Molten Acetamide–Potassium Thiocyanate Eutectic: Spectroscopy of First-row Transition Metal Compounds in a Room Temperature Melt

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The eutectic point of the acetamide–potassium thiocyanate system has been redetermined as 26 °C at 26.3 mol% KSCN, though the melting point is temporarily lowered to 16 °C after heating above 50 °C as a result of a reversible structural change. Electronic spectra of Ni^{II} and Cr^{III} solutions are reported and indicate octahedral co-ordination, while Co^{II} solutions have tetrahedral co-ordination, in each case mainly by thiocyanate anions, with both sulphur and nitrogen ligand atoms, and some co-ordinated acetamide. Comparison with molten alkali metal thiocyanate solutions suggests that in these melts also, mixed co-ordination by sulphur and nitrogen occurs. Variation of the absorption bands of the solutions with temperature was also recorded.

Acetamide forms a large number of low-melting binary (and ternary, *etc.*) eutectics with a vast range of inorganic salts. The resulting non-aqueous solvents, often molten at room temperature, have a high ionicity (as compared to the more usual room-temperature non-aqueous solvents) and are stable as well as being unreactive to air, and generally to water. They are usually excellent solvents, molten acetamide having long been known to dissolve very many inorganic and organic compounds.[1]

The acetamide–potassium thiocyanate system is particularly interesting because, in addition to having an eutectic which is liquid at room temperature, there is the potential of co-ordination of transition metal cations through both nitrogen and sulphur of thiocyanate as well as through oxygen of acetamide [extensive i.r. absorption measurements with a great variety of cations have shown that neutral acetamide does not co-ordinate through nitrogen, though the acetamide anion (CH_3CONH^-) clearly does[2]]. This system has been previously studied,[3–5] but measurements have been largely directed to physical properties rather than chemical effects.[6–8] The position of the eutectic has been quoted as 26 mol% at 25.5 °C[4] and as 24.7 mol% at 28.5 °C,[5] but although this variation is comparatively small a further determination was made as the first stage of the work reported here.

Because of the number of potential ligand atoms in eutectic solutions, electronic spectroscopy was carried out on a series of stable first-row transition metal salts, and the results compared with those for solutions of these salts in molten alkali metal thiocyanates (mainly with KSCN but also with NaSCN–KSCN eutectic)[9,10] and in pure molten acetamide,[2] making allowance for the necessarily different temperatures of measurement. The results illustrate a considerable variation in co-ordination by thiocyanate and have compelled a considerable change in understanding of thiocyanate melt spectra.

Experimental

Materials.—Hydrated nickel(II), cobalt(II), and chromium(III) chlorides (AnalaR, BDH) were dehydrated using the method of Freeman and Smith[11] (Found: Cl, 55.1; Ni, 44.8. Calc. for Cl_2Ni: Cl, 54.7; Ni, 45.3%. Found: Cl, 55.0; Co, 45.2. Calc. for Cl_2Co: Cl, 54.6; Co, 45.4%. Found: Cl, 67.3; Cr, 32.2. Calc. for Cl_3Cr: Cl, 67.2; Cr, 32.8%).

Eutectic.—Acetamide was purified by solution in hot methanol and precipitation with sodium-dried diethyl ether. It was filtered and vacuum dried over potassium hydroxide (m.p.

80 °C). Potassium thiocyanate (AnalaR, BDH) was evacuated for 6 h at 200 °C (m.p. 174 °C).

The composition of the eutectic was redetermined by the visual method (determining the temperatures of initial and complete melting), samples of a series of compositions being prepared in a dry-box. The temperatures of first and of complete melting indicated a eutectic temperature of 26 °C, with 26.3 mol% potassium thiocyanate.

It was observed that heating the eutectic above 50 °C, as was customary for the eutectic solutions used in this work, gave rise to a lower melting point, *ca.* 16 °C. The structural change in the melt was found to be slowly reversible on standing, and will be discussed in more detail in a later paper. This melt was not particularly hygroscopic, but a dry-box was used for preparations and all vessels were kept closed against atmospheric air.

Spectra were determined using a Unicam SP 700 spectrophotometer adapted with reversed optics below 13 000 cm^{-1}, and a RF-heated cell holder. Absorption maxima and molar absorption coefficients are derived from 3—12 separate measurements.

Results and Discussion

Nickel(II).—Nickel(II) chloride dissolves slowly in the eutectic to give green solutions with three absorptions (Table 1). The co-ordination is octahedral, in agreement with all the references cited in Table 1, with the exception of De Haas *et al.*[12] who considered it tetrahedral or square planar.

The ligands involved would seem not to be only acetamide, since the maxima are well to the blue region of those measured in molten acetamide[13] {and also for the complexes [$Ni(CH_3CONH_2)_6$]$^{2+}$ and [$Ni(CH_3CONH_2)_4(H_2O)_2$]$^{2+}$ in other media,[14,15] Table 1}, the higher energy transition being attributed to co-ordination to nitrogen-bonded thiocyanate.

Here we note that though the spectra reported from pure alkali metal thiocyanate melts vary somewhat (all published values are given in Table 1) and though conditions are not identical, they all indicate a quite small ligand field (certainly smaller than for aqueous solution and for the acetamide eutectic) even though nitrogen-bonded thiocyanate (in > 5 mol% solutions) has long been accepted as established by i.r. measurements.[16] The customary explanation of this anomaly has been to attribute it to the presence of potassium cations close to the sulphur end of the thiocyanate anions which somewhat diminish the ligand field of the co-ordinated nitrogen,[17] rather than to a temperature effect.

A more plausible alternative hypothesis can now be advanced, that in the dilute nickel(II) solutions in pure

Table 1. Spectroscopic data[a] for nickel(II) in melts and other solutions

Compound/solvent/temperature	Ref.	v_1 Transition $[^3T_{2g} \longleftarrow {}^3A_{2g}]$	v_2 Transition $[^3T_{1g}(F) \longleftarrow {}^3A_{2g}]$	v_3 Transition $[^3T_{1g}(P) \longleftarrow {}^3A_{2g}]$
NiCl$_2$ in CH$_3$CONH$_2$–KSCN eutectic, 24 °C	This work	9 000 ± 150 (11.3 ± 1.7)	15 000 ± 50 (9.5 ± 1.6)	25 000 ± 125 (27.5 ± 3.3)
NiCl$_2$ in CH$_3$CONH$_2$, 85 °C	13	7 800 (4.4)	12 800 (3.9)	23 700 (10)
[Ni(CH$_3$CONH$_2$)$_6$][ClO$_4$]$_2$ reflectance, r.t.	18	8 730	14 800	25 100
[Ni(CH$_3$CONH$_2$)$_6$]$^{2+}$ in acetone, r.t.	14	8 240	13 370	24 510
[Ni(CH$_3$CONH$_2$)$_4$(H$_2$O)$_2$]Cl$_2$ in ethanol, r.t.	13, 15	7 900 (4.4)	12 600 (4.7)	23 700 (13.7)
NiCl$_2$ in KSCN, 200 °C	b	8 300 (17)	13 700 (20)	
Ni^{II} in KSCN, 185 °C	17	8 550 (13)	14 300 (18)	
Ni^{II} in NaSCN–KSCN eutectic, 160 °C	12	8 300 (16)	14 300 (14)	
NiCl$_2$ in KSCN, 200 °C	c	8 500 (35)	12 800 (45)	22 500 (100)
NiCl$_2$ in KSCN, 177 °C	d		14 000 (4.6)	
Ni^{II} in aqueous 3 mol dm^{-3} KSCN, r.t.	e		15 300 (7)	25 500 (16)
[Ni(NH$_3$)$_6$]Cl$_2$ in aqueous 10 mol dm^{-3} NH$_4$OH, r.t.	This work	10 800 (4.2)	17 500 (4.0)	28 200 (6.0)
Ni^{II} in aqueous 10 mol dm^{-3} NH$_4$OH, r.t.	e	10 750 (4.0)	17 500 (4.8)	28 200 (6.3)
Ni^{II} in H$_2$O, r.t.	f	8 500 (2.2)	13 800 (2.1)	25 300 (5.0)

[a] Absorption maxima (cm^{-1}), with molar absorption coefficients (dm^3 mol^{-1} cm^{-1}) in parentheses; r.t. = room temperature. [b] D. H. Kerridge and S. J. Walker, *J. Inorg. Nucl. Chem.*, 1976, **38**, 1795. [c] S. V. Volkov, N. I. Buryak, and N. P. Evtushenko, *Zh. Neorg. Khim.*, 1973, **18**, 2986. [d] G. W. Harrington and B. Sundheim, *Ann. N.Y. Acad. Sci.*, 1960, **79**, 950. [e] C. K. Jorgensen, *Acta Chem. Scand.*, 1955, **9**, 1362. [f] C. K. Jorgensen, *Adv. Chem. Phys.*, 1963, **5**, 33.

Table 2. Spectroscopic data[a] for cobalt(II) in melts and other solutions

Compound/solvent/temperature	Ref.	v_2 Transition $[^4T_1(F) \longleftarrow {}^4A_2]$	v_3 Transition $[^4T_1(P) \longleftarrow {}^4A_2]$	
CoCl$_2$ in CH$_3$CONH$_2$–KSCN eutectic, 24 °C	This work	7 790 ± 135 (240 ± 10)	16 100 ± 100 (1 566 ± 96)	17 070 ± 40 (895 ± 132) (sh)
[Co(CH$_3$CONH$_2$)$_6$][ClO$_4$]$_2$ reflectance, r.t.	18	7 800	15 200 (sh)	19 000
CoCl$_2$ in KSCN, 200 °C	b	7 300 (45)	16 500 (290)	16 800 (210) (sh)
Co^{II} in KSCN, 185 °C	17	7 692 (64)	16 000 (510)	17 100 (320) (sh)
Co^{II} in NaSCN–KSCN eutectic, 160 °C	12		16 000 (515)	16 700 (407) (sh)
CoCl$_2$ in KSCN, 177 °C	c		16 000	17 400
[NMe$_4$]$_2$[Co(NCS)$_4$] in Me$_2$CO, r.t.	19	7 780 (265)	16 250 (1 800)	17 250 (1 000) (sh)
[NBu$^n_4$]$_2$[CoCl$_4$] in CH$_2$Cl$_2$, r.t.	d	5 440 (78) 5 180 (75) 4 820(71)	14 310 (75)	15 800 (650) 15 770 (450) 15 000 (630)

[a] Absorption maxima (cm^{-1}), with molar absorption coefficients (dm^3 mol^{-1} cm^{-1}) in parentheses; r.t. = room temperature. [b] D. H. Kerridge and S. J. Walker, *J. Inorg. Nucl. Chem.*, 1976, **38**, 1795. [c] S. V. Volkov, N. I. Buryak, and N. P. Evtushenko, *Zh. Neorg. Khim.*, 1973, **18**, 2986. [d] F. A. Cotton, D. M. L. Goodgame, and M. Goodgame, *J. Am. Chem. Soc.*, 1961, **83**, 4690.

thiocyanate melts, co-ordination is by both sulphur and nitrogen (i.r. measurements would not necessarily detect a small proportion of sulphur bonding since the diagnostic band is very weak, and in addition co-ordination might vary with concentration) and that in the acetamide eutectic co-ordination is also by sulphur as well as nitrogen but with a higher proportion of nitrogen-bonded ligands. However, probably not all six co-ordination positions are occupied by nitrogen since the v_2 and v_3 values are still less than those of aqueous thiocyanate solutions (Table 1), in which some, though probably not much, aquation of the nickel cations may also be occurring. In addition it is likely that in the eutectic solution acetamide may also be acting as an additional ligand.

The probable presence of these different ligand atoms in the eutectic solution (O of acetamide, S and N of thiocyanate), and therefore the formation of highly unsymmetrical complexes, is indeed the most likely explanation for the much larger molar absorption coefficients found for the eutectic solutions, as compared to the values for aqueous solutions (illustrated in Table 1 by the aqua and ammine complexes). Similarly the rather larger molar absorption coefficient for aqueous thiocyanate solution may support the suggestion of partial hydrolysis, or of mixed co-ordination by thiocyanate, but the latter and possibly the higher temperatures are probably the explanation of the very large values found with pure thiocyanate melts. Also, it should be borne in mind that M–SCN is angular (100°) though M–NCS is straight, so that even the presence of one or two thiocyanato ligands would considerably decrease the symmetry of the complex, and hence give rise to larger absorption coefficients.

Temperature made little difference to the spectrum of nickel(II) dissolved in the acetamide eutectic [a green solution at 60 °C, 9 050 cm^{-1} (ε = 9 dm^3 mol^{-1} cm^{-1}), 14 750 (10), 24 650 (31) (sh), and a yellow-green solution at 100 °C, 8 750 (10), 14 450 (11.5), 23 550 (57) (sh)] apart from encroachment by a broadening charge-transfer band in the u.v. region.

Table 3. Spectroscopic data ^{a} for chromium(III) in melts and other solutions

Compound/solvent/temperature	Reference	v_1 Transition $[^4T_{2g} \longleftarrow {}^4A_{2g}]$	v_2 Transition $[^4T_{1g}(F) \longleftarrow {}^4A_{2g}]$
CrCl$_3$ in CH$_3$CONH$_2$–KSCN eutectic, 24 °C	This work	18 000 ± 250 (94 ± 15)	24 500 ± 350 (85 ± 15)
[Cr(CH$_3$CONH$_2$)$_6$][ClO$_4$]$_3$ in CH$_3$NO$_2$, r.t.	14	16 450 (53)	22 940 (41.3)
K[Cr(SCN)$_4$(CH$_3$CONH$_2$)$_2$] in CH$_3$OH, r.t.	b	17 950 (41)	24 100 (46)
CrCl$_3$ in KSCN, 200 °C	21	16 520 (127)	22 700 (sh)
Cr^{III} in KSCN, 185 °C	17	16 739 (191)	23 255 (sh)
CrCl$_3$ in KSCN, 177 °C	c	16 700 (15)	
[Cr(NCS)$_6$]$^{3-}$ in H$_2$O, 20 °C	d	17 700 (160)	23 800 (130)
K$_3$[Cr(NCS)$_6$] reflectance, r.t.	21	18 200	23 800 (sh)
[Cr(H$_2$O)$_6$]$^{3+}$ in H$_2$O, r.t.	d	17 400 (13)	24 600 (15)
[Cr(NH$_3$)$_6$]$^{3+}$ in H$_2$O, r.t.	d	21 550 (30)	28 500 (27)

^{a} Absorption maxima (cm^{-1}), with absorption coefficients (dm^3 mol^{-1} cm^{-1}) in parentheses. ^{b} G. Conteras and R. Schmidt, *J. Inorg. Nucl. Chem.*, 1970, **32**, 127. ^{c} G. W. Harrington and B. Sundheim, *Ann. N.Y. Acad. Sci.*, 1960, **79**, 950. ^{d} C. K. Jorgensen, *Adv. Chem. Phys.*, 1963, **5**, 33.

Cobalt(II).—Cobalt(II) chloride dissolved readily in the eutectic to give a bright blue solution. The absorption maxima of the most intense bands are given in Table 2. Three weaker absorptions were also found with maxima and molar absorption coefficients of 20 050 cm^{-1} (ε = 23 dm^3 mol^{-1} cm^{-1}), 21 200 (12), and 23 500 (5) which were assigned to spin-forbidden transitions between the ground state [$^4A_2(F)$] and excited states (^2G), which gain some intensity from spin–orbit coupling mechanisms.

The absorption pattern clearly indicates tetrahedral co-ordination, which was also found for thiocyanate melt solutions and contrasts with the reflectance spectrum of the hexa-acetamide complex (Table 2) which was considered to be octahedral.[18]

The very high values of the molar absorption coefficients may again indicate an unsymmetrical complex, and can be parallelled by the values of > 10^3 obtained for a four-co-ordinate thiocyanate complex, [NMe$_4$]$_2$[Co(NCS)$_4$].[19] In the latter case bonding by sulphur as well as nitrogen of the thiocyanate was not considered, because an early X-ray crystallographic study had shown this complex in the solid state to be tetrahedrally bonded through nitrogen.[20] However, it may be noted that the solid complex gave a very broad reflectance peak centred some 400 cm^{-1} higher than the maximum found in acetone solution, as well as a smaller peak at *ca.* 20 000 cm^{-1}, so there remains the possibility that some switching of the thiocyanate co-ordination occurred in acetone solution. Alternatively, of course, the higher absorption coefficients may arise from some additional distortion occurring both in the eutectic and in the acetone solution.

The position and intensity of the spin-forbidden bands changed little with temperature [*e.g.* at 60 °C, 19 850 cm^{-1} (ε = 24 dm^3 mol^{-1} cm^{-1}), 21 000 (15), and 23 150 (8); at 100 °C, 19 400 (25), 20 750 (14), and 23 150 (7)] but eventually became unobservable as the spin-allowed bands broadened with increasing temperature which evidently explains why these weaker bands have not been reported for thiocyanate melt solutions.

Chromium(III).—A violet solution was formed on dissolving mauve anhydrous chromium(III) chloride in the eutectic. Its absorption bands (Table 3) clearly indicated octahedral co-ordination with a ligand field rather greater than that of water or acetamide which can only be attributed to some nitrogen-bonded thiocyanate. However, the ligand field is also substantially greater than that in molten potassium thiocyanate, a system generally assumed until now to consist entirely of nitrogen bonded thiocyanate on the basis of i.r. measurements

made on much more concentrated (> 5 mol%) solutions.[16] The anomalous red shift of thiocyanate melt solutions from aqueous solutions was again attributed to the polarizing effect of potassium cations on co-ordinated thiocyanate.

As in the case of nickel(II) solutions it is now possible to offer the alternative explanation that in fact sulphur- as well as nitrogen-bonded thiocyanate is present in these co-ordination spheres and that the proportion of nitrogen increases with respect to the thiocyanate melt in the aqueous solution of the thiocyanate complex and in the eutectic, although probably not to the extent of six nitrogen-bonded ligands. Acetamide may also be a ligand in the eutectic solution and this spectrum was similar to that of the only solid thiocyanate–acetamide chromium(III) complex so far reported which contained only four thiocyanates (Table 3).

The values of the molar absorption coefficients for thiocyanate melts and the eutectic were certainly much larger than for the regular octahedra obtained with water or ammonia and would thus support the suggestion of mixed nitrogen- and sulphur-bonded thiocyanate. Again the absence of i.r. evidence for sulphur-bonded thiocyanate in thiocyanate melts is probably due to the extreme weakness of the diagnostic absorption.

Further support for the above hypothesis is obtained from consideration of the change in reflectance spectrum when potassium thiocyanate melt solutions of chromium(III) were frozen. It was reported earlier that the v_1 maximum was considerably blue shifted to 18 000 cm^{-1},[21] and explained as either a distortion in the solid structure imposing a stronger ligand field from thiocyanate, or a removal of the potassium cation polarization effect found in thiocyanate melts. However, the simpler explanation is that some reversal of thiocyanate co-ordination occurs on freezing giving a higher proportion of nitrogen bonding in the solid. The reflectance maximum is certainly close to that of the solid potassium hexaisothio-cyanatochromate(III) (Table 3) where nitrogen bonding is supported by i.r. and chemical evidence.[22,23]

On increasing the temperature of the eutectic solution the colour remained violet and the absorption bands shifted only a little towards the red [at 65 °C, 17 800 cm^{-1} (ε = 100 dm^3 mol^{-1} cm^{-1}), 24 000 (108); at 100 °C, 17 650 (102), 23 700 (110)] indicating a broadly similar co-ordination.

Conclusions

The spectra of the nickel(II) and particularly of the chromium(III) solutions suggest a reassessment of thiocyanate co-ordination in solution and in thiocyanate melts, the most reasonable explanation being co-ordination of thiocyanate by

sulphur as well as nitrogen even with hard Lewis acid cations. This explanation can be extended to the spectra of cobalt(II) solutions and so may be generally applicable at least to first-row transition metal complexes.

The acetamide–potassium thiocyanate eutectic has been shown to be a useful new room-temperature non-aqueous solvent for spectroscopy, and would probably also have potential as a solvent for inorganic and organic reactions, electrochemistry, and some industrial processes.

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