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THERMAL DECOMPOSITION OF SOLID ISOTHIOCYANATE COMPLEXES

PART I. THERMOCHEMICAL PROPERTIES

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ABSTRACT

A series of metal complexes of the type $MPy_4(NCS)_2$ (M = Mn, Fe, Co, Ni, and Zn; Py = pyridine) has been investigated by differential enthalpimetric analysis. The heats of decomposition to the dipyridine complexes and, in some cases, to the anhydrous isothiocyanates are reported and compared with earlier, qualitative data. Variations are noted, and speculative evidence for the formation of the intermediate $NiPy_3(NCS)_2$ is presented.

INTRODUCTION

The physicochemical properties of pyridine complexes of transition metal halides and pseudohalides have been extensively investigated, and many qualitative thermal measurements have been reported[1]. Mortimer and co-workers[2-4] have measured the heats of decomposition of some solid metal halide complexes, and Nelson *et al.*[5] have studied the equilibrium

$$MPy_4X_2 \rightleftarrows MPy_2X_2 + 2Py \qquad (M = Co \text{ or } Ni;\ X = Cl, Br, I, \text{ or } NCS)$$

both in solution and in the solid phase. Bowman and Rogers[6] have reported thermogravimetric data for the complexes $MPy_2(NCS)_2$ (M = Mn, Co, Ni, Cu, or Zn).

The present paper constitutes an extension of previous studies of dihalogeno complexes[2-4]. We have studied a wider variety of complexes than Nelson *et al.*[5] and have also been able to study, in some cases, the reaction

$$MPy_2(NCS)_2\,(\text{cryst.}) \rightarrow M(NCS)_2\,(\text{cryst.}) + 2Py\,(g)\ (M = Mn, Ni, \text{ and } Cu) \quad (1)$$

Inasmuch as the same technique was employed as that of Mortimer *et al.*[2-4] in their studies of the dihalogeno complexes, a direct comparison of our results with theirs is possible.

EXPERIMENTAL

Preparation of Complexes

The isothiocyanatopyridine compounds investigated in this study were prepared by the reaction between a salt (nitrate, sulfate, or chloride) of the appropriate transition metal, ammonium thiocyanate and pyridine in aqueous solution[7-9]. The products were dried in a desiccator until constant weight was attained.

Thermal measurements

A Perkin–Elmer differential scanning calorimeter (DSC-1), calibrated by the heat of fusion of pure indium at its melting point (429 °K), was used. The experimental technique was the same as that previously reported[2]. All decompositions were carried out under a nitrogen atmosphere at a heating rate of $16\,°K \cdot min^{-1}$ and uncertainties are expressed as the standard deviation of the mean.

RESULTS AND DISCUSSION

Tetrapyridine complexes

With the exception of the nickel complex, these all decomposed to the dipyridine complexes according to the reaction

$$MPy_4(NCS)_2\ (cryst.) \rightarrow MPy_2(NCS)_2\ (cryst.) + 2Py\ (g) \qquad (2)$$

The decomposition of the nickel complex has been the subject of much controversy. Duval[10] states that the tripyridine complex is the first product, whereas Erdey and Liptay[11], and Wendlandt and Ali[12] found the dipyridine complex to be the first product. In the thermogram which we have obtained (Fig. 1), each major peak represents the loss of two pyridine molecules. The first peak exhibits a shoulder at 435 °K, and the weight loss at this temperature (14.8%) approximates that required for the loss of one pyridine molecule (16.1%) according to the reaction

$$NiPy_4(NCS)_2\ (cryst.) \rightleftarrows NiPy_3(NCS)_2\ (cryst.) + Py\ (g)$$

The infrared spectrum of the homogeneous, pale blue-green product was similar to that of the di- and tetra-pyridine complexes except for the band at about $2100\ cm^{-1}$, corresponding to the C–N stretching vibration. This band was split into two components at 2085 and $2150\ cm^{-1}$. Inasmuch as the absorptions in the di- and tetra-pyridine complexes were found at 2080 and $2140\ cm^{-1}$, the presence of two types of thiocyanate bonding[13] in the tripyridine complex is possible, although low-site symmetry might equally well be responsible[14]. The tripyridine complex may be similar to the compound $Ni(\gamma\text{-Pic})_3(NCS)_2$ (γ-Pic = 4-methylpyridine) isolated by Kemula and Czarnecki[15].

The heats of decomposition (ΔH) for Reaction 2 are shown in Table I, together with temperature parameters T_i (at which the pen first deviates from the baseline), T_p (at which the enthalpy change is at a maximum), and T (at which the pen returns to the baseline). Strictly speaking, gas phase enthalpies are required, but inasmuch as the complexes are all of similar structure[9] and the temperature limits are similar, only small Kirchoff corrections would be required. The heat capacities for these corrections

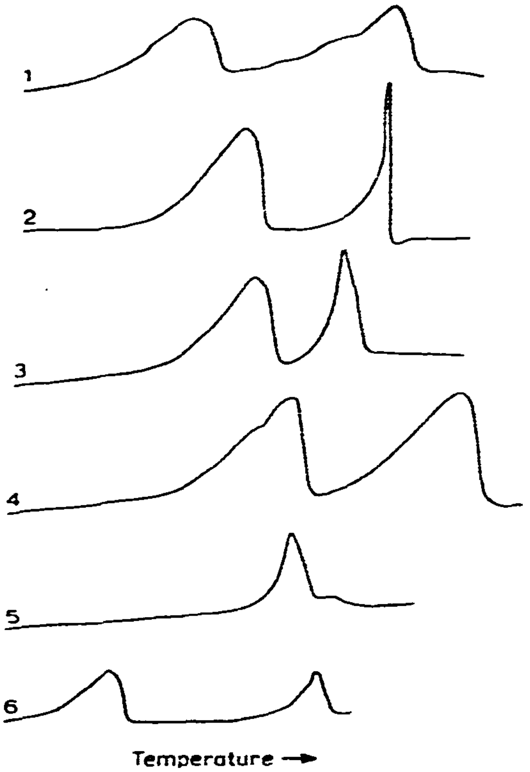

Fig. 1. Thermograms of MPy$_4$(NCS)$_2$; M = Mn (1), Fe(2), Co(3), Ni(4), Cu(5), and Zn(6).

TABLE I

THERMOCHEMICAL DATA FOR ISOTHIOCYANATO TETRA- AND DI-PYRIDINE COMPLEXES

M	*Reaction*	*T$_i$*	*T$_p$*	*T$_f$*	*Weight loss (%)*		*ΔH kcal·mole^{-1}*
			(°K)		*Obs.*	*Calc.*	
Mn(II)	2	350	425	435	32.0	32.4	31.0 ± 0.6
	1	450	520	535	63.8	64.9	33.7 ± 1.0
Fe(II)	2	365	440	455	32.4	32.7	31.0 ± 0.2
	1	480	[a]	—	—	—	—
Co(II)	2	385	450	460	33.7	32.2	27.6 ± 0.5
	1	465	490	[a]	—	—	—
Ni(II)	2	380	435[b] 455	465	32.6	32.2	31.2 ± 0.5
	1	470	530	550	64.3	64.4	36.0 ± 0.7
Cu(II)	1	470	460[b] 480	490	47.5	46.8	25.3 ± 0.3
Zn(II)	2	315	370	380	31.1	31.8	27.4 ± 0.6

[a] Pen did not return to baseline; fusion detected. [b] Two peaks were observed.

and the heats of vapourisation cannot be determined because of the instability of the complexes.

For a given metal ion, the values of ΔH for Reaction 2 are greater for the isothiocyanates than for the analogous chlorides and bromides[4]. If the crystal-packing forces in theses complexes are similar to those which prevail in the chlorides, our results may indicate that the metal-pyridine bonds are strengthened in the isothiocyanates. Nelson *et al.*[5] have shown that the thiocyanate ligand is not likely to promote metal-pyridine π-bonding because of the strong π-bonding in the M–NCS bond. If this is so, then the greater metal-pyridine bond strength may be explained as a steric effect due to the smaller size of the coordinating atom in the NCS ligand, as was first suggested by Graddon *et al.*[16]. We consider that there may well be an interplay of steric and π-bonding effects, the latter being minimal, with respect to metal-pyridine, in the isothiocyanate complexes.

Dipyridine complexes

Each of the compounds studied (M = Mn, Ni, and Cu) decomposed to the anhydrous isothiocyanates by Reaction 1. The compounds are reported to possess polymeric octahedral structures[6], but the copper complex is presumably distorted in a manner similar to $CuPy_2Cl_2$ (ref. 17) which possesses two different Cu–Cl bond lengths. Although Bowman and Rogers[6] detected the formation of intermediate compounds $MPy(NCS)_2$ and $M_3Py_2(NCS)_2$, we were unable to detect such compounds.

Our thermograms (Fig. 1) do not exhibit any shoulders in the temperature range for Reaction 1. For a given metal, the heats of Reaction 1 are each greater than those of Reaction 2, a fact which suggests that the metal-pyridine bond may be strengthened because of the decreased steric crowding in the dipyridine complexes, which permits a closer approach of the pyridine molecules to the metal atom. The anomalously low heat of reaction for the copper complex agrees with Bowman and Rogers' qualitative observations[6] and may result from the distortion present in this complex. Except for the copper complex, the heats of decomposition are again higher than those reported for the analogous chloride and bromide complexes. An explanation for this fact may be similar to that proposed for the tetrapyridine complexes.

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