

Preparation, spectroscopic and thermal studies on the new solid complex $\text{Co}_2(\text{NH}_2)_2(\text{H}_2\text{O})_2(\text{SO}_4)_2$

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Abstract

The preparation and characterization is reported of the new solid bimolecular Co(III)-bridged sulphato complex $\text{Co}_2(\text{NH}_2)_2(\text{H}_2\text{O})_2(\text{SO}_4)_2$ formed by the reaction of urea with $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ in aqueous media at 85°C . The infrared spectrum of the complex was recorded and the observed bands are assigned. Thermogravimetric (TG) and differential thermal analysis (DTA) measurements on the complex, and the infrared spectrum of the final decomposition product were also recorded. The data obtained agree quite well with the expected structure and show that the complex finally decomposes to form CoSO_4 . Detailed mechanisms for the complex formation and its thermal decomposition are given, together with the activation energy for each decomposition step.

INTRODUCTION

Urea possesses two potential donor atoms, the carbonyl oxygen and the amide nitrogen, and much interest has been shown in its bonding in transition metal complexes. The reaction of urea with transition metal ions at room temperature has been studied extensively [1–6], and various metal–urea complexes have been isolated and characterized. In these complexes, urea may coordinate via either its oxygen or nitrogen atom, depending on the type of metal ion [6, 7]. However, the majority of the evidence suggests that the oxygen atom is the preferred coordination site in most of the cases studied. Infrared spectroscopy has been widely used as a powerful means of distinguishing between the two possibilities. A shift in the carbonyl stretching frequency to lower values is usually taken to indicate a metal–oxygen linkage, while a shift in $\nu(\text{CO})$ to higher frequencies indicates a metal–nitrogen bond.

Discussion of the reaction of urea with metal ions at high temperature is rare in the literature, and the available publications describe an interesting feature: the reaction products depend not only on the type of metal ions but also on the metal salt used in the reaction [8–10].

The present investigation was undertaken to study the nature of the reaction products of urea and CoSO_4 in aqueous solutions at high

temperature (approx. 85°C). Thermogravimetric (TG) and differential thermal (DTA) analyses were carried out. The complex and the decomposition products were identified by means of infrared spectroscopy.

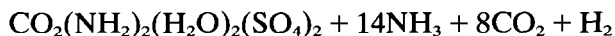
EXPERIMENTAL

The blue solid complex $\text{Co}_2(\text{NH}_2)_2(\text{H}_2\text{O})_2(\text{SO}_4)_2$ was prepared by mixing equal volumes of aqueous solutions of 0.1 M $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ and 0.6 M urea. The mixture was heated on a water bath to approx. 85°C for about 12 h. The complex was precipitated, filtered off, washed several times with boiled water, dried at 80°C in an oven for 2 h, and then in vacuo over phosphorous pentoxide. The complex was characterized by its elemental analysis, infrared spectrum and thermal properties (DTA and TG). Analysis: H, 2.01 (2.11); N, 7.23 (4.70); Co, 31.1 (31.21); SO_4 , 50.25 (50.79), where the calculated values are shown in parentheses.

The infrared spectra of the complex obtained, $\text{Co}_2(\text{NH}_2)_2(\text{H}_2\text{O})_2(\text{SO}_4)_2$, and of the DTA decomposition products were recorded from KBr discs using a Perkin-Elmer 1430 ratio-recording infrared spectrophotometer. Thermogravimetric (TG) and differential thermal (DTA) analyses of the complex were carried out using a Shimadzu DT-40 computerized thermal analysis system. The system includes programs which process data from the thermal analyser with the Chromotpac C-R3A. The rate of heating of the samples was kept at 5°C min⁻¹. A 3.4 mg sample was analysed under N₂ flow at 40 ml min⁻¹. α -Alumina powder was used as the DTA standard material.

RESULTS AND DISCUSSION

The formation of the solid complex $\text{Co}_2(\text{NH}_2)_2(\text{H}_2\text{O})_2(\text{SO}_4)_2$ during the reaction of urea with CoSO_4 in aqueous solution indicates that Co(II) ions decompose the coordinated urea at high temperatures. The mechanism of this decomposition is best understood with reference to the following points. Cobalt ions shows a particular affinity for nitrogen donors [11]; hence, we propose that urea coordinates to Co(II) ions through its nitrogen atom. Gentile et al. [12] have indicated that $\text{Co}(\text{NO}_3)_2$ reacts with urea at room temperature to form the complex $[\text{Co}(\text{urea})_4](\text{NO}_3)_2$ and have suggested the presence of bidentate as well as monodentate urea. Cobalt as Co(II) is easily oxidized by air in the presence of ammonia solution to give cobalt(III). From the elemental analysis and the infrared spectra, we suggest the formation of the complex $\text{Co}_2(\text{NH}_2)_2(\text{H}_2\text{O})_2(\text{SO}_4)_2$, where the cobalt is present as Co(III), in the reaction of urea with CoSO_4 at high temperatures. The following reaction may take place



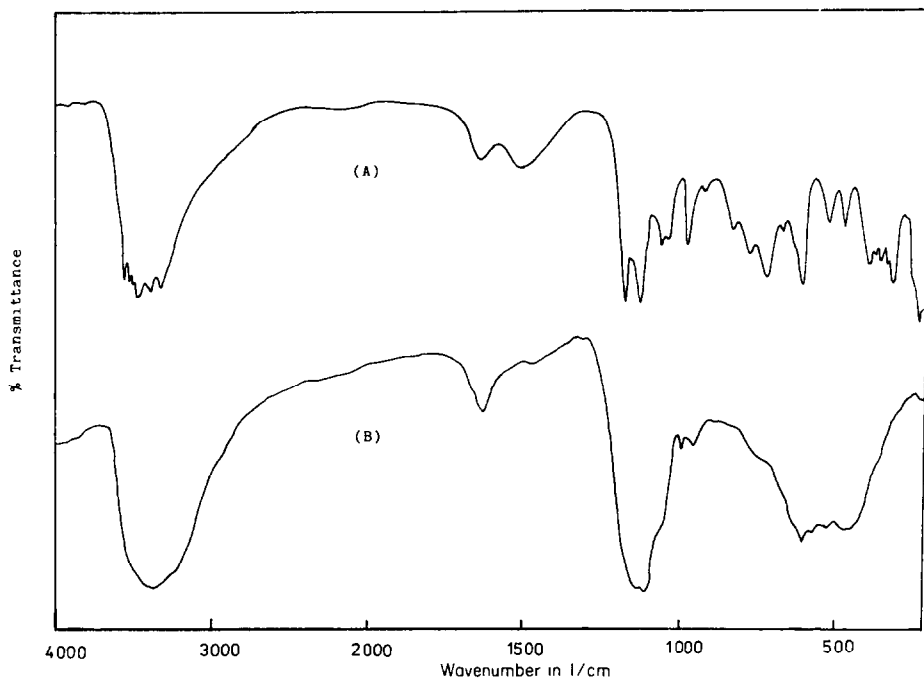


Fig. 1. The IR spectra of (A) $\text{Co}_2(\text{NH}_2)_2(\text{H}_2\text{O})_2(\text{SO}_4)_2$; (B) the final thermal decomposition product, CoSO_4 .

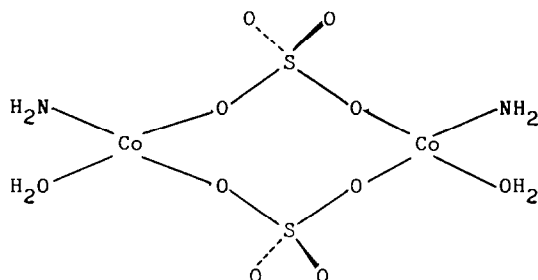
The infrared spectrum of the complex is shown in Fig. 1 and its band assignments are given in Table 1. The most probable structure according to the complex formula and the infrared spectrum is shown in Formula 1 where the complex contains two bridged sulphato ligands and possesses C_{2v}

TABLE 1

IR frequencies (cm^{-1}) and assignments for the complex

Frequency	Assignments	Frequency	Assignments
3550 m	$\nu_{\text{as}}(\text{O-H})$	920 w	$\delta_{\text{t}}(\text{NH}_2)$
3520 m		842 m	$\delta_{\text{r}}(\text{H}_2\text{O})$
3485 w		770 m	
3460 m	$\nu_{\text{s}}(\text{O-H})$	700 s	$\delta(\text{SO}_4)^{2-}$
3360 m		654 m	
3280 m	$\nu_{\text{s}}(\text{N-H})$	600 s	
1680 mbr	$\delta(\text{H}_2\text{O})$	516 m	$\nu(\text{CO-N})$
1512 mbr	$\delta(\text{NH}_2)$	490 m	$\delta(\text{SO}_4)^{2-}$
1170 vs	$\nu(\text{SO}_4)^{2-}$	382 m	$\nu(\text{CO-O})$
1118 vs		365 vw	
1050 m		352 w	
1005 ms	324 w		
970 ms	$\delta_{\text{w}}(\text{NH}_2)$	315 m	
	$\nu(\text{SO}_4)^{2-}$		

Key: br, broad; m, medium; s, strong; w, weak; v, very; ν , stretching; δ , bending; δ_{w} , wagging; δ_{t} , twisting; δ_{r} , rocking.



Formula 1.

symmetry. The infrared spectrum of the complex clearly indicates the absence of bands due to coordinated urea and the presence of four O–H stretching vibrations, characteristic of coordinated water, at 3550, 3520, 3485 and 3460 cm^{-1} . The appearance of these four bands is expected for such a C_{2v} symmetry and can be assigned as follows: the first two bands are assigned to the two anti-symmetric vibrations of the type, $\nu_{\text{as}}(\text{O–H})$, B_2 , while the other two bands are associated with the two symmetric vibrations of the type, $\nu_{\text{s}}(\text{O–H})$, A_1 .

The coordinated $-\text{NH}_2$ groups show a set of bands that agree quite well with those previously reported [6, 13, 14] for related complexes. The two bands at 3360 and 3280 cm^{-1} are assigned to the N–H stretching modes corresponding to the anti-symmetric and symmetric motions, respectively. The broad band at 1512 cm^{-1} can be considered to arise from the $-\text{NH}_2$ bending vibration, while the two bands at 970 and 920 cm^{-1} are due to the wagging and twisting vibration of the coordinated $-\text{NH}_2$ group, respectively. The Co–N stretching frequency is of particular interest, because it provides direct information about the coordination bond. According to Nakamoto [15], the band at 512 cm^{-1} is attributed to the Co(III)–N stretching mode.

It is well known that the free sulphate ion belongs to the highly symmetrical point group T_D . If the ion is coordinated to a metal, the symmetry is lowered and splitting of the degenerate modes occurs, together with the appearance of new bands in the infrared spectrum corresponding to Raman-active bands in the free ion. Bidentate chelating and bridging sulphato groups belong to the C_{2v} symmetry, so that it is not possible to distinguish them from the number of SO stretching bands alone. However, it should be noted that, in the related Co(III)–sulphato complexes, the SO stretching frequencies for bidentate chelating sulphato groups occur at higher frequencies than those of the bridging complexes [16, 17]. For the sulphate ligands in the complex under investigation, a total of eight bands can be assigned for the various SO_4^{2-} vibrations. Three bands occur in the region above 1000 cm^{-1} at 1170, 1118 and 1050 cm^{-1} , while four bands of

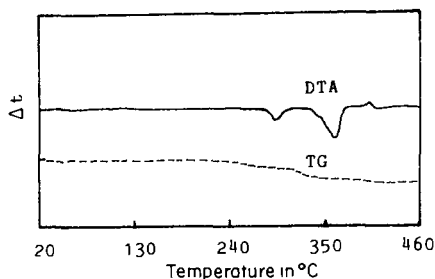
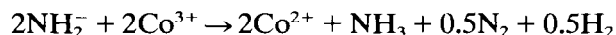


Fig. 2. DTA and TG curves for the $\text{CO}_2(\text{NH}_2)_2(\text{H}_2\text{O})_2(\text{SO}_4)_2$ complex.

different intensities occupy the region below 1000 cm^{-1} at 970, 700, 654 and 600 cm^{-1} . The last band appears at medium intensity at 470 cm^{-1} . The assignment of these bands agrees quite well with those for related complexes containing typical bridged sulphato ligands with C_{2v} symmetry [16–18].

Finally, the group of bands observed at 382, 365, 352, 324 and 315 cm^{-1} is associated with the Co–O stretching modes. This assignment is consistent with those known for other related complexes [19, 20].

Thermogravimetric (TG) and differential thermal analyses (DTA) were carried out for the $\text{Co}(\text{NH}_2)_2(\text{H}_2\text{O})_2(\text{SO}_4)_2$ complex under a N_2 flow. Figure 2 shows the DTA and TG curves, and Table 2 gives the maximum temperature values θ_{max} for the decomposition, together with the corresponding activation energy E . These data support the proposed complex structure and also indicate that the decomposition of the complex occurs in three degradation steps. The first stage of decomposition occurs at 280°C and is accompanied by a weight loss of 9.22% and an activation energy of 97.02 kJ mol^{-1} (endothermic), corresponding to the loss of the two H_2O molecules. The next decomposition step occurs at 363.2°C with a weight loss of 8.40% and an activation energy of 449.5 kJ mol^{-1} (endothermic); this is associated with the loss of the amide groups, as follows



The last degradation step occurs at 401.8°C with an activation energy of

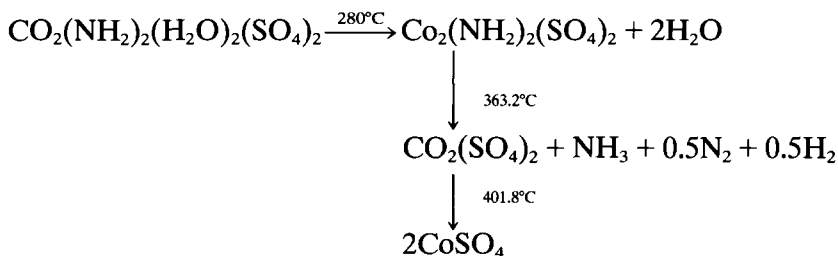
TABLE 2

The maximum temperature θ_{max} and activation energies E of the decomposition steps for the complex

Decomposition	$\theta_{\text{max}}/^\circ\text{C}$	$E/\text{kJ mol}^{-1}$
First step	280	–97.02
Second step	363.2	–449.5
Third step	401.8	15.45

15.45 kJ mol⁻¹ (exothermic), with no weight loss; this is associated with the rupture of the coordination bonds of the sulphato groups. The infrared spectrum of the final product of the thermal analysis supports these conclusions: it shows the absence of any bands due to the amido and bridged sulphato groups, but instead there is a group of bands characteristic of ionic sulphate, CoSO₄.

According to the above discussion, the mechanism for the thermal decomposition of Co(NH₂)₂(H₂O)₂(SO₄)₂ is



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