# THERMOGRAVIMETRIC STUDY OF COBALT(II)-HALIDE COMPLEXES IN A MOLTEN NITRATE EUTECTIC

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## ABSTRACT

The temperatures and stoichiometries of reaction of cobalt(II) nitrate, chloride and bromide have been established by analysis, infrared, X-ray diffractometry and thermogravimetric analysis. Tricobalt tetraoxide and nitrogen dioxide were produced together with oxygen and nitrite from the first two reactants, but with nitric oxide and bromine from the third reactant. Reaction pathways are suggested. Addition of potassium chloride caused a large (150–200°) increase in temperature of maximum reaction rate, which was ascribed to the formation of chloro "complexes". No stabilisation was observed on addition of potassium bromide, though broadening of the weight loss maxima when chloride and bromide were present suggested the formation of mixed complexes.

## INTRODUCTION

The study of association between transition metal cations and halide anions in molten salt solution, besides providing scope for philosophical argument as to whether or not the association has a sufficiently long life for the term "complex" to be used[1], is important as a means to understanding the general behaviour of such ions and has been pursued for as long as any other aspect of molten salt chemistry.

Such associations are, of course, most manifest in halide melts, but molten nitrates have frequently been used for measurements and a considerable list may now be tabulated[2]. In many cases, the measurements have been made on quite dilute solutions by electrochemical, physical or spectroscopic methods. In the case of cobalt(II), despite its being a readily available oxidation state, existing knowledge, apart from two e.m.f. studies[3, 4], is largely confined to the very well known spectroscopic measurements of Gruen et al.[5], demonstrating the classic change from octahedral coordination in a pure nitrate melt to tetrahedral when a high ratio of chloride to cobalt was present. These measurements were largely confirmed by those of Tanaev and Dzhurinskii[6, 7] and Volkov and Buryak[8].

Evidence for more concentrated solutions is necessarily missing, as is the influence that association may have on the properties of such solutions. Bearing in

mind that data is now accumulating on a number of first row transition metals, for example titanium(IV)[9], iron(III)[10], and zinc(II)[11], which shows that halide "complexes" considerably modify the properties of such cations, including their thermal stability and Lux-Flood acidity, a thermogravimetric study of cobalt(II) with both chloride and bromide in nitrate melts was undertaken.

In addition, such studies have defined the thermal stability of pure cobalt(II) solutions (i.e. without additional halide) where the presently available information is imprecise, being derived incidentally from other studies. For example, in lithium nitrate–potassium nitrate, cobalt(II) was evidently stable at 160° for chromatographic[12], solvent extraction[13], and solubility studies[14] as well as spectroscopic measurements at 223° (ref. 5) and 240° (ref. 6) but was found to precipitate at 255° during electromigration[15]. In sodium nitrate–potassium nitrate, the kinetics of the formation of insoluble tricobalt tetraoxide have been reported[16] from 350° to 400°, thus setting an upper temperature limit.

EXPERIMENTAL

*Materials*

The melt was prepared as previously described[9]. Analar (B.D.H.) potassium chloride. potassium bromide and cobalt(II) chloride were all dried at 110° for 12 h (found: Co, 45.2; Cl, 54.4; calc. for $CoCl_2$: Co, 45.4; Cl, 54.6%). Cobalt(II) bromide (B.D.H.) was dried at 250° for 1 h (found: Co, 27.1; Br, 72.0; calc. for $CoBr_2$: Co, 26.9; Br, 73.1%). Analar cobalt(II) nitrate hexahydrate was used as received.

*Analysis*

Chloride and bromide were analysed volumetrically by Volhard's method and cobalt gravimetrically as cobalt(II) sulphate. Infrared spectra of the gases produced from a reaction under vacuum were obtained using a 10 cm cell with KBr windows on a Unicam SP200. X-Ray diffractometry was carried out on a Philips (Eindhoven) instrument using Ni-filtered $CuK_x$ radiation. Thermogravimetric analyses were performed on a Stanton TR-1 thermobalance with a heating rate of 2°/min in a 10 ml silica crucible covered with perforated porcelain disc to prevent the emission of solid particles.

RESULTS AND DISCUSSION

Analar cobalt(II) nitrate hexahydrate dissolved slowly in lithium nitrate–potassium nitrate eutectic at 150° to give a blue solution. When dehydrated under vacuum for four hours, the loss of weight was 35.0% [calc. for loss of $6H_2O$ from $Co(NO_3)_2 \cdot 6H_2O = 37.1\%$]. The melt remaining was a clear blue with no precipitate as would have been observed if hydrolysis had occurred. Nujol mulls of the solidified melt solution gave no evidence of water by infrared. On further heating, a mixture of nitrogen dioxide and oxygen was slowly evolved at 250° confirming the
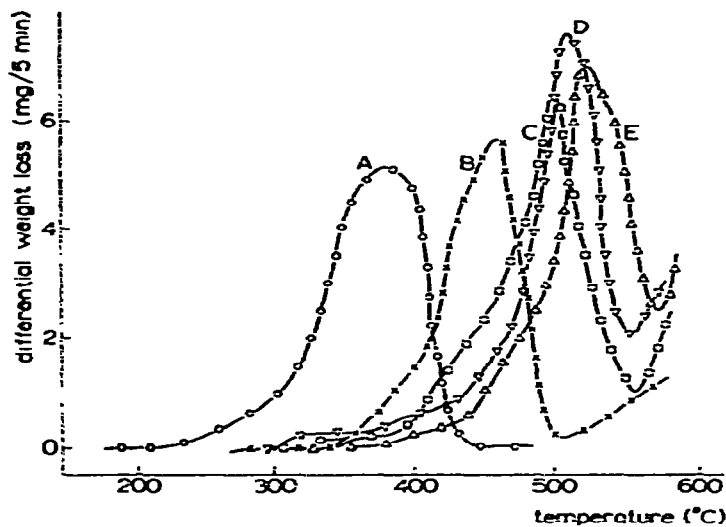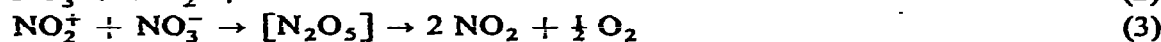
Fig. 1. Thermogravimetric analysis of cobalt(II) nitrate in molten lithium nitrate–potassium nitrate eutectic with additions of potassium chloride. Curve A, $\bigcirc$, 0.159 m $Co(NO_3)_2$; curve B, $\times$, 0.116 m $Co(NO_3)_2$ and 0.29 m KCl; curve C, $\square$, 0.136 m $Co(NO_3)_2$ and 2.03 m KCl; curve D, $\triangle$, 0.120 m $Co(NO_3)_2$ and 2.70 m KCl; curve E, $\triangle$, 0.110 m $Co(NO_3)_2$ and 3.30 m KCl.

inference to be made from the temperatures used by Tanaev and Dzhurinskii[6] and Bailey and Steger[15]. Reaction proceeded at an increasing rate to 350°, whilst a black precipitate of tricobalt tetraoxide was formed, as shown by analysis (found: Co, 73.7; calc. for $Co_3O_4$: Co, 73.4%) and confirmed by X-ray diffraction ["$d$" values 2.88(30), 2.43(100), 2.02(30), 1.55(30), 1.43(40). A.S.T.M. Index 2.860(40), 2.438(100), 2.021(25), 1.555(35), 1.429(45)].

Thermogravimetric analysis (Fig. 1, curve A) showed the rate of gas evolution to increase from 200°, with a maximum at 340°, the total loss of 61.5% and the products identified corresponding reasonably with the stoichiometry
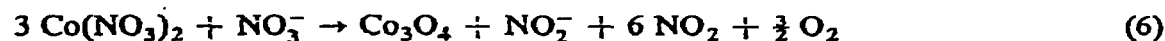
$$3\ Co(NO_3)_2 \rightarrow Co_3O_4 + 6\ NO_2 + O_2 \tag{1}$$

(calc. weight loss 56.3%) which would be deduced if the cobalt(II) cation had behaved as a Lux-Flood acid initially forming cobalt(II) oxide, i.e.

$$NO_3^- \rightleftharpoons NO_2^+ + O^{2-} \tag{2}$$
$$NO_2^+ + NO_3^- \rightarrow [N_2O_5] \rightarrow 2\ NO_2 + \tfrac{1}{2}\ O_2 \tag{3}$$
$$Co^{2+} + O^{2-} \rightarrow CoO\downarrow \tag{4}$$

and the cobalt(II) oxide being oxidised by the liberated oxygen. However, if the postulated oxide were to react as it does in a pure melt with production of the equivalent quantity of nitrite[17], i.e.

$$3\ CoO + NO_3^- \rightarrow Co_3O_4 + NO_2^- \tag{5}$$

the overall reaction, becomes

$$3\ Co(NO_3)_2 + NO_3^- \rightarrow Co_3O_4 + NO_2^- + 6\ NO_2 + \tfrac{1}{2}\ O_2 \tag{6}$$

(calc. weight loss 59.0%) in better conformity with the observed loss.

TABLE 1

REACTION OF COBALT(II) NITRATE IN MOLTEN LITHIUM NITRATE–POTASSIUM NITRATE EUTECTIC WITH
ADDITION OF POTASSIUM CHLORIDE

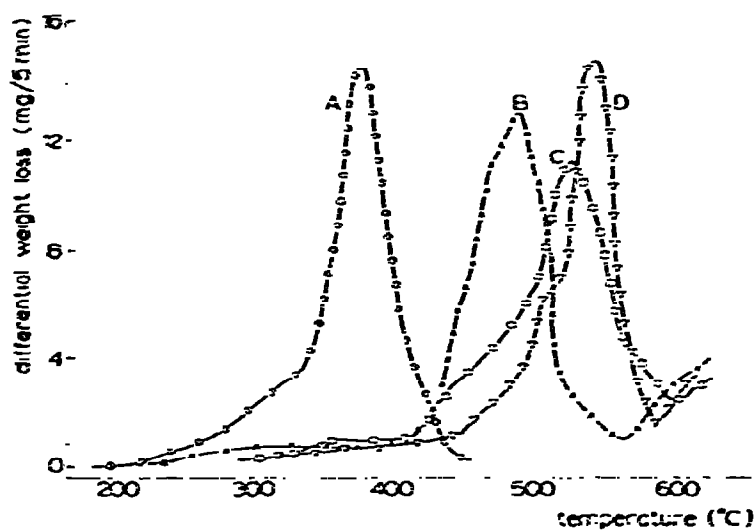| Reactants | | | | Co:Cl ratio | Temperature of maximum rate of weight loss (°C) | Experimental weight loss (%) |
|---|---|---|---|---|---|---|
| $Co(NO_3)_2$ | | KCl | | | | |
| mole | m | mole | m | | | |
| $3.99 \times 10^{-4}$ | 0.159 | | | 1:0 | 380 | 61.5 |
| $3.99 \times 10^{-4}$ | 0.116 | $10.0 \times 10^{-4}$ | 0.29 | 1:2.5 | 460 | 50.7 |
| $3.99 \times 10^{-4}$ | 0.136 | $59.8 \times 10^{-4}$ | 2.03 | 1:15 | 500 | 58.9 |
| $3.99 \times 10^{-4}$ | 0.120 | $89.9 \times 10^{-4}$ | 2.70 | 1:22.5 | 505 | 61.5 |
| $3.99 \times 10^{-4}$ | 0.110 | $120.0 \times 10^{-4}$ | 3.30 | 1:30 | 520 | 60.2 |



Fig. 2. Thermogravimetric analysis of cobalt(II) chloride in molten lithium nitrate–potassium nitrate eutectic with additions of potassium chloride. Curve A, ○, 0.42 m $CoCl_2$; curve B, ×, 0.367 m $CoCl_2$ and 1.83 m KCl; curve C, □, 0.228 m $CoCl_2$ and 2.28 m KCl; curve D, △, 0.277 m $CoCl_2$ and 5.52 m KCl.

When potassium chloride was present in the melt, a very considerable slowing down of the reactions occurred though the products remained the same. The weight losses (Table 1) were somewhat variable, partly because of the difficulty of separating the reaction from that ensuing at higher temperatures, i.e. the thermal decomposition of the melt, but they were broadly in agreement with equation (6). However, the temperatures of maximum rate of weight loss (Table 1 and Fig. 1, curves B–E) increased dramatically by 100–150° depending on the mole ratio of cobalt to chloride.

Cobalt(II) chloride reacted in the nitrate eutectic to form the same products. Analysis of the melt after heating to 500°, showed that no chloride had volatilised [mole ratio initial cobalt(II) chloride to chloride remaining in the melt = 1:1.97].

## TABLE 2

REACTION OF COBALT(II) CHLORIDE IN MOLTEN LITHIUM NITRATE–POTASSIUM NITRATE EUTECTIC WITH ADDITION OF POTASSIUM CHLORIDE

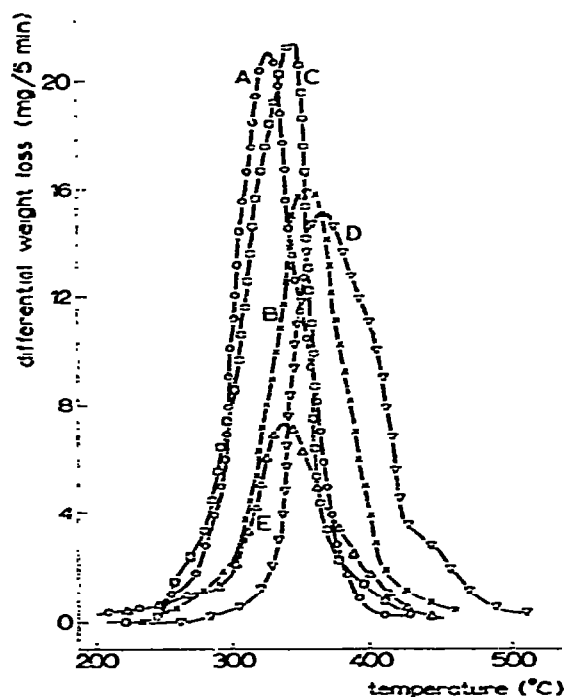| Reactants | | | | $Co:Cl$ ratio | Temperature of maximum rate of weight loss (°C) | Experimental weight loss (%) |
|-----------|---|-----|---|------|------|------|
| $CoCl_2$ | | KCl | | | | |
| mole | m | mole | m | | | |
| $8.47 \times 10^{-4}$ | 0.42 | | | 1:2 | 380 | 80.9 |
| $8.47 \times 10^{-4}$ | 0.367 | $42.3 \times 10^{-4}$ | 1.83 | 1:7 | 490 | 81.7 |
| $8.47 \times 10^{-4}$ | 0.228 | $84.7 \times 10^{-4}$ | 2.28 | 1:12 | 525 | 86.4 |
| $8.47 \times 10^{-4}$ | 0.277 | $169.4 \times 10^{-4}$ | 5.52 | 1:22 | 540 | 89.9 |



Fig. 3. Thermogravimetric analysis of cobalt(II) bromide in molten lithium nitrate–potassium nitrate eutectic with additions of potassium bromide. Curve A, O, 0.274 m CoBr₂; curve B, ×, 0.400 m CoBr₂ and 1.20 m KBr; curve C, □, 0.307 m CoBr₂ and 1.22 m KBr; curve D, △, 0.242 m CoBr₂ and 3.63 m KBr; curve E, △, 0.134 m CoBr₂ and 4.02 m KBr.

The black precipitate was again tricobalt tetraoxide ["$d$" values 2.84(30), 2.43(100), 2.00(25), 1.55(40), 1.43(50)]. The weight loss of 80.9% (Fig. 2, curve A) agreed reasonably with a stoichiometry analogous to equation (6), i.e.

$$3\,CoCl_2 + 7\,NO_3^- \rightarrow Co_3O_4 + NO_2^- + 6\,NO_2 + \tfrac{3}{2}\,O_2 \tag{7}$$
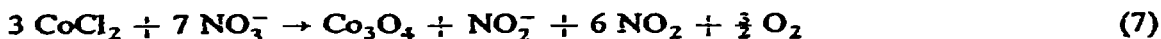
(calc. weight loss 83.0%) as did the weight losses obtained when additional potassium

chloride was present (Table 2). Once again, the temperature of maximum rate of weight loss increased sharply with the cobalt:chloride ratio (Fig. 2, curves B–D).

When cobalt(II) bromide was added to the nitrate eutectic at 200°, the green crystals dissolved again to a blue melt which decomposed only very slowly at this temperature. At 250° reaction was more rapid and at 300° bromide was being evolved as well as nitrogen dioxide mixed with smaller amounts of nitric oxide. The black precipitate was again shown to be tricobalt tetraoxide (found: Co, 72.4%) ["$d$" values 2.88(70), 2.43(100), 2.03(40), 1.56(45), 1.43(60)]. Analysis of the bromide remaining in the melt also demonstrated the loss of bromine [mole ratio of initial cobalt(II) bromide to bromide remaining in melt to liberated bromine = 1 : 0.99 : 0.94] while thermogravimetric analysis (Fig. 3, curve A) showed a total weight loss of 52.9%, close to that indicated by the equation

$$3\,CoBr_2 + 3\,NO_3^- \rightarrow Co_3O_4 + 3\,Br^- + \tfrac{1}{2}\,Br_2 + 2\,NO_2 + NO \qquad (8)$$

(calc. weight loss 55.1%) which may be understood as a Lux–Flood acid–base reaction analogous to equation (6) followed by oxidation of cobalt(II) oxide, i.e.

$$3\,CoBr_2 + 7\,NO_3^- \rightarrow Co_3O_4 + NO_2^- + 6\,NO_2 + \tfrac{1}{2}\,O_2 \qquad (9)$$
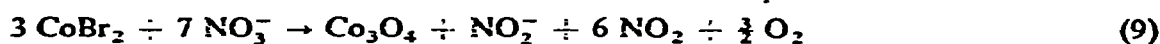
(calc. weight loss 49.3%) accompanied by the already known reactions of the oxidation of bromide ions by nitrogen dioxide[18]

$$Br^- + NO_2 \rightarrow NO_2^- + \tfrac{1}{2}\,Br_2 \qquad (10)$$
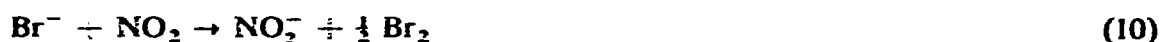
oxidation of nitrite with nitrogen dioxide[19]

$$NO_2^- + NO_2 \rightarrow NO_3^- + NO \qquad (11)$$

and reaction of nitric oxide

$$NO + \tfrac{1}{2}\,O_2 \rightarrow NO_2 \qquad (12)$$

Since there seems no obvious reason why precisely half the bromide should react via

TABLE 3

REACTION OF COBALT(II) BROMIDE IN MOLTEN LITHIUM NITRATE–POTASSIUM NITRATE EUTECTIC WITH ADDITION OF POTASSIUM BROMIDE

| Reactants | | | | Co:Br ratio | Temperature of maximum rate of weight loss (°C) | Experimental weight loss (%) |
|---|---|---|---|---|---|---|
| CoBr | | KBr | | | | |
| mole | m | mole | m | | | |
| 8.48 × 10⁻⁵ | 0.274 | | | 1:2 | 330 | 52.9 |
| 8.48 × 10⁻⁵ | 0.400 | 25.4 × 10⁻⁵ | 1.20 | 1:5 | 350 | 53.5 |
| 8.48 × 10⁻⁵ | 0.307 | 42.3 × 10⁻⁵ | 1.22 | 1:7 | 345 | 55.6 |
| 8.48 × 10⁻⁵ | 0.242 | 127.0 × 10⁻⁵ | 3.63 | 1:17 | 360 | 56.2 |
| 4.24 × 10⁻⁵ | 0.134 | 127.0 × 10⁻⁵ | 4.02 | 1:32 | 335 | 54.0 |

TABLE 4

REACTION OF COBALT(II) BROMIDE IN MOLTEN LITHIUM NITRATE–POTASSIUM NITRATE EUTECTIC WITH ADDITION OF POTASSIUM CHLORIDE

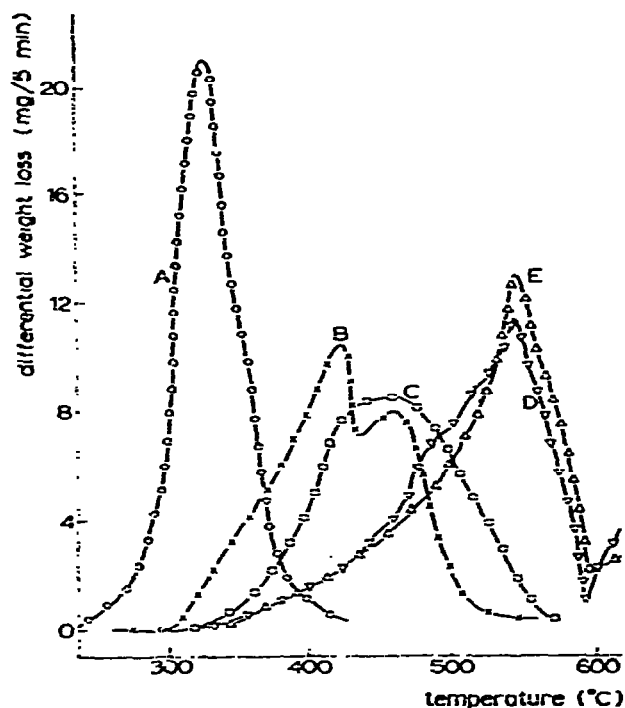| Reactants | | | | $Co:Br$ ratio | Temperature of maximum rate of weight loss (°C) | Experimental weight loss (%) |
|---|---|---|---|---|---|---|
| $CoBr_2$ | | KCl | | | | |
| mol | m | mole | m | | | |
| $8.48 \times 10^{-4}$ | 0.274 | | | 1:0 | 330 | 52.9 |
| $8.48 \times 10^{-4}$ | 0.307 | $25.4 \times 10^{-4}$ | 0.81 | 1:3 | 420 | 50.9 |
| $8.48 \times 10^{-4}$ | 0.236 | $42.3 \times 10^{-4}$ | 1.03 | 1:5 | 450 | 53.2 |
| $8.48 \times 10^{-4}$ | 0.287 | $84.7 \times 10^{-4}$ | 2.25 | 1:10 | 540 | 53.5 |
| $8.48 \times 10^{-4}$ | 0.280 | $127.0 \times 10^{-4}$ | 3.06 | 1:15 | 540 | 55.1 |



Fig. 4. Thermogravimetric analysis of cobalt(II) bromide in molten lithium nitrate–potassium nitrate eutectic with additions of potassium chloride. Curve A, O, 0.274 m $CoBr_2$; curve B, ×, 0.307 m $CoBr_2$ and 0.81 m KCl; curve C, □, 0.234 m $CoBr_2$ and 1.03 m KCl; curve D, △ 0.287 m $CoBr_2$ and 2.25 m KCl; curve E, △, 0.280 m $CoBr_2$ and 3.06 m KCl.

equation (10), the weight loss may be expected to vary both up and down by approximately 3% for each bromide which does not conform to equation (9). When additional potassium bromide was present in the nitrate melt (Table 3), similar reactions occurred though it was noteworthy that the temperature at which the maximum rate of weight loss occurred remained constant (Fig. 3, curves B–E). In contrast, when
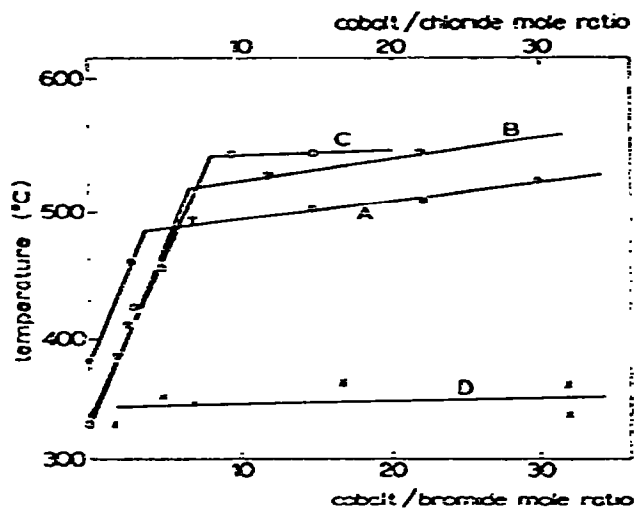
Fig. 5. Stabilisation of cobalt(II) cations by halide anions: temperature of maximum rate of weight loss against cobalt:halide ratio. Curve A, ○, Co(NO₃)₂:KCl; curve B, △, CoCl₂:KCl; curve C, □, CoBr₂:KCl; curve D, ×, CoBr₂:KBr. The top scale refers to curves A–C and the bottom to curve D.

TABLE 5

SPECTRA OF COBALT(II) CHLORIDE IN MOLTEN LITHIUM NITRATE–POTASSIUM NITRATE AT 160°

| Solute concentration (M) | Co:Cl ratio | Absorption maximum (nm) | Molar extinction coefficient (l mole⁻¹ cm⁻¹) | Ref. |
|---|---|---|---|---|
| 0.00229 | 1:2 | 554 | 73 ± 8 | 14 |
| 0.0566 | 1:2 | 588 | 122 ± 5 | 14 |
| 0.187 | 1:2 | 617 | 146 ± 10 | 14 |
|  |  | 676 | (Shoulder) |  |
| 0.0115 | 1:0 | 560 | 80 | 5 |
| 0.00501 | 1:16 | 590 | 125 | 5 |
| 0.00864 | 1:24 | 630 | 180 | 5 |
|  |  | 680 | (Shoulder) |  |

additional potassium chloride was present (Table 4), a considerable increase in the temperature of this maximum was observed (Fig. 4, curves A–E). The weight losses obtained were in close conformity with equation (9).

The increase in temperature of maximum rate of weight loss with the cobalt to chloride is evidently to be attributed to formation of chloro complexes of an increased stability towards Lux–Flood acid–base reactions as has been previously observed with transition metal cations[9–11]. Plotting this ratio against temperature (Fig. 5) indicates little change beyond the 1:10 value suggesting that at this point complete substitution to form the most highly coordinated complex (in this case tetrachloro) has occurred. The ratio is, of course, much less than the 1:1213 reported from the spectroscopic

studies[5] for the highest cobalt to chloride ratio in nitrate (though actually for $NH_4Cl$ in $LiNO_3/NH_4NO_3$). However, to a first approximation, conversion of say 90% of the cobalt(II) to the tetrachloro complex is proportional to the absolute concentration of chloride and not to the ratio. In this case complete conversion, i.e. as shown by a roughly constant temperature for maximum rate of loss, occurs close to 2 m chloride for curves A, B, and C of Fig. 5 compared with 5.7 m in the spectroscopic studies using a different melt at a lower temperature. The relatively small differences between curves A, B and C follow the same pattern, the constant temperature for maximum rate of loss being lower with lower cobalt concentrations (i.e. A < B < C) and occurring at lower chloride concentrations. A similar dependence of chloro complex formation on the absolute value of the chloride concentration was also found in the course of spectroscopic measurements[14]. A decided red shift of the $d–d$ absorption band, accompanied by an increasing extinction coefficient and incipient fine structure, was obtained as the concentration of cobalt(II) chloride increased (Table 5) and which were strikingly similar to the results of Gruen et al.[5] who used more dilute cobalt solutions but roughly comparable concentrations of chloride.

The evidence against effective thermal stabilisation of cobalt(II) by the bromide anion, probably because of much lower stability constants for such complexes, is also clearly seen in Fig. 5 (compare curve B with curve D). Also noteworthy is the much broader maximum of the weight loss curves, particularly at lower ratios when potassium chloride stabilised cobalt(II) bromide solutions (Fig. 4) than when only chloride or bromide anions were present. This may be understood by envisaging a range of chloro-bromo complexes which would, of course, have a wider spread of thermal stabilities, since the presence of some chloride ligands might well increase coordination by the usually reluctant bromide (cf. Fig. 3).

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