}(\text{NH}_3)_4]_2[\text{Mo}_7\text{O}_{24}]^b$	3290	1620	1370	865	480	335	835	1620	1400	835	360	

TABLE 3  
THERMAL STUDIES AND WEIGHT LOSS DATA  
OF THE PRESENT COMPLEXES

Complex	% loss	Temp °C	Significance of loss
$[\text{Ni}(\text{NH}_3)(\text{H}_2\text{O})_5]_3\text{Mo}_7\text{O}_{21}$	6.0	150	$6\text{H}_2\text{O}$
	10	380	$9\text{H}_2\text{O}$
	15	520	$12\text{H}_2\text{O}$
	20	630	$3\text{NiO}\cdot 7\text{MoO}_3$
$[\text{Cu}(\text{NH}_3)_5(\text{H}_2\text{O})]_3\text{Mo}_7\text{O}_{21}\cdot 3\text{H}_2\text{O}$	3.0	150	$3\text{H}_2\text{O}$
	11	290	$9\text{H}_2\text{O}$
	14	310	$12\text{H}_2\text{O}$
	17	840	$3\text{CuO}\cdot 7\text{MoO}_3$

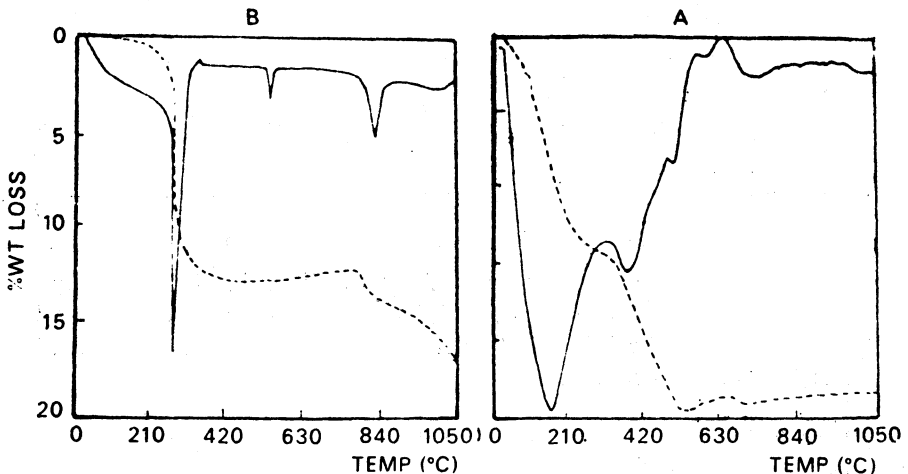


Fig. 1. DTA and TG of the paramolybdates of nickel ammine (A) and copper ammine (B) complexes

sharp in case of copper correspond to the evolution of water of crystallisation together with water and ammonia of coordination.

The strong exothermic peak between  $450^{\circ}$ – $500^{\circ}\text{C}$ , in case of  $\text{Co}(\text{II})$ , attributed to crystallisation of mixed oxides diminished in case of  $\text{Ni}(\text{II})$  and disappeared in  $\text{Cu}(\text{II})$ . This is most probably due to the relatively higher rate of reaction in the present two cases.

The suggested structures are: 1.  $3\text{NiO}\cdot 7\text{MoO}_{21}$ , 2.  $3\text{CuO}\cdot 7\text{MoO}_{21}$ , 3.  $3\text{CoO}\cdot 7\text{MoO}_{21}$

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**SYMPOSIUM ON FREE RADICALS**

An international symposium of free radicals in biotechnology and medicine relating to analytical determination of free radicals will be held at the Scientific Societies Lecture Theatre, Savile Row, London on 7 February 1990.

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