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SYNTHESIS AND THERMAL DECOMPOSITION OF DITHIOCYANATOBIS(PIPERIDINE)CADMIUM(II)

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ABSTRACT

Piperidine hydrothiocyanate has been used as a molten salt medium for the synthesis of dithiocyanatobis(piperidine)cadmium(II). This compound decomposes in five steps. The decomposition begins at 126 °C, with the first step being the loss of one molecule of piperidine per molecule of complex. The resulting $[Cd(pip)(SCN)_2]$ appears to contain bridging thiocyanate ions. This reaction, the only one for which reliable kinetic parameters could be determined, appears to be of zero order with an activation energy of 63.6 ± 5.2 kJ mol^{-1}.

INTRODUCTION

Molten salts provide one way to synthesize thiocyanate complexes of metals, using salts such as an amine hydrothiocyanate or potassium thiocyanate. Kerridge [1] has reported the use of molten KSCN in the synthesis of potassium hexathiocyanatochromate(III). Molten piperidine hydrothiocyanate has been used in the synthesis of piperidinium hexathiocyanatochromate(III) [2]. In the present study, we used molten piperidine hydrothiocyanate to synthesize dithiocyanatobis(piperidine)cadmium(II).

The decomposition reactions of cyanide and thiocyanate complexes are of particular interest because of the possibility that HCN or HSCN, respectively, will be liberated. During the decomposition of the Reinecke's salt, $(NH_4)[Cr(NH_3)_2(NCS)_4]$, two HSCN and NH_3 are lost in the first step [3]. Piperidinium hexathiocyanatochromate(III) decomposes in one step to piperidine hydrothiocyanate and $Cr(NCS)_3$ [4]. As a continuation of our study of thermal properties of thiocyanate complexes, the present work describes the synthesis and decomposition of dithiocyanatobis(piperidine)cadmium(II).

EXPERIMENTAL

Piperidine hydrothiocyanate, pipHSCN, was prepared by a previously described method [4]. The product was recrystallized from acetone and allowed to dry in air.

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Dithiocyanatobis(piperidine)cadmium(II), [Cd(pip)$_2$(SCN)$_2$], was prepared by reacting pipHSCN and cadmium carbonate. A 10:1 ratio of pipHSCN to cadmium carbonate was used. The reaction was carried out by adding the cadmium carbonate slowly with occasional stirring to molten pipHSCN at 100 ° C, and heating the mixture for an additional 2 h. The complex is soluble in molten pipHSCN. Separation of the complex from the unreacted pipHSCN was accomplished by recrystallization from ethanol. The [Cd(pip)$_2$(SCN)$_2$] crystallized as a white solid. It was removed by filtration, washed with cold ethanol, and allowed to dry in air.

Analysis for [Cd(pip)$_2$(SCN)$_2$]: calculated, $C = 36.18$ and $H = 5.53$; found, $C = 36.45$ and $H = 5.74$.

The IR spectrum of [Cd(pip)$_2$(SCN)$_2$] was recorded using a Perkin–Elmer 783 IR spectrophotometer with samples in the form of Nujol and fluorinated hydrocarbon mulls on CsI plates. The IR spectra of the residue remaining after heating [Cd(pip)$_2$(SCN)$_2$] to 180 and 550 ° C were also recorded in the same manner.

Thermal studies were carried out using a Perkin–Elmer thermogravimetric system Model TGS-2. A dry nitrogen atmosphere and a heating rate of 10 ° C min^{-1} were used. Sample weights were in the range 3.0–7.5 mg. Kinetic parameters were determined using the Coats and Redfern method [5]. The n values used were 0, 1/3, 2/3,…,2, and the calculations were carried out on a microcomputer using a program written in BASIC.

RESULTS AND DISCUSSION

The IR spectrum of dithiocyanatobis(piperidine)cadmium(II) contains the following peaks: N–H stretch as a strong sharp peak at 3250 cm^{-1}; C≡N stretch as a strong sharp peak at 2100 cm^{-1}; C–S stretch as a sharp peak at 870 cm^{-1}; and NCS bend as two sharp peaks at 465 and 455 cm^{-1}. Figure 1 shows the C≡N stretching region of the IR spectrum. The sharpness of the peak corresponding to the N–H stretching vibration indicates that there is no hydrogen bonding between the piperidine and the thiocyanate ions. This suggests that the thiocyanate ions and the piperidine are both coordinated to the cadmium in a manner that does not allow them to form hydrogen bonds.

It is possible to determine the bonding mode of the thiocyanate ion to the metal ion by examining the peaks which are due to C≡N stretching, C–S stretching, NCS bending and metal–thiocyanate stretching vibrations [6]. Nakamoto has suggested the following guidelines for determining the bonding mode of the thiocyanate ion. (1) For N-bonded thiocyanate, the C≡N stretching frequency is at 2050 cm^{-1}; for S-bonded thiocyanate it is at about 2100 cm^{-1}; and for bridging thiocyanate it is above 2100 cm^{-1}. (2) For N-bonded thiocyanate the C–S stretching frequency is at 780–860 cm^{-1}; and for S-bonded thiocyanate it is at 690–720 cm^{-1}. (3) For N-bonded

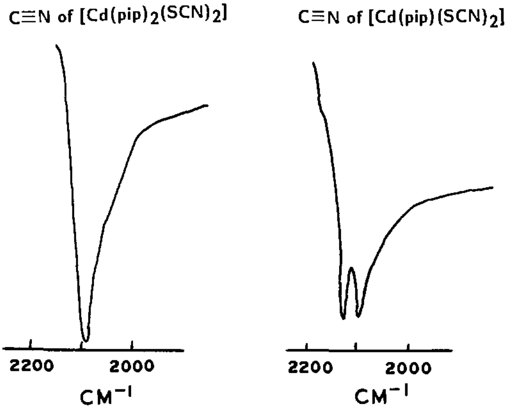

Fig. 1. IR spectra in the cyanide stretching region for $[Cd(pip)_2(SCN)_2]$ and $[Cd(pip)(SCN)_2]$.

thiocyanate, the NCS bending frequency is a single peak near 480 cm^{-1}; and for S-bonded thiocyanate it appears as several low intensity peaks near 420 cm^{-1}. (4) The metal–thiocyanate stretching frequency is higher in N-bonded compounds than in S-bonded compounds [6]. The C≡N stretching and the NCS bending frequencies found for $[Cd(pip)_2(SCN)_2]$ fit Nakamoto's criteria for S-bonded thiocyanate. The peak that may correspond to the C–S stretching vibration appears to fit the criterion for N-bonded thiocyanate. However, it is possible that this peak may correspond to an N–H rocking vibration of the piperidine molecules. The hard–soft acid–base principle [7] predicts that thiocyanate would bond through sulphur to Cd^{2+}, because Cd^{2+} is a soft acid and the sulphur end of thiocyanate is the softer base. Thus, the preponderance of the evidence indicates that the thiocyanate ions in dithiocyanatobis(piperidine)cadmium(II) are bonded to the cadmium through the sulphur.

A typical TG curve for the decomposition of $[Cd(pip)_2(SCN)_2]$ is shown in Fig. 2. The decomposition occurs in five steps. The first takes place between 126 and 180 °C. This reaction results in a 22.3 ± 1.8% mass loss, which corresponds to 88.7 ± 7.1 mass units. Thus, the first reaction appears to be

$$[Cd(pip)_2(SCN)_2](s) \rightarrow [Cd(pip)(SCN)_2](s) + pip(g) \qquad (1)$$

for which the calculated mass loss is 21.4%.

This first step in the decomposition of $[Cd(pip)_2(SCN)_2]$ is the only one for which kinetic parameters could be determined reproducibly. The Coats and Redfern method was used to determine the reaction order and the activation energy [5]. These values were calculated using α values between 0.1 and 0.8. The best fit of the data occurs with $n = 0$. For this reaction order, the average activation energy from nine trials was found to be 63.6 ± 5.2 kJ mol^{-1}. This value for activation energy is somewhat lower than

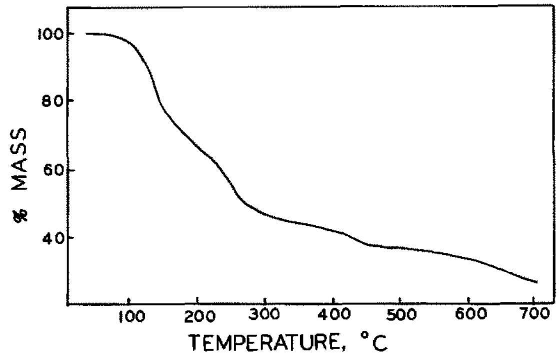

Fig. 2. Typical TG curve for the decomposition of dithiocyanatobis(piperidine)cadmium(II).

the values observed for the decomposition of other thiocyanate complexes. An activation energy this low reflects a relatively weak coordinate bond between the cadmium ion and a first row donor atom.

There are significant differences between the IR spectrum of the solid product after the first reaction, $[Cd(pip)(SCN)_2]$, and that of $[Cd(pip)_2(SCN)_2]$. Most dramatic is the C≡N stretching vibration shown in Fig. 1, which reveals two peaks at 2128 and 2100 cm^{-1}, indicating a change in bonding mode for some of the thiocyanate ions. These peaks are of about equal intensity, which is consistent with only half of the thiocyanate ions having changed in bonding mode. A peak above 2100 cm^{-1} is consistent with bridging thiocyanate ions [6]. Coordination through the nitrogen atom of a thiocyanate ion already S-bonded to a cadmium would replace the piperidine lost from the coordination sphere. With minimal disruption, this could give a polymeric structure in which the coordination number of cadmium remains four. This light yellow solid product was found to be a hard, intractable mass. It may be that the ability of this product to form easily with little reorientation of coordination spheres accounts for the low activation energy for its formation. The N–H stretching bond for the remaining piperidine molecules is sharp, indicating no hydrogen bonding of piperidine to thiocyanate in $[Cd(pip)(SCN)_2]$.

The second step takes place in the temperature range 180–226 °C and involves a mass loss of 12.2 ± 1.6%, which corresponds to 48.5 ± 6.2 mass units. The second reaction appears to be a loss of 2/3 mole of piperidine per mole of complex, which corresponds to a calculated mass loss of 14.2%.

$$[Cd(pip)(SCN)_2](s) \rightarrow Cd(pip)_{1/3}(SCN)_2(s) + 2/3pip(g) \qquad (2)$$

This type of reaction has been observed in cadmium complexes of picolines [8] and ethylenediamine [9].

The third step takes place between 226 and 335 °C. This step results in a mass loss of 18.6 ± 1.3%, which corresponds to 74.0 ± 5.0 mass units, but not all of the products of this decomposition step have been determined.

This reaction may be written as

$$Cd(pip)_{1/3}(SCN)_2(s) \rightarrow \text{Product A}(s) + 1/3pip(g) + \text{Product B}(g) \quad (3)$$

In the range 335–550 ° C there occurs a fourth reaction, which results in a mass loss of 10.9 ± 1.5% or 43.4 ± 6.0 mass units. This reaction appears to be the gradual decomposition of Product A(s) to yield CdS.

$$\text{Product A}(s) \rightarrow CdS(s) + \text{Product C}(g) \quad (4)$$

The residue remaining after this fourth reaction is believed for several reasons to be CdS. The percent mass remaining is consistent with that expected for CdS, and the residue has a bright yellow colour characteristic of CdS. Also, the IR spectrum of the residue does not show a CN peak, nor any other vibrations arising from SCN^-.

At temperatures above 550 ° C there occurs a fifth reaction, which appears to be the gradual loss of sulphur to give cadmium metal. At 700 ° C the final mass is 31.1 ± 2.4% of the original and appears to be continuing to decrease. For $[Cd(pip)_2(SCN)_2]$, the percent cadmium is 28.1%. Thus, the expected final mass is only slightly less than that actually observed at 700 ° C.

The decomposition reactions shown in eqns. (2)–(4) were found to give somewhat indistinct mass losses. Consequently, no kinetic parameters are presented here for these reactions.

CONCLUSIONS

This work has shown that molten amine hydrothiocyanates are useful in the synthesis of complexes. In this case, an unusual cadmium complex, $[Cd(pip)_2(SCN)_2]$, was prepared. The bonding mode of thiocyanate in $[Cd(pip)_2(SCN)_2]$ has been elucidated, and it has been shown that thiocyanate bridges form when piperidine is lost from the complex. The decomposition pattern of $[Cd(pip)_2(SCN)_2]$ has also been elucidated.

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