Spectroscopy and Reactions of Copper(II), Nickel(II), and Cobalt(III) Compounds in Molten Nitrites

By **Sabah S. Al Omer** and **David H. Kerridge,*** Department of Chemistry, The University, Southampton SO9 5NH

Copper(II) sulphate and nickel(II) chloride formed green solutions in lithium nitrite–potassium nitrite eutectic at 120 °C. The electronic-absorption bands indicate bonding by both nitro- and nitrito-ligands $\{[Cu(NO_2)_4(ONO)_2]^{4-}$ and $[Ni(NO_2)_3(ONO)_3]^{4-}\}$. The i.r. bands of the solidified melt also indicate both forms of nitrite ligand. At higher temperatures the cations are precipitated as the oxides by Lux–Flood acid-base reactions with the melt. Cobalt(III) $\{$as $Na_3[Co(NO_2)_6]$ or $[Co(NH_3)_6]Cl_3\}$ is not soluble, but decomposes ultimately to form the oxide Co_3O_4 *via* a series of reactions which include thermal decomposition, acid-base, cation exchange, and formation of the more stable complex $K_3[Co(NO_2)_6]$. The last reaction is facilitated by the presence of lower-melting nitrite eutectics.

THE chemistry of molten alkali-metal nitrites has been much less explored than that of corresponding nitrates as is shown even for the usually better known first-row transition-metal compounds, where very few studies have been carried out. For example, for copper there is only a brief report of the oxidation of CuS_2 in sodium nitrite at 400 °C,[1] while for nickel and cobalt the dichlorides have been found to react at or below the melting point of the sodium nitrite–potassium nitrite eutectic (220 °C) to give the thermodynamically most stable oxides (NiO and Co_3O_4).[2] Metallic nickel has been anodically oxidised largely to the oxide but some nickel(II) cations (<10%) were also reported to be formed in the same eutectic at 230—300 °C.[3] In contrast, cobalt in $Na[NO_2]$ at 300 °C was found in two investigations to give a dark red melt, although on eventual addition of water Bartlett and Johnson[4] reported a cobalt(III) solution while Temple and Thickett[5] found a precipitate of cobalt(II) oxide. The latter workers also reported the unexpected finding that addition of sodium peroxide to the melt produced a deep blue colour which was attributed to cobaltate(V).[5]

In those cases where a direct comparison can be made it is apparent that transition-metal oxides are formed at much lower temperatures in molten nitrites than in molten nitrates. This increase in Lux–Flood basicity may be correlated with the more ready ionisation (1),

$$[NO_2]^- \rightleftharpoons [NO]^+ + O^{2-} \qquad (1)$$

---

[1] S. A. Tariq, *Chem. and Ind.*, 1972, 122.

[2] D. H. Kerridge and S. A. Tariq, *Inorg. Chim. Acta*, 1970, **4**, 499.

[3] A. J. Arvia, R. C. V. Piatti, and J. J. Podesta, *Electrochim. Acta*, 1972, **17**, 889.

[4] H. E. Bartlett and K. E. Johnson, *J. Electrochem. Soc.*, 1967, **114**, 64.

[5] R. B. Temple and G. Thickett, *Austral. J. Chem.*, 1973, **26**, 1137.

found by Kust and Burke[6] to have the comparatively large self-ionisation constant of 1.3×10^{-9} as compared to 10^{-19} mol dm^{-3} for Na[NO$_3$]-K[NO$_3$] at 300 °C. Thus the possibility of obtaining stable molten nitrite solutions of transition-metal cations ought to be larger at lower temperatures, suggesting the desirability of using lower melting eutectics.

In this paper, investigations using lithium nitrite–potassium nitrite (40.7 : 59.3 mol %, m.p. 104 °C) and sodium nitrite–potassium nitrite–barium nitrite eutectics (36.4 : 42.4 : 21.2 mol %, m.p. 102 °C) are reported as well as some comparative measurements with sodium nitrite–potassium nitrite. These have enabled the first electronic *d–d* spectra ever reported in molten nitrites to be obtained, as well as the elucidation of a somewhat complex series of reactions undergone by cobalt(III) complexes.

EXPERIMENTAL

Materials.—Lithium nitrite was prepared from equimolar quantities of potassium nitrite and lithium sulphate (Hopkins and Williams, G.P.R.). After filtration and evaporation of the aqueous solution to dryness, the lithium nitrite was extracted with absolute ethanol. After evaporation of the solvent, the monohydrate was dehydrated *in vacuo* for 16 h at increasing temperatures up to 110 °C (Found: Li, 12.8; [NO$_2$]$^-$, 81.2. Calc. for Li[NO$_2$]: Li, 13.2; [NO$_2$]$^-$, 86.7%). AnalaR sodium nitrite (B.D.H.) and reagent-grade potassium nitrite and barium nitrite were dried at 130 °C for 30 h. The salts were mixed in the eutectic proportions,[7,8] melted, and filtered through a no. 4 sinter. Before use the melt was further dehydrated *in vacuo* ($<10^{-2}$ Torr) * for 20 h.

AnalaR nickel(II) chloride and cobalt(II) chloride (B.D.H.) were dehydrated with thionyl chloride[9] (Found: Cl, 54.1; Ni, 44.8. Calc. for NiCl$_2$: Cl, 54.7; Ni, 46.3. Found: Co, 45.3. Calc. for CoCl$_2$: Co, 45.4%). AnalaR copper(II) sulphate (B.D.H.) was dehydrated at 200 °C for 3 h (Found: Cu, 39.3; SO$_4$, 59.7. Calc. for Cu[SO$_4$]: Cu, 39.8; SO$_4$, 60.2%). AnalaR sodium hexanitrocobaltate(III) and hexa-amminecobalt(III) chloride (B.D.H.) were dried at 110 °C for 2 h.

Procedure.—Reactions were observed in Pyrex tubes fitted with B.24 sockets, closed with silica-gel guard tubes, and heated in a resistance furnace connected to an Ether Transitol controller. Anions and cations were detected qualitatively and estimated quantitatively by standard gravimetric and volumetric methods: nitrite with permanganate, nitrate in the presence of excess of nitrite by Leithe's method,[10] chloride as silver chloride, sulphate as barium sulphate, copper as the thiocyanate, nickel with dimethylglyoxime, and cobalt with ethylenediaminetetra-acetate (edta) and colorimetrically. *X*-Ray diffraction was carried out with a Phillips (Eindhoven) diffractometer using nickel-filtered Cu-K_α radiation. Gas samples collected *in vacuo* were analysed by mass spectroscopy, using an A.E.I. MS12 instrument and by i.r. spectroscopy using a Unicam 200G spectrometer equipped with a 10-cm cell with silicon windows. Nujol mulls were examined on the same instrument.

Electronic spectra of melts were obtained in 1-mm quartz cells using a Unicam SP 700 spectrometer with resistance heating and reversed optics for high-temperature use, and the reflectance spectra with a Unicam SP 800 spectrometer. Thermogravimetric analysis (t.g.a.) was carried out in silica crucibles (10 cm^3) on a Stanton TR-1 thermobalance modified for use with air or purified nitrogen atmospheres at a heating rate of 2° min^{-1}. Weight losses are reported as a weight percentage of the solute.

RESULTS AND DISCUSSION

Copper(II) sulphate dissolved in lithium nitrite–potassium nitrite eutectic at 120 °C to form a green solution. A small amount of reaction occurred forming black particles. The latter, after dissolution of the quenched melt in water, filtering, and drying, gave the *X*-ray diffraction lines of copper(II) oxide. A more rapid reaction began at 185 °C with liberation of nitrogen dioxide and nitrogen monoxide which was shown by t.g.a. to have a maximum rate of gas evolution at 210 °C [Figure 1 (*a*)] and again copper(II) oxide was precipitated. The total experimental weight loss was 41.3% which after correcting for some reaction of NO$_2$ to form nitrate, *i.e.* as in (2), gave a weight loss of

$$\mathrm{NO_2} + [\mathrm{NO_2}]^- \longrightarrow \mathrm{NO} + [\mathrm{NO_3}]^- \qquad (2)$$

$$\mathrm{Cu[SO_4]} + 2[\mathrm{NO_2}]^- \longrightarrow \mathrm{CuO} + [\mathrm{SO_4}]^{2-} + \mathrm{NO_2} + \mathrm{NO} \qquad (3)$$

44.1% corresponding to the stoicheiometry (3) (calc. weight loss of 2N + 3 O per Cu[SO$_4$] : 44.7%).

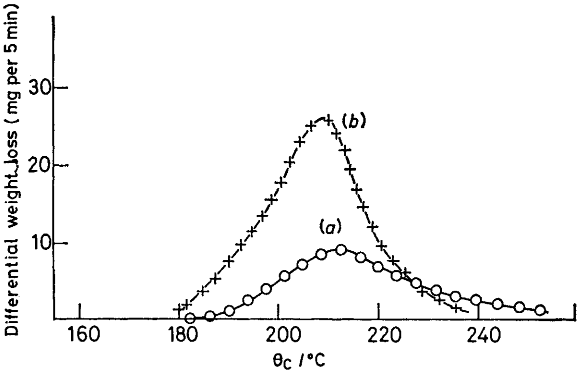

FIGURE 1 Thermogravimetric analysis in sodium nitrite–potassium nitrite eutectic: (*a*) 0.49 mol kg^{-1} NiCl$_2$; (*b*) 0.24 mol kg^{-1} Cu[SO$_4$]

After filtration the green melt was stable for some hours at 120 °C and showed two electronic-absorption bands, one at 24 500 cm^{-1} (ε 860 dm^3 mol^{-1} cm^{-1}) and a very broad band centred at 14 400 cm^{-1} (ε 107 dm^3 mol^{-1} cm^{-1}), Figure 2 (*a*). A Nujol mull of the solidified and powdered melt showed i.r. absorption bands at 1 380 and 1 350 with a shoulder at 1 208 cm^{-1} if main-

---

* Throughout this paper: 1 Torr = (101 325/760) Pa.

[6] R. N. Kust and J. D. Burke, *Inorg. Nuclear Chem. Letters*, 1970, **6**, 333.

[7] P. I. Protshenko and O. N. Shukina, *Zhur. neorg. Khim.*, 1959, **4**, 1178.

[8] P. I. Protshenko and G. S. Zhilina, *Izvest. Vysshikh. Uchebn. Zavedini khim. Tekhnol.*, 1967, **10**, 377.

[9] J. Freeman and M. L. Smith, *J. Inorg. Nuclear Chem.*, 1958, **7**, 224.

[10] W. Leithe, *Electrochim. Acta*, 1960, 762.

tained anhydrous, but if the powdered melt had been exposed to water vapour bands at 1 350 and 1 325 cm^{-1} were obtained. The last two bands may be attributed to nitro-groups and the absorptions at 1 380 and 1 208 cm^{-1} to nitrito-groups.[11]

The presence of both types of bonding in the melt may also be deduced from the position of the lower-energy electronic-absorption band which arises from *d*–*d* transitions. This lay between the energy calculated for a hexanitro-complex (15 850 cm^{-1}) and that for a hexanitrito-complex (10 450 cm^{-1}, using Jørgensen's rule that the octahedral field splitting is the product of a ligand and a cation function whose values are approximately constant and may be derived from other complexes of known structure [12]). Further, calculation using Jørgensen's rule of average environment suggested that the band at 14 400 cm^{-1} could be attributed to four nitro- and two nitrito-ligands. The unusually large molar absorption coefficient for an octahedral complex may have arisen partly from the non-equivalence of the ligands and partly from the Jahn–Teller effect.[13] The highest-energy band is assigned to a charge-transfer transition.

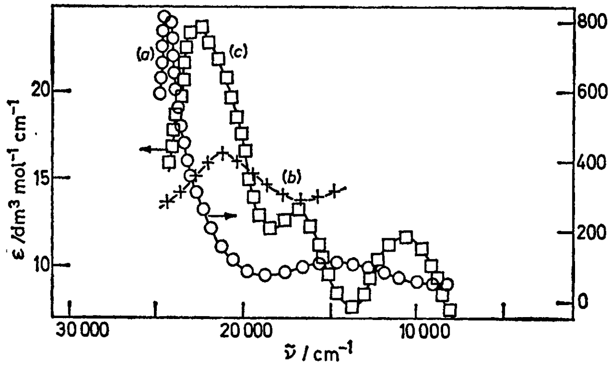

FIGURE 2 Electronic spectra in lithium nitrite–potassium nitrite eutectic: (*a*) Cu[SO$_4$]; (*b*) reflectance spectrum of NiCl$_2$ (ordinate is arbitrary optical-density scale); and (*c*) NiCl$_2$

Nickel(II) chloride dissolved only slowly in the nitrite eutectic at 120 °C but within 3 h a green solution had formed together with a few black particles. After filtration the green melt was stable for 24 h but then slowly formed a black precipitate shown to be nickel(II) oxide by *X*-ray diffraction. The black particles initially formed were also nickel(II) oxide and, as also in the case of copper(II) sulphate, were considered to be produced by the oxide impurity present in the original melt. Thermogravimetric analysis showed the reaction to reach a measurable rate of weight loss at 180 °C [Figure 1 (*b*)] with a maximum rate at 210 °C. The total experimental weight loss averaged 51.4% but on correction for nitrate formation [equation (2)] became 57.9% corresponding to equation (4) (calc. weight loss: 58.6%).

On solidification the colour of the nickel(II) solution changed to orange-red, the reflectance spectrum [Figure 2 (*b*)] showing only one absorption band at 20 500 cm^{-1}

$$\mathrm{NiCl_2} + 2[\mathrm{NO_2}]^- \longrightarrow \mathrm{NiO} + 2\mathrm{Cl}^- + \mathrm{NO_2} + \mathrm{NO} \qquad (4)$$

close to the higher-energy reflectance bands found by Goodgame and Hitchman [11] {20 700 cm^{-1} for the orange-brown K$_4$[Ni(NO$_2$)$_6$]·H$_2$O and 19 200 cm^{-1} for red K$_4$[Ni(NO$_2$)$_4$(ONO)$_2$]}. Infrared spectroscopy on the solidified powdered anhydrous melt gave bands in the nitrite-stretching region at 1 386, 1 350, 1 325, and 1 208 cm^{-1}, while the powdered melt which had been allowed to absorb water showed absorption bands only at 1 350 and 1 325 cm^{-1}. These absorptions were again close to those found previously for the potassium salts,[11] where the hydrate {K$_4$[Ni(NO$_2$)$_6$]·H$_2$O, bands at 1 346 and 1 318 cm^{-1}} was shown to contain nitro-groups only but the anhydrous complex gave four bands {K$_4$[Ni(NO$_2$)$_4$(ONO)$_2$], 1 387, 1 347, 1 325, and 1 216 cm^{-1}} indicating the presence of both nitro- and nitrito-ligands. Some small shifts may be attributed to the presence of lithium cations as well as potassium.

The green melt solution had three electronic-absorption bands [Figure 2 (*c*)]. Their relatively low molar absorption coefficients indicated octahedral co-ordination although the Dq value of 1 080 cm^{-1} was much less than that found for six nitro-ligands {*cf.* 1 340 cm^{-1} for K$_4$[Ba(NO$_2$)$_6$], or 1 320 for K$_4$[Ni(NO$_2$)$_6$]·H$_2$O} but more than that calculated using Jørgensen's equation for six nitrito-ligands (*i.e.* 820 cm^{-1}). Using the average-environment rule, the absorption was close to that expected for three nitro- and three nitrito-ligands. The Dq value was close to that found for six ammonia ligands (bands at 10 750, 17 500, and 28 200 cm^{-1}) and the three absorptions in the melt should probably be assigned to the same transitions, *i.e.* $^3A_{2g}\rightarrow{}^2T_{2g}$, $^3A_{2g}\rightarrow{}^3T_{1g}(F)$, and $^3A_{2g}\rightarrow{}^3T_{1g}(P)$ respectively. In the case of the solidified melt the one observed band is attributed to the second of these transitions (both the higher- and lower-energy transitions would fall outside the range of the reflectance spectrometer). The blue shift suggested that one, or possibly two, nitrito-ligands isomerise to the nitro-form, probably from steric considerations of accommodation in the eutectic structure. However, the considerable red shift of the highest-energy band of the melt is likely to be due to an instrumental effect arising from the very strong charge-transfer band of nitrite at 27 100 cm^{-1} as was previously found for chromate.[14] The somewhat asymmetric shape of the band supported this hypothesis. Similar considerations also apply to the higher-energy band of the copper(II) solution [Figure 2 (*a*)].

Sodium hexanitrocobaltate(III) did not dissolve in sodium nitrite–potassium nitrite eutectic at 230 °C although it could form red-brown suspensions. It reacted within 5 min producing a black precipitate and a brown gas, which was shown to be a mixture of NO$_2$

---

[11] D. M. L. Goodgame and M. A. Hitchman, *Inorg. Chem.*, 1967, **6**, 813.

[12] C. K. Jørgensen, 'Absorption Spectra and Chemical Bonding in Complexes,' Pergamon, Oxford, 1962.

[13] H. Elliott, B. J. Hathaway, and R. C. Slade, *Inorg. Chem.*, 1966, **5**, 669.

[14] D. H. Kerridge and S. A. Tariq, *Inorg. Chim. Acta*, 1969, **3**, 667.

and NO by i.r. spectroscopy. The precipitate was shown by analysis to be the thermodynamically most stable cobalt oxide (Found: Co, 73.5. Calc. for Co_3O_4: Co, 73.4%) and confirmed by *X*-ray diffraction. The overall reaction may be represented by (5). Attempts to obtain cobalt(III) solutions were never successful. For example, in acidic melts, to which $K_2[S_2O_7]$ had been added the reaction produced the same products. Nor did solution occur in lower melting eutectics ($Li[NO_2]$–$K[NO_3]$ and $Na[NO_2]$–$K[NO_2]$–$Ba[NO_2]_2$) either pure or containing disulphate, although on increasing the temperature to 220 °C reaction began, forming brown gas and a black precipitate of Co_3O_4. However, prolonged contact (*e.g.* 1—2 h) at 220 °C with the just molten sodium nitrite–potassium nitrite eutectic resulted in the formation of a greenish yellow solid, insoluble both in the melt and in water, which was identified as $K_3[Co(NO_2)_6]$.

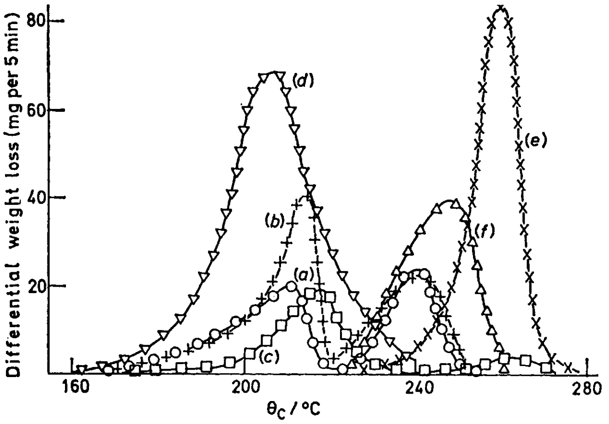

FIGURE 3 Thermogravimetric analysis of $Na_3[Co(NO_2)_6]$ in various nitrite eutectics: (*a*) 0.32 mol kg^{-1}, in $Na[NO_2]$–$K[NO_2]$ (m.p. 220 °C); (*b*) 0.51 mol kg^{-1} as in (*a*); (*c*) 0.72 mol kg^{-1} in $Na[NO_2]$–$K[NO_2]$ (m.p. 240 °C); (*d*) $Na_3[Co(NO_2)_6]$ alone (1.1 g); (*e*) 0.25 mol kg^{-1} in $Na[NO_2]$–$K[NO_2]$–$Ba[NO_2]_2$; (*f*) 0.11 mol kg^{-1} in $Li[NO_2]$–$K[NO_2]$

$$3Na_3[Co(NO_2)_6] \longrightarrow Co_3O_4 + 9Na[NO_2] + 5NO_2 + 4NO \quad (5)$$

Thermogravimetric analysis of $Na_3[Co(NO_2)_6]$ in sodium nitrite–potassium nitrite eutectic showed the presence of two reactions [Figure 3(*a*) and (*b*)], the total weight loss varying between 21.5 and 24.2%, but after correction for the formation of nitrate [equation (2)] the average loss was 28.7%, in agreement with equation (5) {Calc. for loss of 3 N + $4\frac{2}{3}$ O per $Na_3[Co(NO_2)_6]$: 28.9%}. However, the amount of decomposition occurring in each stage was found to be dependent on the melting point and thus on the composition of the melt used. For example, the second weight loss was 4.1% with the sodium nitrite–potassium nitrite eutectic (m.p. 220 °C), but when the melting point had been increased to 240 °C by addition of sodium nitrite the second-stage weight loss was only 1.5% [Figure 3 (*c*)]. In contrast, the first stage of weight loss was always closely similar to the thermal decomposition of $Na_3[Co(NO_2)_6]$ without melt [Figure 3 (*d*)]. The weight loss of the latter was 18.3—22.1% in accordance with a reaction lying between the limiting stoicheiometries previously reported,[15] *i.e.* equation (5) (Calc. weight loss: 28.9%) and (6) (Calc. weight loss: 17.0%).

$$3Na_3[Co(NO_2)_6] \longrightarrow Co_3O_4 + 9Na[NO_3] + 5NO + 2N_2 \quad (6)$$

It followed that if the first weight loss was ascribed to this thermal decomposition and the overall reaction to equation (5) then the second phase of weight loss must be a closely similar reaction. In fact, the latter could be understood as the formation of the more stable $K_3[Co(NO_2)_6]$ and its subsequent thermal decomposition, since the decomposition temperature for the potassium compound had already been reported as higher than that for the sodium compound [15] (210—290 as opposed to 170—210 °C). Thus the diminishing weight loss for the second-stage reaction may be explained as the extent to which the exchange of alkali-metal cations had proceeded between the liquid melt and the compound. In confirmation, when other nitrite melts of lower melting point were used, complete cation exchange was possible before the decomposition temperature of the sodium compound was reached, and only one weight loss was observed although at the higher-temperature characteristics of the potassium compound. For example, in sodium nitrite–potassium nitrite–barium nitrite (m.p. 170 °C) decomposition began at 225 °C with a maximum rate at 260 °C [Figure 3 (*e*)] with a weight loss varying between 23.5 and 26.5%, averaging 30.1% after correction for nitrate formation; while in lithium nitrite–potassium nitrite eutectic (m.p. 110 °C) weight loss began at 225 °C with a maximum at 250 °C [Figure 3 (*f*)] with losses between 24.2 and 29.7% which averaged 29.9% after correction for nitrite formations. Thus the overall reaction was again in accordance with equation (5).

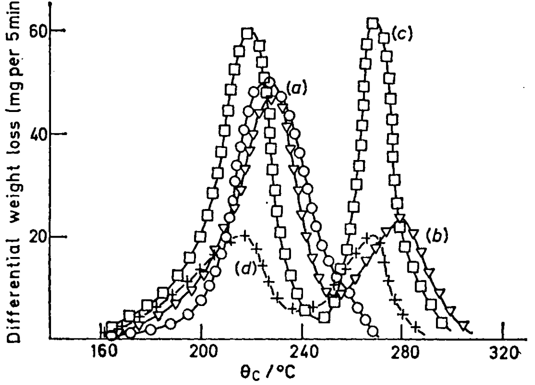

FIGURE 4 Thermogravimetric analysis of $[Co(NH_3)_6]Cl$, in nitrite eutectics: (*a*) 0.25 mol kg^{-1} in $Na[NO_2]$–$K[NO_2]$; (*b*) $[Co(NH_3)_6]Cl_3$ alone (0.45 g); (*c*) 0.43 mol kg^{-1} in $Na[NO_2]$–$K[NO_2]$–$Ba[NO_2]_2$; and (*d*) 0.34 mol kg^{-1} in $Li[NO_2]$–$K[NO_2]$

Hexa-amminecobalt(III) chloride reacted immediately with the sodium nitrite–potassium nitrite eutectic at

---

[15] M. B. Davies and J. W. Lethbridge, *J. Inorg. Nuclear Chem.*, 1972, **34**, 2171.

230 °C with evolution of a brown gas mixture of NO_2 and NO and precipitation of black Co_3O_4, confirmed by *X*-ray diffraction. Thermogravimetry showed only a one-stage weight loss [Figure 4 (*a*)] commencing at 170 °C, below the melting point, when blue particles were observed to form. The reaction became more rapid on melting, reached a maximum rate at *ca.* 230 °C, and was complete by 270 °C. The overall weight loss originally near 74.9 became 77.6% after correction for formation of nitrate in accordance with the stoicheiometry (7)

$$3[Co(NH_3)_6]Cl_3 + 6[NO_2]^- \longrightarrow Co_3O_4 + 6Cl^- + 3[NH_4]Cl\uparrow + 14NH_3\uparrow + NO_2\uparrow + 6NO\uparrow \quad (7)$$

(Calc. weight loss: 77.8%). This unexpectedly complicated representation is probably the result of a series of reactions. In the first place the compound is known to decompose thermally. This was found to occur in two stages [Figure 4 (*b*)], the final solid product being cobalt(II) chloride by analysis (Found: Co, 45.2. Calc. for $CoCl_2$: Co, 45.4%) and i.r. spectroscopy. The overall weight loss averaged 50.4% in agreement with the stoicheiometry (8) suggested by Wendlandt.[16] (Calc. weight loss: 51.4%).

$$6[Co(NH_3)_6]Cl_3 \longrightarrow 6CoCl_2 + 6[NH_4]Cl + 28NH_3 + N_2 \quad (8)$$

It was not possible to identify the intermediate solid product, nor was one suggested by the earlier worker.[16] The second reaction postulated is the Lux–Flood acid-base reaction, accompanied by oxidation, found earlier in sodium nitrite–potassium nitrite, at a temperature largely above the melting point of the eutectic,[17] *i.e.* (9)

$$3CoCl_2 + 6[NO_2]^- \longrightarrow Co_3O_4 + 6Cl^- + 2NO_2 + 4NO \quad (9)$$

(Calc. weight loss: 54.4%), while any undecomposed compound may also have reacted directly with the nitrite melt. It was considered that these reactions overlapped sufficiently that only one maximum was observed [Figure 4 (*a*)].

In the nitrite eutectics of lower melting point, in contrast, the $[Co(NH_3)_6]Cl_3$ showed two distinct stages of decomposition in the thermogram [Figure 4 (*c*) and (*d*)]. In both melts, if the temperature was held constant at 220 °C (*i.e.* before the second weight loss had begun), a yellow-green precipitate, insoluble in water, was produced. This solid contained potassium and cobalt and had the *X*-ray diffraction lines of $K_3[Co(NO_2)_6]$. The higher-temperature weight loss was attributed to decomposition of this compound [*i.e.* as in equation (5)]. The overall weight losses of 70.8—71.1, corrected to 78.2% (for the $Na[NO_2]$–$K[NO_2]$–$Ba[NO_2]_2$ melt), and 74.4, corrected to 78.4% (for the $Li[NO_2]$–$K[NO_2]$ melt), were close to the calculated value for equation (7). In both cases the final black product was confirmed to be Co_3O_4 by *X*-ray diffraction.

Finally, addition of cobalt(II) chloride to lithium nitrite–potassium nitrite at 120 °C produced insoluble yellow-green solid $K_3[Co(NO_2)_6]$, probably by a reaction such as (10), although the additional products were not identified.

$$CoCl_2 + 7K[NO_2] \longrightarrow K_3[Co(NO_2)_6] + 2KCl + K_2O + NO \quad (10)$$

The lower-temperature reaction in the lower-temperature nitrite melts [Figure 4 (*c*) and (*d*)] may therefore be understood as thermal decomposition of $[Co(NH_3)_6]Cl_3$ [equation (8)] followed by the formation of $K_3[Co(NO_2)_6]$ [equation (10)]. The overall weight losses were consistent with these two reactions, followed by reaction (5), provided that the potassium oxide of equation (10) reformed nitrite by reaction with acidic nitrogen oxides and the nitrogen eventually produced in reaction (8) reacted at an earlier stage as a nitrogen oxide.

We thank the Iraqi Ministry of Industry for the award of a maintenance grant (to S. S. Al O.).

[8/174 *Received*, 1st *February*, 1978]

---

[16] W. W. Wendlandt, *Texas J. Sci.*, 1958, **10**, 392.

[17] D. H. Kerridge and S. A. Tariq, *Inorg. Chim. Acta*, 1970, **4**, 499.