Higher Ammoniates of Cobalt(II) Thiocyanate

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Summary: Seven and eight cobalt (II) thiocyanate ammoniates have been detected by a tensimetric study of the ammonia - cobalt(II) thiocyanate system at – 35.4°C. Dissociation enthalpy measurements have yielded values of 33.8 and 37.5 kJ mol^{-1} for the seven and eight ammoniates respectively.

Introduction

Among the cobalt(II) amines, the complexes $Co(NH_3)_6X_2$ (X=Cl, Br, I, NO_3, NO_2 IO_3) have been extensively investigated (1-6). Some of their stepwise dissociation products Co $(NH_3)_nX_2$ are also reported: n=2, 1 for the chloride and bromide (2,3); n=2 for the iodide (1,3) and n=4, 2 for the nitrite (1,6). Apart from a deca-ammoniate of cobalt(II) chloride reported by Biltz and Rahlfs (3), very little is known concerning higher ammoniates (n > 6) of cobalt(II) salts. Two excellent reviews (7,8) covering ammonia complexes of cobalt (II) salts are available. In the present work, a low temperature (– 35.4°C) in the vicinity of the liquid ammonia boiling point (– 33°C) has been employed to study the reaction of cobalt(II) thiocyanate with ammonia by the tensimetric technique thus facilitating the detection of new ammoniates $Co(NCS)_2$ nNH_3 (n= 7,8). A thermoanalytical stepwise dissociation study of $Co(NH_3)_6(NCS)_2$ will be the subject of a later paper.

Starting from a high NH_3 : $Co(NCS)_2$ mole ratio of a reaction mixture at –35.4°C, the ammonia vapour pressure over the system is measured when equilibrium is attained after every small stagewise removal of ammonia. Characteristic univariant portions appear in the resulting P_{NH_3} versus NH_3 : $Co(NCS)_2$ isotherm if stable ammoniates are present at the experimental temperature within the composition range studied. Ammonolytic reactions (akin to hydrolysis) of the type reported for vanadium (IV) and titanium (IV) (10,11) were not observed.

Dissociation enthalpy measurements involve plotting $\log_{10} P_{NH_3}$ versus 1/T for a range of temperatures at a selected composition conforming to the required dissociation. From the vant Hoff's relation,

$$\log P_{NH_3} = \Delta H/2.303\ RT + C$$

The linear plot thus obtained has a slope

$$\Delta H/2.303\ R$$

from which the ΔH value can be calculated.

Experimental

Cobalt(II) thiocyanate: The brown reagent (ex. B.D.H.) is probably a hemihydrate (15) and was dehydrated by dissolving in ethanol followed by evacuation at 100°C to obtain the green anhydrous form (13).

Liquid ammonia: Ammonia gas from a cylinder was condensed at – 78°C (acetone/solid CO_2 bath) and dried by addition of sodium metal. The solution was distilled and the anhydrous solvent collected on the high vacuum apparatus. A detailed description of the construction and operation of the high vacuum apparatus for use with liquid ammonia is given elsewhere (7).

Tensimetric studies: The technique involves addi-

tion of known amounts of ammonia to a weighed sample of reagent and measuring the equilibrium vapour pressure at − 35.4°C over a range of NH_3 : $Co(NCS)_2$ compositions on a tensimetric apparatus attached to the high vacuum line. Details of the technique can be consulted in the aformentioned reference (7).

Dissociation enthalpy measurements: In separate experiments, the ammonia dissociation pressure of two fixed - composition reaction mixtures (NH_3 : $Co(NCS)_2$ = 7.80 and 6.76) was measured over a range of temperatures. The results are given as linear Log P_{NH_3} versus 1/T plots (see fig. 2 and 3).

Thermostatic baths: Thermostatic baths for various temperatures were prepared from selected solvents of the required melting point. Liquid nitrogen was stirred into a Dewar flask containing each solvent to obtain a "freezing point slurry". Solvents used were: chloroform (− 63.5°C); dichlorobenzene (− 45.6°C) 1-2 dichloroethane (−35.4°C) bromobenzene (−30.8°C); carbon tetrachloride (−23°C). The ice point was employed for 0°C.

Results and Discussion

For high NH_3 : $Co(NCS)_2$ mole ratio range (> 8) the isotherm for the ammonia - cobalt (II) thiocyanate system obeys Rault's Law (see fig. 1). and is expected to approach the P_{NH_3} value of about 680 mm Hg (the value for liquid ammonia at −35.4°C). This value has been computed from the vapour pressure expression for liquid ammonia (7).

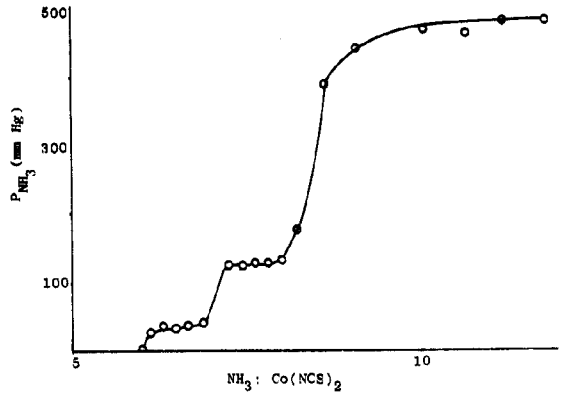

Fig. 1. Tensimetric curve for the ammonia cobalt (II) thiocyanate at -35.4°C.

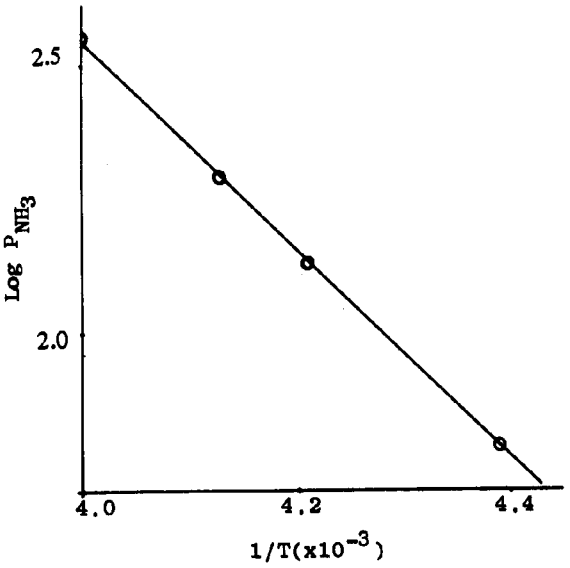

Fig. 2. Isochore plots for the dissociation of the ammoniate of cobalt (II) thiocyanate.

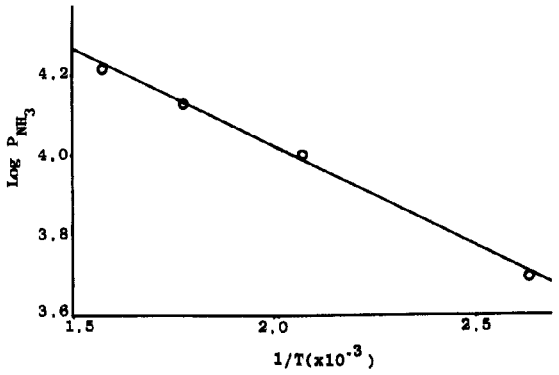

Fig. 3. Isochore plots for the dissociation of the seven ammoniate of cobalt (II) thiocyanate.

$$\text{Log } P = 9.95028 - 1473.17/T - 0.003803T$$

The presence of stable ammoniate species in the system can be identified by a constant P_{NH_3} portion,

	Colour	P_{NH_3} (diss.) at $-35.4^{\circ}C$ (mm Hg)	Slope ($\Delta H/2.303R$)	ΔH (kJ mol^{-1})	Dissociation product
$Co(NCS)_2\ 8NH_3$	deep pink	130	-1.96×10^3	37.5	$Co(NCS)_2\ 7NH_3$
$Co(NCS)_2\ 7NH_3$	pink	50	-1.76×10^3	33.8	$Co(NCS)_2\ 6NH_3$
$Co(NCS)_2\ 6NH_3$	pink	0	–	–	$Co(NCS)_2\ 4NH_3$ (reference 9)

and dissociation into lower ammoniates according to

$$Co(NCS)_2\ nNH_{3(s)} \rightleftharpoons Co(NCS)_2\ (n\text{-}1)NH_{3(s)} + NH_{3(g)}$$
$$+ NH_{3(g)}$$

and the equilibrium constant expression has the form

$$K = P_{NH_3}$$

since all other reactant/product moieties are solids (concn. = unity). Therefore each ammoniate has its own unique P_{NH_3} (dissociation) value determined by the value of the equilibrium constant.

Thermochemical data and colours of ammoniates identified from the tensimetric study (fig. 1) are listed below. The ΔH values have been calculated from the slopes in fig. 2 and 3.

$Co(NCS)_2\ 6NH_3$ has a thermal stability extending to room temperature as observed for other familiar hexamminecobalt(II) salts.

The magnitude of the H values obtained in this study for the dissociation of the octa-and hepta-ammoniates indicate very weak bonding for the eighth and seventh ammonia molecules to the rest of the system. These molecules therefore exist outside the M-NH_3 co-ordination sphere and are presumably bound to the $M(NH_3)_6^{2+}$ structure by weak ion - dipole type forces. Other workers (14) have proposed a similar mode of bonding in some higher ammoniates of titanium (III) halides.

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