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PREPARATION, CHARACTERIZATION AND THERMAL STUDIES OF THE PARAMOLYBDATES OF SOME COBALTAMMINE COMPLEXES

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ABSTRACT

Five cobaltammine–paramolybdate ion-pair complexes have been prepared and characterized via their nitrogen content and IR study. The complexes were subjected to thermogravimetric and differential thermal analyses. The IR study suggests that the compounds prepared are of the ion-pair type. Thermal treatment showed that molybdenum in complexes containing five or six ammonia ligands per cation is reduced from oxidation state VI to V, a phenomenon which did not take place in complexes containing four ammonia ligands. The IR study of the thermally decomposed compounds revealed the resolution of the originally broad Mo=O and Mo–O–Mo bands.

INTRODUCTION

There is very little work described in the literature concerning the paramolybdates of transition-metal complexes. Very few of such ion-pairs have been characterized [1–3], and preparations utilizing oxomolybdate clusters have been described [4–6]. Coomber and Griffith [7] studied the electronic and IR spectra of the hexammine Co(III) molybdate. Mironov et al. [8] were concerned with the heats and entropies of coordination of the cobaltammine molybdate and tungstate complexes.

Amperometric and conductometric titrations have been used to determine the composition of Co(II), Ni(II), Cu(II) and Zn(II) hydroxocyanomolybdates [9]. The thermodynamics of some outer-sphere molybdate and tungstate complexes of some cobalt ammoniates have also been determined [10].

EXPERIMENTAL

Materials

A 1-M ammonium molybdate, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, stock solution was prepared in distilled water, from the A.R.-grade chemical. The following

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cobaltammine complexes were prepared as described in the literature [10]: hexamminecobalt(III) chloride, chloropentamminecobalt(III) chloride, nitratopentamminecobalt(III) nitrate, carbonatotetramminecobalt(III) chloride, and hexamminecobalt(II) chloride.

Ammonium molybdate solution was added with continuous stirring to the solutions of the prepared complexes in the proper ratios. The pH of the solutions were found to be slightly below 7.0. Instant precipitation was observed; however, the mixtures were left overnight to ensure complete precipitation. The precipitates were filtered, washed with water and dried at 100–105 °C.

Methods

The following techniques and/or measurements were carried out on the prepared cobaltammine *p*-molybdate complexes. (i) Elemental analysis for nitrogen at the microchemical analysis centre, Cairo University. (ii) The IR spectra were recorded on a Perkin–Elmer spectrometer over the range 4000–200 cm^{-1} using the KBr disc technique. (iii) Magnetic susceptibility measurements were carried out at 20 °C using the Gouy method. (iv) Thermogravimetric (TG) and differential thermal analysis (DTA) data were obtained using a Stanton RedCroft STA-78, simultaneous thermal analyser (rate 2 °C min^{-1}, 50 ml min^{-1}; N_2 at atmospheric pressure).

It is interesting to note that, when the carbonatopentamminecobalt(III) complex was dissolved in water mixed with ammonium molybdate, the bicarbonatoaquotetramine *p*-molybdate was obtained on precipitation. Again the hexammine complex of Co(II) gave, after mixing with ammonium molybdate, the diaquotetraminecobalt(II) ion-pair.

RESULTS AND DISCUSSION

Table 1 shows the nitrogen content and the magnetic susceptibility of the prepared complexes.

IR study

Assignment of vibrational modes

Ammine complexes vibrations. The vibrational spectra of metal–ammine complexes have been studied extensively and have been reviewed by Schmidt and Müller [11]. It is stated that the antisymmetric and symmetric NH_3 stretchings, the NH_3 degenerate deformation, the NH_3 symmetric deformation and the NH_3 rocking vibrations appear in the regions of 3400–3000, 1650–1550, 1370–1000 and 950–590 cm^{-1}, respectively. The metal–ammine stretches and deformation (ν_{M-N} and δ_{N-M-N}) are observed near 500 cm^{-1} and 300 cm^{-1}, respectively [12].

TABLE 1

Nitrogen content and magnetic susceptibility $(v_s$ of some *p*-molybdate cobaltammine complexes

Complex	Colour	N(%)		u_s
		Calc.	Exp.	
$[Co(NH_3)_6]_2 \cdot Mo_7O_{24}$	Clear orange	12.2	12.6	Diamagnetic
$[Co(NH_3)_5Cl]_3Mo_7O_{24} \cdot 3H_2O$	Pink	12.8	12.8	Diamagnetic
$[Co(NH_3)_5NO_3]_3Mo_7O_{24}3H_2O$	Pink	14.6	14.6	Diamagnetic
$[Co(NH_3)_4H_2OHCO_3]_3Mo_7O_{24}$	Clear violet	10.4	10.4	Diamagnetic
$[Co(NH_3)_4(H_2O)_2]_3Mo_7O_{24}$	Lilac	10.9	11.4	1.64

$MO_7O_{24}^{6-}$ vibrations (paramolybdate ion). When a basic solution containing only MoO_4^{2-} and NH_4^+ is acidified, the molybdate ions condense in definite steps to form a series of polymolybdate ions. When the pH is lowered to about 6, polymerization is detectable and the main reaction at this stage is to form the paramolybdate ion [13].

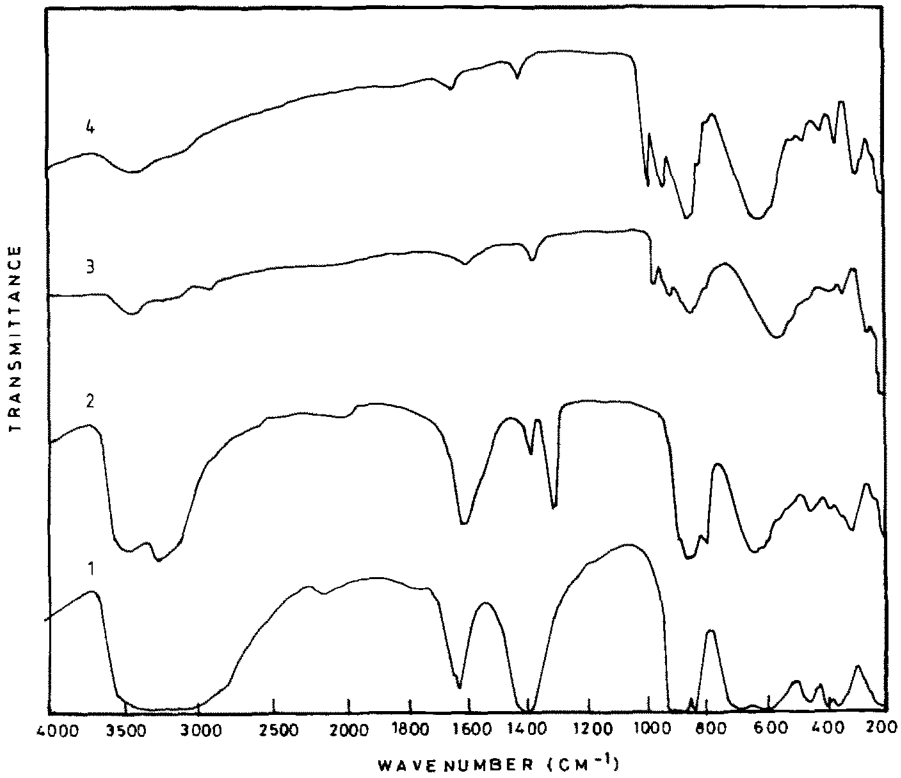

Fig. 1. The IR spectra of ammonium paramolybdates (1) and hexammine cobalt(III) paramolybdates heated at 110 °C (2), 290 °C (3), 450 °C (4).

TABLE 2

Vibrational spectra of [ammine complexes][Mo_7O_{24}] · xH_2O

Complex	$\gamma_a NH_3$	$\delta_a NH_3$	$\delta_s HNH$	$\rho_r NH_3$	$\gamma(H-N)$	$\nu(N-H-N)$	$\nu_1+\gamma_3$	$\nu_2+\nu_4$	$\nu(Mo=O)$	$\nu(Mo=O)$	$\nu(Mo-O-Mo)$	$\nu(Mo-O)$	$\nu(Co-C)$	$\nu(Co-ONO_2)$	$\nu(Co-OCO_2)$
$Mo_7O_{24}^{6-}$							890,	967	1630(s)	1410(s)	840(s)	370(br)			
$[Co(NH_3)_6]Cl_3$ [18]	3240 3160	1619	1329	831											
$[Co(NH_3)_6]_2[Mo_7O_{24}]$	3290(s)	1620(s)	1370(s)	865(s)	480 410(m)	335(m)	835(s)		1620(s)	1400(s)	835(s)	360(br)			
$[Co(NH_3)_5Cl]Cl_2$ [7]		1587(m)	1302	847	488	325							275		
$[Co(NH_3)_5Cl]_3[Mo_7O_{24}]$ $\cdot 3H_2O$	3500 3200	1615	1320 1355	825 880	555 410	340	905	655	1615	1405(s)	785	370	290		
$[Co(NH_3)_5NO_3][NO_3]_2$ [19]			1377 1330	828											
$[Co(NH_3)_5NO_3]_3Mo_7O_{24}$ $\cdot 3H_2O$	3420 3200	1620	1330	840	480	410	890	670	1620	1385	890	330		250 260	
$[Co(NH_3)_4CO_3]Cl$ [20]		1593													673, 430 395
$[Co(NH_3)_4H_2OHCO_3]_3$-Mo_7O_{24}	3446 3280	1630	1305	850	480	370	890	–	1630	1400	885	330			670, 480
$[Co(NH_3)_6Cl_2$ [21]	3330 3250	1602	1163	654	325	292									
$[Co(NH_3)_4(H_2O)_2]_3$-$[Mo_7O_{24}]$	3450 3250	1630	1325	640	480	330	880	650	1630	1400	925	360			

The free MoO_4^{2-} ion has a distorted tetrahedral (Td) symmetry and the major absorption bands arising from the MoO_4^{2-} anion generally occur between 910 and 840 cm^{-1} for $\nu_1 + \nu_3$, and at about 340 cm^{-1} for $\nu_1 + \nu_4$ [14]. In the present study, where the *p*-molybdate ion is involved, some other strong bands are observed at 580, 1000, 1400 and 1600 cm^{-1} (Fig. 1) due to Mo=O and Mo–O–Mo bands which are formed when condensation takes place [15,16], where

$$MoO_4^{2-} + H^+ \rightarrow [MoO_3(OH)]^-$$

$$2[MoO(OH)_5]^- \rightarrow [(HO)_4OMo\text{–}O\text{–}Mo\text{–}O(OH)_4]^{2-} + H_2O$$

$$7MoO_4^{2-} + 8H^+ \rightarrow Mo_7O_{24}^{6-}$$

The structure of the $Mo_7O_{24}^{2-}$ ion was studied by X-ray diffraction, where the Mo atoms lie at the centers of octahedra of oxygen atoms and the structure is built up of these octahedra by means of shared corners and shared edges (but not shared faces) [17]. The shifts in the vibration bands of the cationic ammine complexes and of the *p*-molybdate anion due to ion-pair formation are given in Table 2. The fact that all the shifts are relatively small confirm the assumption that the *p*-molybdate complexes formed are ion-pairs where no appreciable change in bonding inside the cation or the anion takes place, as was previously observed by Coomber and Griffith [7] for $[Co(NH_3)_5Cl]MoO_4$. In all thermally treated compounds the originally broad Mo=O and Mo–O–Mo bands at about 580 and 1000 cm^{-1} have been resolved, while those at about 1400 and 1600 cm^{-1} remained unchanged. The resolution of the former bands may be attributed to the removal of the $\rho r(NH_3)$ vibrations in the resulting mixed oxides. The IR spectrum of the hexamminecobalt(III) *p*-molybdate and its heated product are given as examples in Fig. 1.

Thermal study

The TG curves (Fig. 2) show that all the complexes dissociated in two major steps in the temperature range 130–290 °C, a plateau is then maintained from 450 to 750 °C. A large weight loss takes place above 750 °C due to sublimation of molybdenum oxide. A slow weight loss took place at the first step followed by very rapid decomposition. The slow weight losses began in the temperature range 130–180 °C while the more rapid changes took place in the range 215–290 °C. The first weight losses were due to loss of H_2O of crystallization, if present, together with ammine and aquo ligands probably by the *trans* mechanism [22]. The percentage losses and their significance are given in Table 3.

Two common features were observed in the DTA curves. The first is the presence of two strong endothermic peaks below 290 °C corresponding to the evolution of water of crystallization together with water and ammonia of

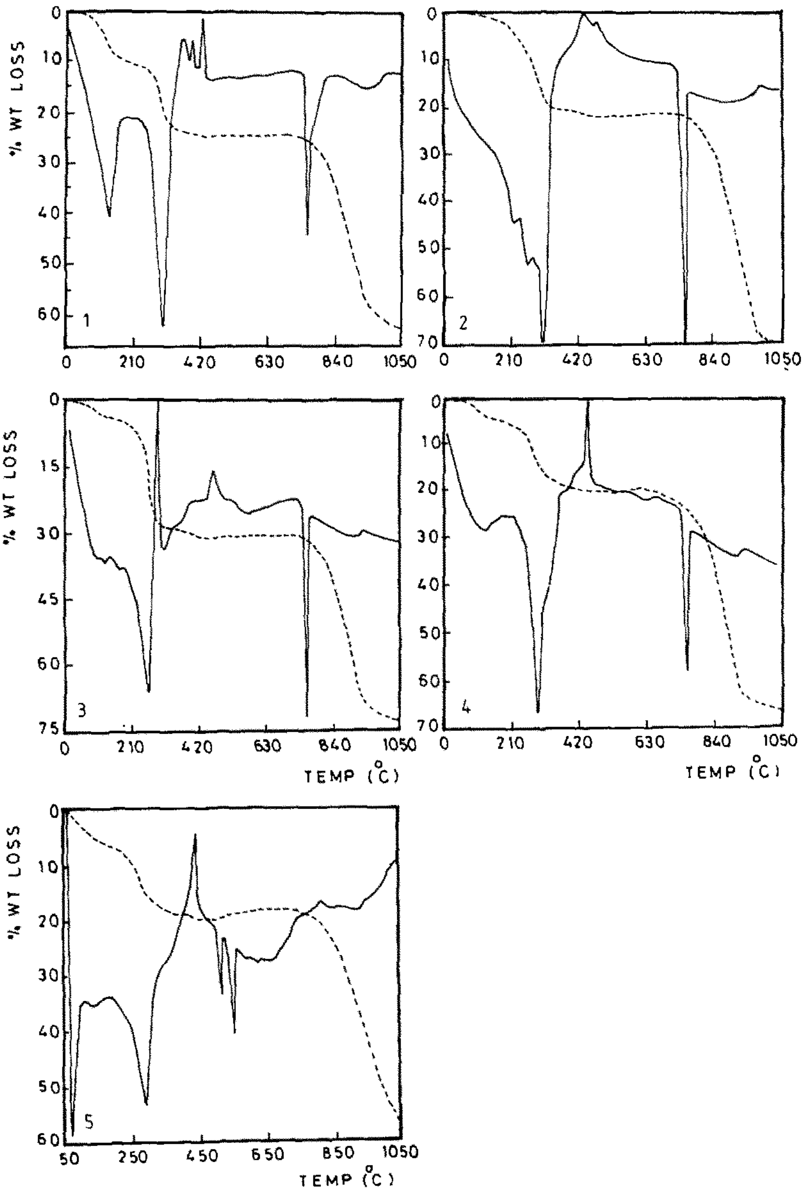

Fig. 2. DTA and TG curves of the paramolybdates of the cobaltammine complexes.

coordination. The second feature is the appearance of a strong exothermic peak between 450 and 500 °C which may be attributed to some sort of crystallization of the mixed oxides formed. The sublimation of molybdenum oxide, above 750 °C, is accompanied by a strong endothermic peak.

The stoichiometries of the resulting mixed oxides are: $Co_2Mo_7O_{20.5}$; $Co_3Mo_7O_{20.5}Cl_3$; $Co_3Mo_7O_{22}$; $Co_3Mo_7O_{25.5}$; and $Co_3Mo_7O_{24}$. In each of

TABLE 3

Results of the thermal studies

Complex	Molecular weight	Temperature (°C)	Loss (%)	Significance of loss
$[Co(NH_3)_6]_2Mo_7O_{24}$	1378	130	10	$8NH_3$
		250	13	$10NH_3$
		310	24	
		790	25	
$[Co(NH_3)_5Cl]_3Mo_7O_{24}\cdot 3H_2O$	1648	150	3	$3H_2O$
		310	20	
		790	22	
$[Co(NH_3)_5NO_3]_3Mo_7O_{24}\cdot 3H_2O$	1728	150	3	$3H_2O$
		250	15	$3H_2O+3NO_3^-$
		290	30	
		770	31	
$[Co(NH_3)_4H_2OHCO_3]_3Mo_7O_{24}$	1674	150	3	$3H_2O$
		230	14	$3H_2O+3HCO_3$
		380	20	
		690	21	
$[Co(NH_3)_4(H_2O)_2]_3Mo_7O_{24}$	1545	150	7	$6H_2O$
		290	18	
		790	20	

the first three complexes the stoichiometry of the resulting oxide is less than that based on the assumption that the oxidation states of Co and Mo are III and VI, respectively, by 3.5 oxygen atoms. This may be explained as being due to the lowering of the oxidation state of Mo from VI to V. Such a reduction is not observed in the oxides resulting from heating complexes 4 and 5. This phenomenon may be attributed to the presence of 5 or 6 ammonia ligands per molecule in the first three complexes (where reduction took place) and only four ammonia ligands in the last two complexes. Ammonia is known to act as a reducing agent at elevated temperatures.

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