Thermochimica Acta, 55 (1982) 327–332
Elsevier Scientific Publishing Company, Amsterdam—Printed in The Netherlands

THERMOGRAVIMETRIC AND SPECTROSCOPIC STUDIES ON *trans*-$[Co(en)_2Cl_2]Cl$ AND *cis*-$[Co(en)_2(NCS)Cl]ClO_4$ IN MOLTEN KSCN AND $ZnCl_2$–KCl EUTECTIC

D.H. KERRIDGE, N. CARTHEY

Department of Chemistry, University of Southampton, Southampton S09 5NH (Gt. Britain)

M. HASSANEIN and A.E. EID

Department of Inorganic Chemistry, National Research Centre, Dokki, Cairo (Egypt)

(Received 30 November 1981)

ABSTRACT

The green *trans*-dichlorobis(ethylenediamine)cobalt(III) chloride and the red *cis*-chloroisothiocyanatobis(ethylenediamine)cobalt(III) perchlorate were prepared and their purity was confirmed by measuring their isobestic point spectrophotometrically. Thermal and spectral behaviour of the two Co(III) complexes in the solid state and in molten KSCN and $ZnCl_2$–KCl eutectic was studied. Results of thermogravimetric analysis showed a difference in decomposition temperature of the two complexes alone and in molten media. Moreover, the end product of the complexes alone was found to be Co_3O_4, but in thiocyanate melt CoS_2. Spectral measurements in the melts show characteristic absorption bands of tetrahedrally coordinated Co(II) suggesting the formation of $[Co(NCS)_4]^{2-}$ and $[CoCl_4]^{2-}$ species after oxidation–reduction reactions. Spectra in the solid state show the characteristic absorption of Co(III) in octahedral coordination.

INTRODUCTION

Although very many cobalt(III) complexes have been prepared and many studies made on their room temperature absorption spectra, kinetics of ligand replacement in aqueous solution, etc, little is so far known on their stability in high temperature non-aqueous solution (i.e. in molten salts) and their behaviour at high temperature, though some thermal decomposition studies have been reported [1–4].

In molten salts the only reports are of two complexes $[Co(NH_3)_6Cl_3$ and $Na_3Co(NO_2)_6]$ whose reactions, and ultimate decomposition to tricobalt tetraoxide, have been reported in lithium nitrite–potassium nitrite eutectic [5] and in the corresponding nitrate eutectic [6], while stepwise replacement of ammonia ligands in the former complex has been studied in sodium hydrogen sulphate–potassium hydrogen sulphate [7] and in ammonium hydrogen sulphate when cobalt(II) and nitrogen were the ultimate products [8]. Both complexes were also studied in potassium thiocyanate where the former complex was found to be reduced to soluble cobalt(II), though with the latter a further slow reaction occurred with nitrite precipitating tricobalt tetraoxide, and with both complexes parathiocyanogen was formed [9].

To broaden the available information the reactions of two further cobalt(III) complexes have been studied in molten potassium chloride–zinc chloride eutectic (KCl 46 mole%, $ZnCl_2$ 54 mole%, m.p. 228°C) since hitherto no cobalt(III) complexes have been studied in any chloride melt, and for comparison in the pseudohalide molten potassium thiocyanate. Thermogravimetric analysis has also been carried out on these two complexes alone, so that the effects of the melts on the temperatures of decomposition and the nature of the products could be more clearly seen.

EXPERIMENTAL

Trans-$[Co(en)_2Cl_2]Cl$ was prepared as reported earlier [10] while *cis*-$[Co(en)_2(NCS)Cl]ClO_4$ was obtained by the method of Werner [11]. The absence of other cobalt(III) complexes in the samples used was confirmed by obtaining sharp isobestic points as the complexes hydrolysed in aqueous solution. Similarly, plots of optical density at constant wavelength, i.e. of $\log(O.D._t - O.D._\infty)$, against time always gave good straight lines. Thermogravimetric analysis was carried out on the Stanton TR 1 thermobalance with a heating rate of 2°C min^{-1}, the weight losses being reported as % of the weight of the reactant complex. X-Ray powder diffraction was carried out on a Phillips (Eindhoven) diffractometer using nickel filtered copper K_α radiation. A Unicam SP700 spectrophotometer modified for high temperature measurements was used to record the melt spectra and a Carl Zeiss DMR 21 spectrophotometer for the diffuse reflectance measurements. Quantitative analysis for cobalt was EDTA titration after dissolving the acid insoluble black solids in molten potassium hydrogen sulphate at 400°C (for 2 h).

RESULTS AND DISCUSSION

The red complex, *cis*-$[Co(en)_2(NCS)Cl]ClO_4$ reacted immediately with potassium thiocyanate at 200°C to give a blue solution which contained cobalt(II) and gave two absorption bands at ~ 8100 and 15900–17000 cm^{-1} which are characteristic of $[Co(NCS)_4]^{2-}$ anions [12]. The green complex, *trans*-$[Co(en)_2Cl_2]Cl$ reacted immediately to give a red solution (possibly indicating initial replacement of chloride by thiocyanate) which changed, after 1 min, to a blue solution also containing cobalt(II) and giving the same two absorption bands. These two bands can be assigned to the transitions $^4A_2 \rightarrow {}^4T_1(F)$ and $^4A_2 \rightarrow {}^4T_1(P)$, respectively. The splitting of the higher frequency band (1100 cm^{-1}) can be attributed to the splitting of the $^4T_1(P)$ excited state by distortion of the tetrahedral symmetry of the absorbing cobalt centres.

The reactions appear to follow an analogous stoichiometry to that of the cobalt(III) complexes studied earlier [9].

$$trans[\mathrm{Co(en)_2Cl_2}]\mathrm{Cl} + \mathrm{KSCN} \rightarrow [\mathrm{Co(NCS)_4}]^{2-} + (\mathrm{SCN})_x + (\mathrm{en})_2 + 3\,\mathrm{Cl}^-$$

$$cis[\mathrm{Co(en)_2(NCS)Cl}]\mathrm{ClO_4} + \mathrm{KSCN} \rightarrow [\mathrm{Co(NCS)_4}]^{2-} + (\mathrm{SCN})_x + (\mathrm{en})_2 + \mathrm{ClO_4^-} + \mathrm{Cl}^- \quad (1)$$

On heating to higher temperatures further reaction took place with the eventual precipitation of cobalt as a black solid which was shown qualitatively to contain sulphur and proved to be cobalt disulphide ($\mathrm{CoS_2}$) by X-ray powder diffraction (see Table 1). Quantitative analysis showed a lower cobalt content (35.3 and 27.5% Co, respectively, compared with 47.9% calculated for $\mathrm{CoS_2}$) considered to be due to mixture with insoluble parathiocyanogen. This suggested that the tetra-coordinated anion had reacted

$$[\mathrm{Co(NCS)_4}]^{2-} \rightarrow \mathrm{CoS_2} + 2\,\mathrm{CN}^- + (\mathrm{SCN})_x \quad (2)$$

So that the overall reactions would be

$$trans[\mathrm{Co(en)_2Cl_2}]\mathrm{Cl} + 5\,\mathrm{SCN}^- \rightarrow \mathrm{CoS_2} + 3\,\mathrm{Cl}^- + 2\,\mathrm{CN}^- + \frac{3}{x}(\mathrm{SCN})_x + 2\,(\mathrm{en}) \quad (3)$$

and

$$cis[\mathrm{Co(en)_2(NCS)Cl}]\mathrm{ClO_4} + 4\,\mathrm{SCN}^- \rightarrow \mathrm{CoS_2} + \mathrm{Cl}^- + \mathrm{ClO_4^-} + 2\,\mathrm{CN}^- + \frac{3}{x}(\mathrm{SCN})_x + 2\,(\mathrm{en}) \quad (4)$$

and the calculated weight losses 42.1 and 32.3%, respectively, for loss only of ethylene diamine, but 103 and 79%, respectively, for loss of ethylenediamine and para thiocyanogen.

In fact thermogravimetric analysis showed the weight loss from the green dichloro-complex to begin at 230°C with a maximum rate of loss at 320°C. The rate of loss then decreased but began to increase again from 450°C probably due to increasing thermal decomposition of thiocyanate and distillation of sulphur from the melt [13].

$$x\mathrm{SCN}^- \rightarrow x\mathrm{CN}^- + \mathrm{S}_x \uparrow \quad (5)$$

TABLE 1

X-Ray powder diffraction pattern of black solids formed by reaction of cobalt(III) complexes in molten potassium thiocyanate—'*d*' spacings and intensities

Green $[Co(en)_2Cl_2]Cl$	Red $[Co(en)_2(NCS)Cl]ClO_4$	ASTM Index for CoS_2	
		Cattierite	Pyrite structure (quenched from 600°C)
3.20 (25)			3.20 (10)
2.76 (100)	2.76 (100)	2.77 (100)	2.77 (70)
2.47 (50)	2.47 (70)	2.48 (60)	2.48 (35)
2.23 (40)		2.25 (48)	2.26 (35)
1.96 (35)	1.95 (70)	1.95 (34)	1.96 (35)
1.67 (70)	1.66 (70)	1.66 (55)	1.67 (100)

The total weight loss was found to be 76% at 450°C, indicating that not all the parathiocyanogen had volatilized at this temperature.

Thermal analysis of the red chloro-isothiocyanato complex in melt showed similar reaction temperatures, as would be expected in view of the above equations, and by isothermal heating at 370°C the rate of weight loss was shown to have fallen to a low value after 2 h when the overall loss was 81%. This would indicate that all parathiocyanogen had volatilized, provided there was no additional loss caused through oxidation by perchlorate (nothing has so far been published on the reactions of perchlorate with molten thiocyanate).

For comparison, thermogravimetric analysis was carried out on both complexes in the absence of thiocyanate melt when it was found that the green complex began to lose weight at 80°C but more rapidly above 225°C with a maximum rate of loss at 530°C, equilibrium being reached at 680°C when the overall loss was 84%, close to the 82.7% calculated for the equation

$$3\,[Co(en)_2Cl_2]Cl + 2\,O_2 \rightarrow Co_3O_4 + 6\,(en) + 4.5\,Cl_2 \qquad (6)$$

and in agreement with the previous study [4].

In contrast, the red complex was apparently stable to heating until it reacted extremely rapidly (explosively) at 200°C, ejecting solid material from the crucible and rendering weight loss measurements unhelpful. This difference in reactivity of the complexes when heated alone is no doubt due to the oxidizing character of the perchlorate in intimate contact with oxidizable ethylene diamine and thiocyanate. The considerable stabilization effected by molten potassium thiocyanate is probably because the perchlorate is then dissolved throughout the melt and its concentration and time of residence near to oxidizable species is thus much lower. The overall course of reaction of the green complex is also very different [cf. eqns. (3) and (6)] again due to the presence of thiocyanate.

Diffuse reflectance of the two solid complexes showed bands at 9000, 16000, 24000 and 28000 cm^{-1} for the green complex (the latter three being strongly absorbing, the first two being split) and 12000, 20000 and 26000 cm^{-1} for the red complex (the latter two being strong and very broad) typical of *trans* and *cis* stereochemistries where the $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ transitions of low spin Co(III) complexes in strong octahedral ligand fields are split by less than octahedral symmetries [14]. Generally, the observed absorption intensities are less for the *trans* complex which has a centre of symmetry, in agreement with the aqueous solution spectra of geometrical Co(III) isomers [15].

In molten potassium chloride–zinc chloride eutectic at 250°C both complexes dissolved to give green solutions which contained cobalt(II) and had absorption bands at 6500, 14000, 14900 and 16400 cm^{-1} characteristic of the tetrahedral species $[CoCl_4]^{2-}$. The much larger splitting of the $^4A_2 \rightarrow {}^4T_1(P)$ transition (2400 cm^{-1}) than was found for the thiocyanate complex may well result from increasing distortion from the regular tetrahedron, probably due either to the changed interaction between a cation with thiocyanate and with chloride, or simply due to the increasing polarizing power of the surrounding cations ($K^+$and Zn^{2+}/K^+) since distortion has been found to become greater with increasing cation potential (Z_+/r_+) and to produce a larger splitting number in melts containing aluminium chloride [16].

The spectrum of cobalt(II) chloride in this melt which has not previously been published, was found to consist of four bands in the same positions as for the red and green complexes, but the melt solution was blue rather than green. This change in colour was due to the presence of ethylenediamine, since a solidified cobalt(II) chloride melt solution when moistened with ethylenediamine and remelted gave a similar green melt. The green melts formed from the complexes in addition to the four maxima previously mentioned, which are identical with those of cobalt(II) chloride, also showed over the range 30000–20000 cm^{-1} the tail of an intense UV band (maximum $>$30000 cm^{-1}) which was probably produced by an ethylenediamine interaction.

REFERENCES

1 F.C. Chang and W.W. Wendlandt, J. Inorg. Nucl. Chem., 32 (1970) 3775.
2 W.W. Wendlandt, W.R. Robinson and W.Y. Yang, J. Inorg. Nucl. Chem., 25 (1963) 1495.
3 F.C. Chang and W.W. Wendlandt, Thermochim. Acta, 7 (1973) 103.
4 W.W. Wendlandt, Texas J. Sci., 10 (1958) 271.
5 S.S. Al Omer and D.H. Kerridge, J. Chem. Soc., Dalton Trans., (1978) 1589.
6 H. Frouzanfar and D.H. Kerridge, J. Inorg. Nucl. Chem., 40 (1978) 1327.

7 J.A. Duffy and W.J.D. Macdonald, J. Chem. Soc. A, (1971) 1160.
8 R.A. Sutula and J.B. Hunt, Inorg, Chem., 11 (1972) 1879.
9 D.H. Kerridge and S.J. Walker, J. Inorg. Nucl. Chem., 38 (1976) 1795.
10 J.C. Bailer, Inorg. Synth., 2 (1946) 223.
11 A. Werner, Annalen, 1 (1912) 386.
12 D.H. Kerridge and M. Moseley, Chem. Commun., (1969) 429.
13 D.H. Kerridge, in A.A. Newman (Ed.), Chemistry and Biochemistry of Thiocyanic Acid and its Derivatives, Academic Press, London, New York, 1975, Chapter 3.
14 A.B.P. Lever, Inorganic Electronic Spectroscopy, Elsevier, Amsterdam, 1968.
15 F. Basolo, C.J. Ballhausen and J. Bjerrum, Acta Chem. Scand., 9 (1955) 810.
16 H.A. Oye and D.M. Gruen, Inorg. Chem., 4 (1965) 1173.