Molten Lithium Carbonate–Sodium Carbonate–Potassium Carbonate Eutectic: Electronic Spectroscopy of First-row Transition Metal Compounds

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Stable solutions containing chromate(VI), cobalt(II), nickel(II), and copper(II) have been obtained at 420 °C in a molten lithium carbonate–sodium carbonate–potassium carbonate eutectic. Electronic spectroscopy has demonstrated the existence of the tetrahedral chromate(VI) in the melt while nickel(II) and copper(II) exhibited six-fold co-ordination by oxygen, the nickel(II) species appearing to change to a more symmetrical octahedral co-ordination on solidification. The cobalt(II) geometry can be interpreted as octahedral or dodecahedral. While chromate(VI) dissolved readily in the melt without apparent decomposition, attempts to prepare more concentrated solutions (>0.01 mol kg^{-1}) of the acidic cobalt(II), nickel(II), or copper(II) cations resulted in the precipitation of the respective metal oxide due to acid–base reactions with the carbonate ion.

In recent years considerable effort has been expended in attempts to develop a molten carbonate fuel cell, allowing the direct production of electricity from carbonaceous fuels with high efficiency. Such cells frequently contain transition and rare-earth metal additives and components; as an example, one recent paper described cells with a nickel oxide cathode and nickel–chromium anode.[1] However, little is known about interactions of the melt with such materials, although in recent years systematic studies have been carried out on the reactions of the acidic oxides of the main group and early transition and lanthanide elements with the ternary eutectic melt,[2–5] and of the less acidic cations of the later first-row transition elements.[6,7]

The surprising fact that first-row transition metal compounds generally can form stable coloured solutions in a molten ternary carbonate eutectic has however not been apparent from the literature, as until now the only reference has been to nickel(II) solutions.[6] Indeed until now it was generally presumed that transition metal cations would be too acidic to have more than a transitory existence in the highly basic carbonate melt.

The stability of such solutions immediately suggests a study of their electronic spectra and the first results from this are now reported here.

Experimental

Materials.—The ternary carbonate eutectic was prepared by drying the individual carbonates (BDH, AnalaR) at 200 °C for 12 h, mixing in the appropriate quantities (Li_2CO_3–Na_2CO_3–K_2CO_3 eutectic, 43.5:31.5:25.0 mol%, m.p. 397 °C) and heating in a platinum crucible at 500 °C under flowing oxygen (500 cm^3 min^{-1}) for 2 h and then carbon dioxide (500 cm^3 min^{-1}) for 2 h. The melt was allowed to cool to room temperature under carbon dioxide, broken up and stored in the dry-box until required. The BDH AnalaR reagents (K_2CrO_4, $CoCl_2$, $NiCl_2 \cdot 6H_2O$) and those of reagent grade ($CuSO_4 \cdot 5H_2O$, Na_2SO_3, KCl) were dehydrated as described by Duval.[8]

Procedure.—The thermogravimetric analyses were carried out on a Stanton TR-1 thermobalance using cylindrical recrystallised alumina crucibles (Thermal Syndicate) with a heating rate of 2 °C min^{-1}. The weight losses reported are the average of three determinations and given as a percentage of the weight of the specified reactant.

The melt transmission spectra were obtained on a Unicam SP700 spectrometer with reversed optics in the i.r. range. The melt solutions were contained in square Pyrex cells, of nominal pathlength 9 mm, for <30 min and, for comparison, in a novel design of windowless cell (of nominal pathlength 10 mm) fabricated in pure gold for greater corrosion resistance,[9] both types of cell being placed in stainless-steel susceptors heated by a Redifon type 1H24B RF generator. The cell compartment was maintained under an atmosphere of carbon dioxide dried over silica gel. Similar results were obtained with both types of cell, indicating negligible corrosion effects at the exposure times involved in these measurements, although the gold cell only produces semi-quantitative data because the curvature of the transmitting melt/air interfaces produces a varying pathlength. Reflectance spectra were obtained using a Unicam SP735 diffuse reflectance attachment on the SP700 spectrometer.

X-Ray powder diffraction was carried out with a Phillips diffractometer employing nickel-filtered Cu-K_α radiation. The experimental 2θ values were converted into d spacings (Å) which were matched, together with the corresponding relative intensities, with values listed for that compound in the JCPDS Index, or other quoted reference.

Results and Discussion

Potassium tetraoxochromate(VI) dissolved readily in the eutectic at 415 °C, forming clear yellow dilute solutions, which became orange at higher concentrations.

The spectra of dilute solutions (*ca.* 10^{-3} mol kg^{-1}) showed only one broad band below 30 000 cm^{-1}, at 26 500 cm^{-1} ($\varepsilon = 2\,750 \pm 250$ dm^3 mol^{-1} cm^{-1}), while the reflectance spectra of a more concentrated solidified solution (0.02 mol kg^{-1}) gave indications of an additional band at *ca.* 37 000 cm^{-1}.

These results are consistent with the presence of the tetrahedral $[CrO_4]^{2-}$ in the melt, and in the cooled solid, the band positions and extinction coefficients being similar to those obtained in other molten media, *e.g.* sulphate, nitrate, and chloride.[10–12]

It may be noted that thermogravimetric analysis carried out previously in this laboratory[3] has shown that the only stable melt species is $[CrO_4]^{2-}$, the more condensed chromium(VI) anions being quantitatively depolymerised below the eutectic melting point, *e.g.* equation (1). The bands at 26 500 and 37 000

$$[Cr_nO_{3n+1}]^{2-} + (n-1)CO_3^{\,2-} \longrightarrow n[CrO_4]^{2-} + (n-1)CO_2 \quad (1)$$

cm^{-1} may therefore be assigned respectively to the $t_2 \longrightarrow {}^2e$ and $t_1 \longrightarrow {}^4t_2$ charge-transfer transitions of the tetrahedral oxoanion.[13,14]

Attempts to prepare soluble chromium(III) species by reduction of the chromate(VI) solutions with sodium sulphite resulted in the quantitative precipitation of chromium as a lithium-containing grey-green solid, suggested to be lithium chromate(III) ($LiCrO_2$) by *X*-ray powder diffraction: *d* spacings 4.80s, 2.47m, 2.05s, 1.53s, and 1.45m (the lines were broad and weak, probably indicating some lack of crystallinity; s = strongest lines, m = lines of medium intensity), as compared with 4.80 (100), 2.48 (28), 2.06 (48), 1.59 (12), and 1.47 (15) (relative size of lines given in parentheses) given by Niki and Laitinen.[15] The insolubility of chromium(III) is probably a consequence of the relatively high acidity of this cation, which would thus be expected to react with the carbonate melt, with the evolution of carbon dioxide.

Cobalt(II) chloride reacted with the eutectic at 420 °C forming a stable clear lilac solution if only small quantities were used (equivalent to *ca.* 10^{-2} mol kg^{-1} solutions), but with larger quantities a black precipitate was formed in addition to the solution with little evidence of gas evolution.

X-Ray diffraction showed that the black precipitate appeared to be a mixture of CoO, possibly together with some Co_3O_4, the *d* spacings being 2.45 (100), 2.12 (100), 1.50 (50), and 1.42 (25), as compared with 2.46 (75), 2.13 (100), and 1.51 (50) (JCPDS index for CoO[16]), and 2.86 (45), 2.44 (100), and 1.42 (45) (JCPDS index for Co_3O_4[16]).

It has been reported[6] that the solid product when cobalt(II) chloride is heated up to 600 °C with the eutectic is tricobalt tetraoxide, equation (2). However the simpler Lux–Flood acid–base[17] reaction (3) presumably took place at lower temperatures,

$$3CoCl_2 + 3CO_3^{2-} \longrightarrow Co_3O_4 + 6Cl^- + 2CO_2 + CO \quad (2)$$

$$CoCl_2 + CO_3^{2-} \longrightarrow CoO + CO_2 + 2Cl^- \quad (3)$$

with progressive oxidation of the cobalt(II) oxide as the temperature increased, becoming complete by 600 °C. The dilute lilac solution gave a spectrum with a band at 17 000 cm^{-1} ($\varepsilon = 85 \pm 10$ dm^3 mol^{-1} cm^{-1}) and a shoulder at 19 000 cm^{-1} ($\varepsilon = 73.5 \pm 8.5$ dm^3 mol^{-1} cm^{-1}). Reflectance spectra of the lilac solids obtained by quenching the lilac solutions also showed a band at *ca.* 17 000 cm^{-1}, with some evidence of a shoulder at 18 500 cm^{-1}. The spectrum of the lilac solution closely resembles that of cobalt(II) in the ternary sulphate eutectic at 580 °C,[18] both in band position and extinction coefficient. However the co-ordination in the latter melt is a matter of some controversy, since the band position and extinction coefficients are intermediate between the values usually expected for octahedral and tetrahedral cobalt(II). For octahedral cobalt(II) in aqueous and molten media, the prominent visible band, corresponding to the highest energy transition ${}^4T_{1g}(F) \longrightarrow {}^4T_{1g}(P)$ occurs between 20 000 and 21 000 cm^{-1} (ε *ca.* 10 dm^3 mol^{-1} cm^{-1}), while for tetrahedral complexes the ${}^4A_2 \longrightarrow {}^4T_1(P)$ band is usually observed between 15 000 and 18 000 cm^{-1} ($\varepsilon > 100$ dm^3 mol^{-1} cm^{-1}).

Consequently, an alternative co-ordination geometry for sulphate melts has been proposed, *i.e.* a basically tetrahedral arrangement of four bidentate groups with overall D_{2d} symmetry.[19] A similar controversy exists for the cobalt(II) species in $LiNO_3$–KNO_3 melts; as well as octahedral co-ordination being suggested, the band maximum occurring at 18 000 cm^{-1} ($\varepsilon = 80$ dm^3 mol^{-1} cm^{-1}) has been assigned to an analogous dodecahedral geometry.[20,21] Thus the absorption band of cobalt(II) in carbonate melts may also arise from either octahedral or dodecahedral oxygen co-ordination.

Orange anhydrous nickel(II) chloride dissolved in the eutectic at 420 °C, completely at low concentrations (10^{-2} mol kg^{-1}) forming orange solutions which showed no signs of decomposition; at higher concentrations a greenish grey precipitate was produced as well as reddish orange solutions, the nickel concentrations in the latter being as much as 0.06 mol kg^{-1}.

X-Ray diffraction showed the precipitate to be nickel(II) oxide, with exact correspondence to the JCPDS index for NiO[16] [*i.e.* 2.41 (60), 2.09 (100), and 1.48 (35)]. Earlier reports of the reaction of nickel(II) chloride in the carbonate eutectic[6,7] also showed the final solid product by reaction above 400 °C to be nickel(II) oxide, equation (4), but no orange solutions were

$$NiCl_2 + CO_3^{2-} \longrightarrow NiO + 2Cl^- + CO_2 \quad (4)$$

observed, probably as a consequence of the comparatively high nickel(II) concentrations employed.

The spectra of the orange solutions obtained in the present work showed a broad band with a maximum at 24 000 cm^{-1}, and an extinction coefficient of 45 dm^3 mol^{-1} cm^{-1}. Reflectance spectra of quenched 0.06 mol kg^{-1} solutions (pale greenish yellow solids) exhibited bands at 24 000 and 14 000 cm^{-1} of approximately equal intensity. These values are not dissimilar to those reported earlier[6] though the maximum stable concentration found here is much lower. The green colour reported earlier[6] may have been due to some greenish nickel(II) oxide product being present and possibly to the additional chloride ligands. The band at 24 000 cm^{-1} occurring in both solid and solution spectra again seems likely to be due to the ${}^3A_{2g} \longrightarrow {}^3T_{1g}(P)$ transition of octahedral nickel(II), while the ${}^3A_{2g} \longrightarrow {}^3T_{1g}(F)$ band can apparently be observed at 14 000 cm^{-1} in the spectrum of the solid but not of the solution. These two bands occur with similar intensities in the spectrum of the regular-octahedral $[Ni(H_2O)_6]^{2+}$ ion in water,[22] together with the ${}^3A_{2g} \longrightarrow {}^3T_{2g}(F)$ band at lower energy. Hence it may be proposed that the change in the spectrum of the nickel(II) solutions on solidification results from the formation of a more symmetrical octahedral geometry.

For comparison, a solution of nickel(II) in the ternary alkali-metal sulphate was prepared by reaction of nickel(II) oxide with potassium pyrosulphate ($K_2S_2O_7$). The pink solution, shown by Dearnaley[23] to have absorption bands at 21 500 ($\varepsilon = 39$) and 9 800 cm^{-1} ($\varepsilon = 11$ dm^3 mol^{-1} cm^{-1}), formed a reddish yellow solid initially on quenching, which changed to green on further cooling to room temperature. The reflectance spectrum of the latter solid showed two bands at 23 000 and 11 500 cm^{-1}, of roughly equal intensity. These spectral changes on solidification are similar to those found in the carbonate melt and evidently a similar transformation of the co-ordination geometry could be occurring, to a more symmetrical octahedral environment in the solid sulphate. In the carbonate melt the lower energy bands may simply be too weak ($\varepsilon <$ *ca.* 1 dm^3 mol^{-1} cm^{-1}) and/or occur at too low an energy to be observed.

Anhydrous copper(II) sulphate reacted rapidly with the melt at 420 °C, evolving gas and forming a green solution and a black precipitate. The latter did not however appear if only small quantities of copper(II) sulphate were employed (equivalent to 10^{-2} mol kg^{-1} solutions), the resultant green solution then apparently being stable indefinitely.

Thermogravimetric analysis of a 0.5 mol kg^{-1} mixture of $CuSO_4$ with the eutectic showed that copper sulphate underwent a one-stage reaction (maximum rate of weight loss at fusion of the mixture), the only detectable products being sulphate ions and a black solid shown to be copper(II) oxide by *X*-ray diffraction: *d* spacings 2.52 (100), 2.32 (95), and 1.87

(25); JCPDF index for CuO,[16] 2.52 (100), 2.32 (96), and 1.87 (25). It was not possible to observe the formation of the green solution due to the intense black colour of the resulting suspension. Total weight loss up to 500 °C was 25.1% of the weight of copper sulphate, consistent with reaction (5) for which

$$CuSO_4 + CO_3^{2-} \longrightarrow CuO + SO_4^{2-} + CO_2 \quad (5)$$

a weight loss of 27.5% is calculated. The discrepancy between the calculated and theoretical weight loss may be at least partly due to the possible formation of some soluble copper species in the melt. An analogous stoicheiometry has been found for copper(II) chloride.[6]

The dilute, green melt solutions (*ca.* 10^{-2} mol kg^{-1}) displayed a relatively intense absorption band at 26 000 cm^{-1} (ε = 300 dm^3 mol^{-1} cm^{-1}), and a weaker band at 14 100 cm^{-1} (ε = 43 ± 5 dm^3 mol^{-1} cm^{-1}). Pale blue solids were formed by quenching the green solutions, giving reflectance spectra with a band at 14 000 cm^{-1}, but with continuously increasing absorption above 20 000 cm^{-1}. The lower energy absorption band at 14 100 cm^{-1} in the melt (14 000 cm^{-1} in the solid) is consistent with the $^2E_g \longrightarrow {}^2T_{2g}$ transition of octahedral copper(II), ε being in the expected range of 20—50 dm^3 mol^{-1} cm^{-1}. [Tetrahedral copper(II) complexes usually give a broad band below 10 000 cm^{-1} (ε *ca.* 100 dm^3 mol^{-1} cm^{-1}).] The band at 26 000 cm^{-1} for the melt is probably due to a charge transfer occurring at relatively low energy due to the comparatively easy reduction of copper(II).

Thus, in conclusion, it has been shown that despite the strong Lux–Flood basicity of the carbonate melt, dilute solutions of the weakly acidic divalent transition metals can be formed, stable enough for absorption spectra to be readily obtained. This stability is undoubtedly due to co-ordination, largely by carbonate anions, but possibly also by oxide anions which would be relatively available in this melt. However, the more strongly acidic chromium(III) cation was evidently not sufficiently stabilised by this co-ordination and reacted quantitatively with the melt.

Comparison of the ligand field of carbonate melts as compared to those reported in other alkali-metal oxyanion salt melts[20–23] shows that carbonate (if that be the only ligand, since oxide is possible) has a greater ligand field than both nitrate and sulphate and indeed marginally larger than that of water itself. However, comparison at such varied temperatures necessarily involves considerable temperature shifts, and can obscure differences in ligand field. But in this case the red shift with temperature merely makes it clearer that the order is $SO_4^{2-} < NO_3^- < H_2O < CO_3^{2-}$.

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