Cobalt(II) Halide Complexes in Aqueous Ammonium Nitrate–Calcium Nitrate Melts: Electronic Spectra and Solvent Extraction†

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Addition of chloride or bromide to cobalt(II) dissolved in a low-temperature aqueous nitrate melt [xNH$_4$NO$_3$·yCa(NO$_3$)$_2$·zH$_2$O] changed the electronic absorption spectrum from near-octahedral co-ordination by both nitrate and water to a tetrahedral (or severely distorted octahedral) symmetry with between two and three halide ligands, the bromide species containing less water. The effects of varying the concentrations and of increasing temperature are discussed. Solvent-extraction measurements were made and the spectra of the organic and salt phases recorded.

Spectroscopic investigations of the co-ordination of 'probe cations' have been frequently used for insight into melt structures; the changes occurring with temperature and with varying concentrations of a second component have both been used, when variable co-ordination is found, to show whether the change is one of gradual distortion or due to two coexisting geometrically distinct species.[1,2]

Cobalt(II) has often been chosen for such work since it gives a striking red shift to the principal visible absorption band on changing from octahedral to tetrahedral co-ordination (the latter exhibits well defined fine structure). This change is clearly seen in aqueous solutions, when for example concentrated hydrochloric acid is added, and is commonly illustrated in text-books.[3] The analogous change also occurs in molten nitrate solution upon addition of chloride, as shown by the classic study of Gruen *et al.*[4]

Similar changes in co-ordination occur when bromide or iodide is added to cobalt(II) solutions in the lithium nitrate–potassium nitrate eutectic,[5] though the initial co-ordination in pure nitrate was later claimed to be dodecahedral[6] because of the spectral similarity to tetranitratocobaltate(II) whose structure had been determined by *X*-ray diffraction,[7] and on the basis of resolution of the spectrum into five bands.[8] Volkov and Buryak[9] showed that complete conversion into the tetrachloro complex required an extremely large excess (× 500—1 000) of added chloride and that alkali-metal chlorides give increased absorption coefficients with increasing cation radius.

Hemmingsson and Holmberg[10] applied a computational treatment to their spectral curves and were able to calculate the stability constants of the mono-, di-, tri-, and tetra-halogeno species, using added chloride and also bromide, while showing added fluoride caused no spectral change, but could not determine the number of co-ordinated nitrate anions nor did they consider their results accurate enough to specify where the change from dodecahedral to tetrahedral co-ordination occurred; however, Griffiths and Potts[11] have attempted this with the analogous nickel(II) species. Similar spectral changes were observed when cobalt(II) was dissolved in molten ammonium nitrate with and without added chloride.[12]

Analogous changes in co-ordination have been reported for other oxyanion melts, particularly the change from octahedral to pseudo-tetrahedral to octahedral and finally, to tetrahedral in potassium sulphate–zinc sulphate glasses with steadily increasing ratios of zinc chloride.[13] Subsequently, in pure sulphate melts, cobalt(II) was shown to be dodecahedral[14] or octahedral, changing to dodecahedral at higher temperature.[15] In acetate, the co-ordination of cobalt(II) changes from octahedral to tetrahedral as the proportion of potassium increases in lead acetate–potassium acetate glasses,[16] though in alkali-metal acetate melts the co-ordination has been reported both as tetrahedral[17] and as dodecahedral.[18] The results from purely chloride melts are rather less relevant but may be summarised as octahedrally co-ordinated cobalt(II) in alkali-metal chlorides,[19] distorted tetrahedral in magnesium chloride,[20] and tetrahedral in lead(II), tin(II), and bismuth(III) chlorides;[21] in aluminium trichloride the co-ordination is octahedral, changing to distorted octahedral and then to tetrahedral as potassium chloride is added.[20]

However, in all the above systems there have been no more than two potential ligands to consider. It thus seemed timely to consider the potential competition for co-ordination to the 'probe cation', cobalt(II), when there are three potential ligands. The only such system reported so far is cobalt(II) in a glass [of composition '6KNO$_3$·4Ca(NO$_3$)$_2$ + 24 mol% H$_2$O doped with 1 mol% KSCN'] where the composition ratio was not changed though the spectrum was determined at two temperatures (20 and 50 °C).[22]

A series of spectral measurements of cobalt(II) in low-melting hydrated nitrate melts [xNH$_4$NO$_3$·yCa(NO$_3$)$_2$·zH$_2$O] with added halide were therefore undertaken as a follow-up to the studies of complex formation using e.m.f.[23–25] and solvent extraction[26] measurements. The high solubility of these nitrates in water enables their study at low water concentrations and such 'aqueous melts' thus have incomplete hydration spheres around the ions and are therefore intermediate between aqueous electrolyte solutions and anhydrous ionic molten salts. The water concentration in the two water-rich mixtures used corresponds to the same hydration number (4.35) for the cobalt(II) ion, according to the simplified calculations of Gal *et al.*,[27] the other to a hydration number of 3.23.

Some metal–ligand association equilibria in these solutions investigated earlier showed both regular and reversed orders of halide complexation with highly polarised bivalent metal ions,[23–26] but no spectroscopy has so far been reported in aqueous melts as opposed to glasses.

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† Supplementary data available (No. SUP 56549, 15 pp.): additional spectra of cobalt(II). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx.

Table. Slopes derived by limiting-logarithm method (ref. 31)

Mole ratio			Concentration (mol dm^{-3})		Temperature	Limiting slope		
NH_4NO_3	$Ca(NO_3)_2$	H_2O	Co^{2+}	X^-	(°C)	Co^{2+}	Cl^-	Br^-
0.6	0.4	1.25	0.002—0.010	0.57	92	1.15		
0.6	0.4	1.25	0.0070	0.07—0.57	92		2.5	
0.6	0.4	1.25	0.0070	0.07—0.57	80		2.7	
0.6	0.4	1.25	0.0070	0.07—0.58	61		2.8	
0.7	0.3	1.075	0.0028	0.43—1.01	92		1.5	
0.7	0.3	0.80	0.0070	0.24—0.58	92		1.9	
0.6	0.4	1.25	0.0075	0.07—0.75	92			2.5
0.7	0.3	1.075	0.0027	0.46—1.06	92			2.3
0.7	0.3	0.80	0.0070	0.40—0.85	92			2.9
0.7	0.3	0.80	0.0025	0.24—0.89	92			3.1

Experimental

Spectrophotometric Measurements.—Solvents of the desired composition were prepared from known weights of carefully dried salts (reagent grade Merck products) and distilled water. Calcium nitrate was dried for 24 h at 220 °C, while ammonium nitrate was dried under vacuum at $\leqslant 80$ °C, in order to avoid possible decomposition above its melting point. Cobalt(II) nitrate hexahydrate (reagent grade), anhydrous ammonium chloride or ammonium bromide were added to the melts to obtain the desired concentrations. The mixtures were premelted at 80 °C in stoppered glass vessels and rectangular quartz spectrophotometric cells of 10-mm pathlength with ground-glass stoppers were filled with the melts, using preheated glass pipettes.

Spectra were recorded on a Beckman DK-1A recording spectrophotometer, with a thermostatted cell compartment. The temperature in the cells was maintained within ± 0.7 °C. The reference cell was always filled either with pure solvent of the corresponding composition, or where stated, with a solution containing the corresponding concentration of cobalt(II) nitrate but without ligand addition. Spectra were recorded at wavelengths between 400 and 750 nm, the baseline being checked immediately before spectra were recorded.

All concentrations in spectrophotometric measurements were expressed in molarities. The densities of the melts were determined picnometrically, so that molar absorption coefficients could be calculated.

Distribution Measurements.—The melt phase in the distribution experiments was prepared in the same way as for spectrophotometric measurements, except that cobalt(II) nitrate solutions were labelled with ^{60}Co. The organic phase was a solution of tri-n-butyl phosphate (0.2 mol dm^{-3}) in an eutectic mixture of biphenyl and naphthalene (55 mol% biphenyl, m.p. 39.5 °C[28]).

The technique of phase equilibration and sampling is described elsewhere.[29] The radioactive tracer concentration was counted in both phases. The molal distribution coefficient was calculated as an average of at least two independent sample equilibrations, which were in agreement within $\pm 2\%$.

In the preliminary experiments it was shown that the pure solvent (eutectic mixture of biphenyl and naphthalene) did not extract cobalt(II) either from nitrate melts or from melts with various ligand concentrations added. The molal distribution coefficient of cobalt(II) was determined as a function of the chloride and bromide ligand concentrations in the melt phase.

The distribution of cobalt(II) species between the two phases was also followed spectrophotometrically. A few distribution experiments were performed without radioactive tracer addition and the spectra of both the organic and inorganic phases were recorded. Pure organic and inorganic solvents were used as corresponding reference solutions. The spectra of both phases were recorded with and without ligand addition in the melt phase before equilibration.

Results

Cobalt(II) spectra were determined at temperatures from 61 to 92 °C in melts with three initial ammonium–calcium–water ratios, and though chloride and bromide were added as ammonium halides the additional ammonium had an insignificant effect on the spectra. Representative spectra at increasing chloride ratios are given in Figures 1 and 2 and at increasing bromide ratios in Figures 3 and 4. The effect of temperature is illustrated in Figure 5 and of water concentration in Figures 6 and 7. In each case a series of cobalt concentrations were studied (the complete results are too extensive to list here but copies of all spectra were available as SUP 56549). Plots of log absorbance at constant chloride concentrations *versus* log cobalt concentration at the wavelengths of the absorbance maxima gave straight lines indicating that Beers law was obeyed.

Attempts were made to calculate the stability constants of individual halogeno-substituted monomeric cobalt complexes and of their absorption coefficients by using the LETAGROP–SPEFO program employed so successfully by Hemmingsson and Holmberg[10] for cobalt halide complexes in the anhydrous lithium nitrate–potassium nitrate eutectic, though in the present case without success. Likewise a newly developed modification of the STEPIT program, which was kindly made available,[30] also gave no consistent results. The older graphical limiting-logarithm method of Bent and French[31] was therefore used, with the results shown in the Table. Plots of log absorbance *versus* log halide molality gave consistent results at wavelengths where there was no absorption due to regular 'octahedral' species.

Solvent extraction showed cobalt(II) complexes to be present in both phases, the spectra of the organic and of the salt phase (after equilibration with 0.5 mol dm^{-3} chloride or bromide) together with that of cobalt(II) nitrate without added halide being given in Figures 8 and 9. The dependence of the distribution of cobalt(II) on halide concentration is given in Figure 10.

Discussion

It is clear that in these hydrate melts chloride and bromide anions cause a change in co-ordination of cobalt(II) which is conventionally referred to as from octahedral to tetrahedral (Figures 1—4) and that the values of $\lambda_{max.}$ show a blue shift from the values in anhydrous melts, thus indicating co-ordination by water as well as by nitrate, at least in the halide-free systems. The octahedral maximum (Figures 1 and 2) appeared at 525 nm,

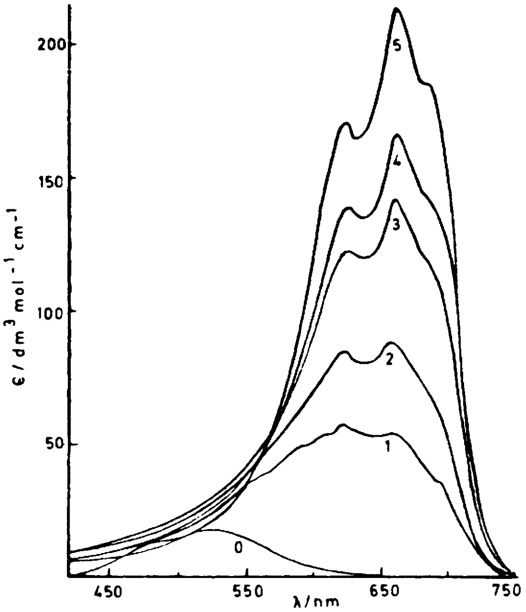

Figure 1. Variation of the spectra of cobalt(II) [(2.75 ± 0.05) × 10^{-3} mol dm^{-3} $Co(NO_3)_2$] in NH_4NO_3-$Ca(NO_3)_2$-H_2O (mole ratio 0.7:0.3:1.075) with added NH_4Cl: zero (0), 0.437 (1), 0.555 (2), 0.717 (3), 0.809 (4), and 1.010 mol dm^{-3} (5)

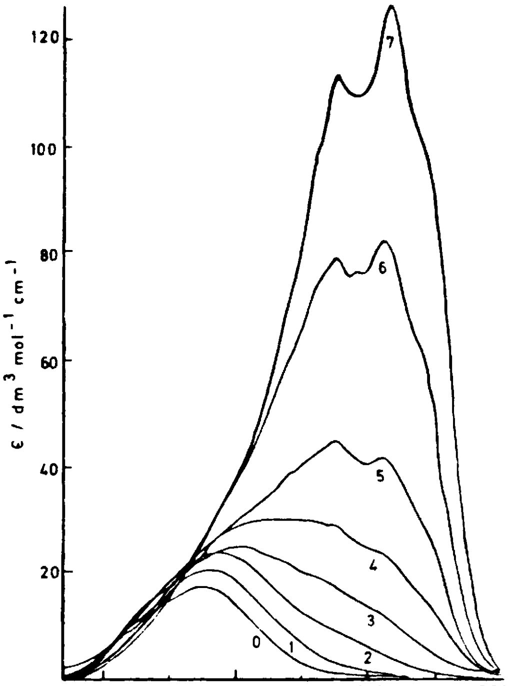

Figure 2. Variation as in Figure 1, except (7.0 ± 0.1) × 10^{-3} mol dm^{-3} $Co(NO_3)_2$ in NH_4NO_3-$Ca(NO_3)_2$-H_2O (mole ratio 0.6:0.4:1.25) at 92 °C. Added NH_4Cl: zero (0), 0.070 (1), 0.136 (2), 0.208 (3), 0.272 (4), 0.355 (5), 0.445 (6), and 0.569 mol dm^{-3} (7)

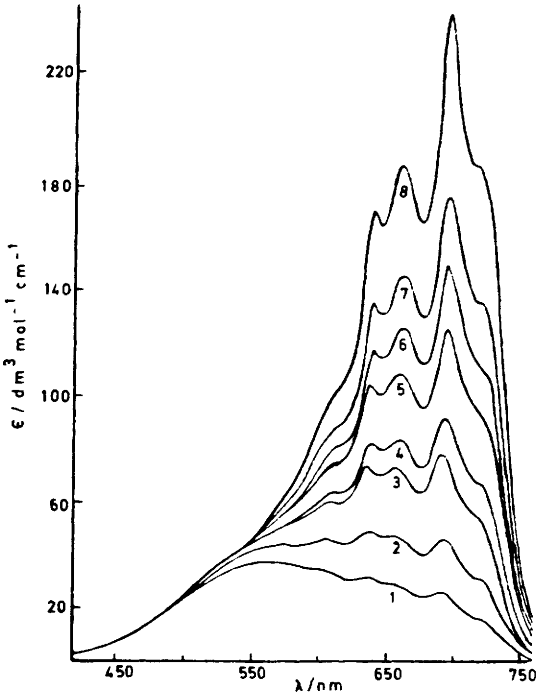

Figure 3. Variation of the spectra of cobalt(II) [(7.0 ± 0.1) × 10^{-3} mol dm^{-3} $Co(NO_3)_2$] in NH_4NO_3-$Ca(NO_3)_2$-H_2O (mole ratio 0.7:0.3:0.8) at 92 °C with added NH_4Br: 0.399 (1), 0.477 (2), 0.558 (3), 0.607 (4), 0.665 (5), 0.711 (6), 0.726 (7), and 0.851 mol dm^{-3} (8)

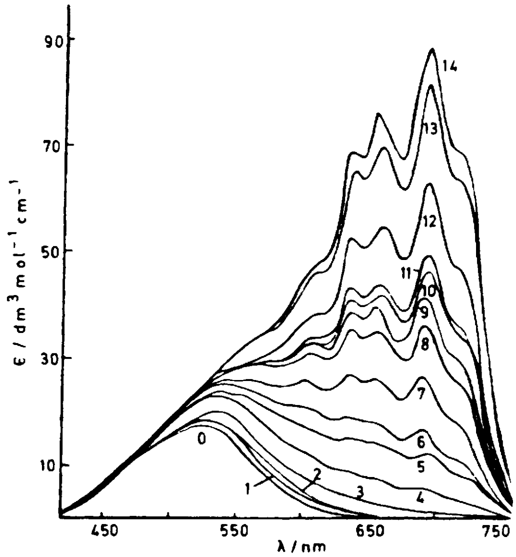

Figure 4. Variation as in Figure 3, except (7.7 ± 1.0) × 10^{-3} mol dm^{-3} $Co(NO_3)_2$ in NH_4NO_3-$Ca(NO_3)_2$-H_2O (mole ratio 0.6:0.4:1.25). Added NH_4Br: zero (0), 0.070 (1), 0.136 (2), 0.206 (3), 0.275 (4), 0.358 (5), 0.449 (6), 0.475 (7), 0.510 (8), 0.547 (9), 0.575 (10), 0.610 (11), 0.677 (12), 0.729 (13), and 0.750 mol dm^{-3} (14)

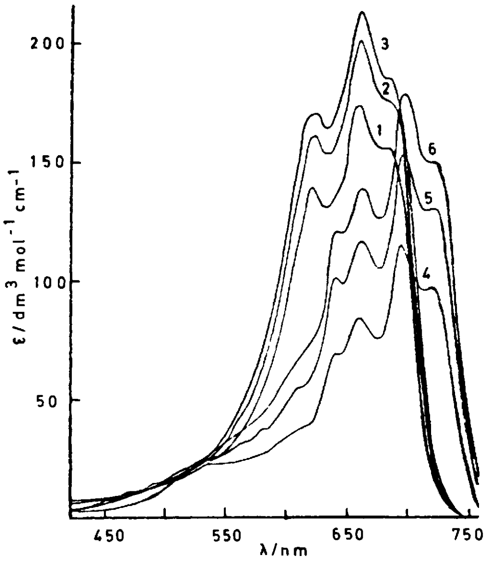

Figure 5. Variation of spectra with temperature. Curves: (1—3), 2.7×10^{-3} mol dm^{-3} $Co(NO_3)_2$ in NH_4NO_3–$Ca(NO_3)_2$–H_2O (mole ratio 0.7:0.3:1.075) with 1.0 mol dm^{-3} NH_4Cl; (4—6), 2.6×10^{-3} mol dm^{-3} $Co(NO_3)_2$ in NH_4NO_3–$Ca(NO_3)_2$–H_2O (0.6:0.4:1.25) with 0.59 mol dm^{-3} NH_4Br. Temperature: 61 (1,4), 80 (2,5), and 92 °C (3,6)

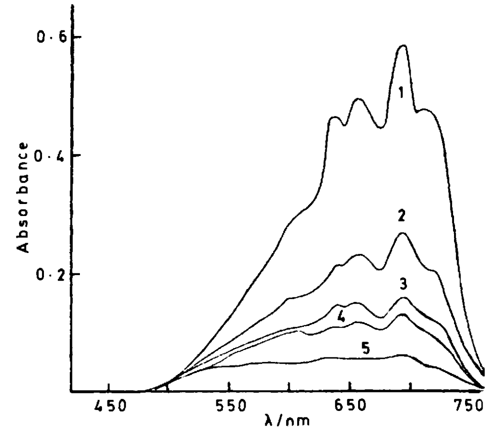

Figure 7. Variation as in Figure 6, except 7.0×10^{-3} mol dm^{-3} $Co(NO_3)_2$ with 0.75 mol dm^{-3} NH_4Br

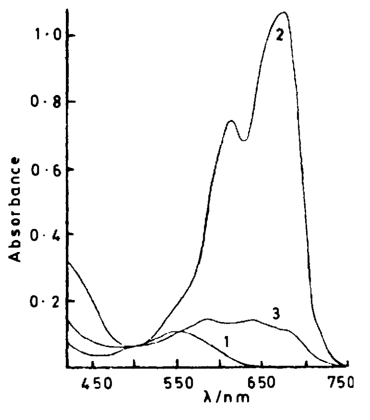

Figure 9. Spectra of the organic phase after equilibration. Details as in Figure 8

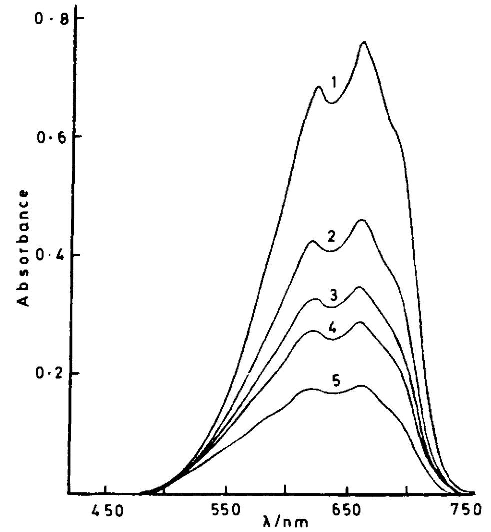

Figure 6. Variation of the spectra of cobalt(II) [6.9×10^{-3} mol dm^{-3} $Co(NO_3)_2$] in NH_4NO_3–$Ca(NO_3)_2$–H_2O (mole ratio 0.6:0.4:*Z*) with 0.56 mol dm^{-3} NH_4Cl at 92 °C. Z = 1.25 (1), 1.50 (2), 1.65 (3), 1.73 (4), and 2.00 (5)

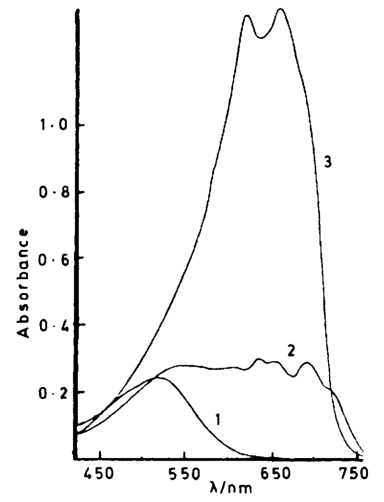

Figure 8. Spectra of the salt phase after equilibration at 92 °C. Initial concentrations: 1.33×10^{-2} mol dm^{-3} $Co(NO_3)_2$. Curves: 1, no Cl^- or Br^-; 2, 0.5 mol dm^{-3} NH_4Br; 3, 0.5 mol dm^{-3} NH_4Cl

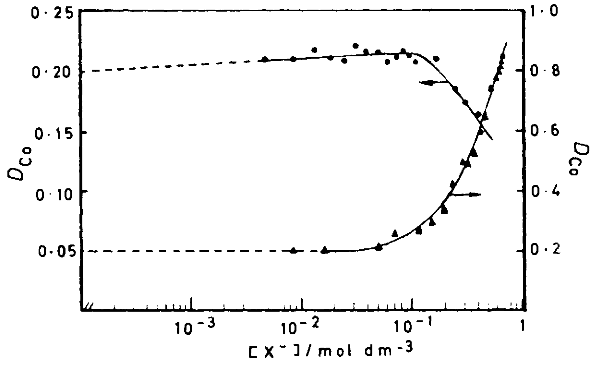

Figure 10. Dependence of the distribution coefficient (D) of cobalt(II) on NH_4X concentration; X = Cl (●), Br (▲). Initial composition of salt phase: NH_4NO_3–$Ca(NO_3)_2$–H_2O (mole ratio 0.6:0.4:1.25), 1.33×10^{-3} mol dm^{-3} $Co(NO_3)_2$

midway between the 510 nm in aqueous solutions[3] and 550 nm in anhydrous $LiNO_3$–KNO_3 at 180 °C,[4] though co-ordination by as many as three water molecules is not necessarily implied since some shift due a change in cation and in temperature could also have occurred.

The tetrahedral maximum is also at a slightly shorter wavelength than in the corresponding pure halide melt (660 nm when chloride is present, Figures 1 and 2, as against 710,[4] 695,[19] or 695—715 nm[20] in anhydrous chloride), again indicating some co-ordination by nitrate and/or by water ($\lambda_{max.}$ at 660 nm in $LiNO_3$–KNO_3 with 0.48 mol dm^{-3} Cl^-, where on average one nitrate is co-ordinated[10]). Similarly with bromide the tetrahedral maximum is at 695 nm (Figures 3 and 4), as compared to 720 nm in the pure bromide melt.[19] Bromide-containing solutions show three maxima plus two shoulders as opposed to two maxima plus one shoulder with chloride-containing melts. The greater number of peaks may well indicate the simultaneous presence of two complexes at significant concentrations and thus less different values of successive stability constants in the case of the bromide spectra, as found earlier with anhydrous nitrate melts.[10] Water would also appear to be involved in the co-ordination process since increasing the water concentrations causes a reduction in the absorption coefficient of the tetrahedral maximum (Figures 6 and 7), though there was no significant change in the wavelength of this maximum.

The multiple absorptions with maxima at 660 nm for chloride and 695 nm for bromide referred to above as 'tetrahedral' could also be attributed to severely distorted octahedral species [*cf.* Co^{II} in KCl–$AlCl_3$ (49.9:50.1 mol%)].[20] Certainly some intermediate octahedrally co-ordinated species might be expected as halide is substituted, before the eventual production of tetrahedral species, as suggested by many authors.[1,2,4,5,32] As is customarily found, 'tetrahedral' co-ordination (as indicated by the size of the absorption coefficient) increases with halide concentration (Figures 1—4). An increase in temperature also causes an increase in this absorption coefficient (Figure 5), indicating either that the tetrahedral complex is relatively more thermally stable, or that the absorbing species is actually severely distorted octahedral, because octahedral species, in contrast to tetrahedral, have increased absorption coefficients with increasing temperature.[33]

Families of curves (*e.g.* Figures 1—4) are ideally treated by computation to obtain a series of stepwise stability constants for increasing halide substitution, exemplified by the studies of Hemmingsson and Holmberg.[10] However with the present data both the programs used in the latter studies and one recently developed by Holmberg[30] gave values for the stability constants and for the absorption coefficients which could not be optimised satisfactorily, primarily because the range of halide concentration was insufficient (the maximum halide concentration used in each case is close to the solubility limit for ammonium halide in the solvent). Nevertheless it must be borne in mind that the programs assume only one ligand activity to be changing, in this case halide, so that the failure to obtain consistent results may thus also indicate changing water and/or nitrate activities within the sets of spectra. However the limiting slope plots (Table) indicated that the complexes were mononuclear in cobalt(II) and contained between two and three halides at highest ligand concentration (*i.e.* at the solubility limit of the halides in the particular solvent).

The number of halide ligands in the limiting complex can be seen to decrease, as might have been anticipated, with increasing temperature, cobalt concentration, water concentration, and ammonium–calcium ratio at constant hydration number. The limiting slope for nitrate ligands indicated virtually no nitrate co-ordination and thus co-ordination by one water molecule, if the absorbing species is four-co-ordinate tetrahedral, in reasonable agreement with the absorption maxima found. Under comparable conditions the number of bromide ligands was greater than that of chloride, though it should be noted that the solubility of ammonium bromide was approximately 50% higher than that of ammonium chloride, and thus that bromide complexes tended to contain less water than chloride complexes, as expected from electrostatic and steric considerations. The finding that bromide co-ordinates to a greater extent is in fact the reverse of the trend found with anhydrous melts.[10] In this connection it is relevant that the order of the stability constants for chloride and bromide complexes of zinc(II), a small highly polarising transition-metal cation like cobalt(II), was also reversed on going from aqueous to anhydrous melts.[25]

The results obtained by solvent extraction broadly support the conclusions from the spectroscopic measurements. The higher distribution coefficients for cobalt(II) bromides than for the chlorides indicate the higher solubility of the former in the organic phase, largely due to lower water co-ordination. The distribution coefficient for the chlorides begins to decrease at the same chloride concentration (0.2 mol dm^{-3}) at which the significant change from octahedral absorption is observed (Figure 2), *i.e.* a concentration where negatively charged species are formed, which are not extractable by tri-n-butyl phosphate.[34,35] However, with bromide, no decrease in distribution coefficient was observed even at the higher possible ammonium bromide concentration, probably because of the presence of one or more complexes with a high solubility in the organic phase, whose concentration even increases as the bromide concentration reaches a maximum.

The phases after equilibration gave spectra which showed cobalt(II) to be tetrahedrally co-ordinated in both the melt and in the organic phase. With chloride the absorption was probably due to tetrahedral species with negative charge in the salt phase, *e.g.* $[CoCl_m(NO_3)_n]^{(m+n-2)-}$ while in the organic phase the spectrum (Figure 8) suggested the simultaneous presence of octahedral as well as tetrahedral species probably containing chloride, nitrate, water, and tri-n-butyl phosphate (tbp) as possible ligands. Conversely with bromides the organic phase showed absorption typical of blue tetrahedral neutral species such as $CoBr_2{\cdot}2tbp$ which is known to be soluble in the organic solvent;[34,36] the salt phase showed absorption due to both octahedral and tetrahedral species similar to that obtained at 0.45—0.5 mol dm^{-3} bromide (Figure 3).

In conclusion, although nitrate is always present as a potential ligand, it competes effectively only when no halide is present, the octahedral complexes then formed having approximately equal numbers of water and nitrate ligands. However in the presence of both chloride and bromide, nitrate ligands are increasingly displaced and eventually also some water ligands, finally giving tetrahedral species with approximately three halides and one water molecule as ligands.

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References

1 C. A. Angell and D. M. Gruen, *J. Phys. Chem.*, 1966, **70**, 1601.
2 W. E. Smith, J. Brynestad, and G. P. Smith, *J. Chem. Phys.*, 1970, **52**, 3890.
3 F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' 3rd edn., Interscience, New York, 1972.

4 D. M. Gruen, S. Fried, P. Graf, and R. L. McBeth, Proc. 2nd. U.N. Int. Conf. Peaceful Uses Atomic Energy, 1958, vol. 28, p. 112.
5 I. V. Tananaev and B. F. Dzhurinskii, *Dokl. Akad. Nauk SSSR*, 1960, **135**, 94.
6 J. A. Duffy and M. D. Ingram, *J. Am. Ceram. Soc.*, 1968, **51**, 544.
7 F. A. Cotton and J. G. Bergman, *J. Am. Chem. Soc.*, 1964, **86**, 2941.
8 K. W. Fung and K. E. Johnson, *Can. J. Chem.*, 1970, **47**, 4699.
9 S. N. Volkov and N. I. Buryak, *Ukr. Khim. Zh.* (*Russ. Ed.*), 1972, **38**, 663.
10 S. Hemmingsson and B. Holmberg, *Inorg. Chem.*, 1980, **19**, 2242.
11 T. R. Griffiths and P. J. Potts, *Inorg. Chem.*, 1975, **14**, 1039.
12 A. G. Keenan and I. J. Ferrer, *J. Phys. Chem.*, 1972, **76**, 2844.
13 M. D. Ingram and J. A. Duffy, *J. Chem. Soc. A*, 1968, 2575.
14 J. R. Dickinson and K. E. Johnson, *J. Mol. Spectrosc.*, 1970, **36**, 1.
15 J. R. Dickinson and M. E. Stone, *Can. J. Chem.*, 1972, **50**, 2946.
16 M. D. Ingram, G. G. Lewis, and J. A. Duffy, *J. Phys. Chem.*, 1972, **76**, 1035.
17 R. A. Bailey, M. El Guindy, and J. A. Walden, *Inorg. Chem.*, 1969, **8**, 2526.
18 J. A. Duffy and M. D. Ingram, *J. Chem. Soc. A*, 1969, 2398.
19 B. R. Sundheim and M. Kukk, *Discuss. Faraday Soc.*, 1961, **32**, 49.
20 H. A. Øye and D. M. Gruen, *Inorg. Chem.*, 1965, **4**, 1173.
21 K. W. Fung and K. E. Johnson, *Can. J. Chem.*, 1970, **48**, 3635.
22 A. Barkatt and C. A. Angell, *J. Phys. Chem.*, 1978, **82**, 1972.
23 I. J. Zsigrai, R. M. Nikolić, and I. J. Gal. *J. Chem. Soc., Dalton Trans.*, 1976, 879.
24 I. J. Zsigrai, I. J. Gal, and R. M. Nikolić, *J. Chem. Soc., Dalton Trans.*, 1978, 549.
25 R. Nikolić and D. Stojić, *Electrochim. Acta*, 1980, **25**, 165.
26 R. M. Nikolić and I. J. Gal. *J. Inorg. Nucl. Chem.*, 1974, **36**, 3827.
27 I. J. Gal, R. M. Nikolić, and G. Heraković, *J. Chem. Soc., Dalton Trans.*, 1976, 104.
28 V. H. Troutner, U.S. Atomic Energy Commission, Report No. HW-57431, 1958.
29 R. M. Nikolić and I. J. Gal, *J. Inorg. Nucl. Chem.*, 1968, **30**, 1963.
30 B. Holmberg, personal communication.
31 H. E. Bent and C. L. French, *J. Am. Chem. Soc.*, 1941, **63**, 568.
32 K. E. Johnson and T. S. Piper, *Discuss. Faraday Soc.*, 1962, **32**, 32.
33 G. Pedro Smith, in 'Molten Salts Chemistry,' ed. M. Blander, Interscience, New York, 1964, p. 445.
34 L. I. Katzin, *J. Inorg. Nucl. Chem.*, 1957, **4**, 187.
35 M. Zangen, *Inorg. Chem.*, 1968, **7**, 1202.
36 H. Irving and D. N. Edgington, *J. Inorg. Nucl. Chem.*, 1959, **10**, 306.

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