Optically Active Co-ordination Compounds. Part XXVIII.† Resolution of the Triscarbonatocobaltate(III) Anion

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The nature of the triscarbonatocobaltate(III) species in aqueous solution and in some salts has been studied by i.r. spectroscopy. The presence of the trischelated species $[Co(CO_3)_3]^{3-}$ is demonstrated by an optical resolution, using $(+)[Co(en)_3]^{3+}$.

THE nature of anionic apparently tris-chelated complexes involving metals in the oxidation state III and bidentate ligands chelating through oxygen has been the subject of some debate. In particular, the role of water in the crystal lattice is of interest. We recently studied[1] the trisoxalato-complexes of formulae $K_3[M(C_2O_4)_3],xH_2O$ and describe here our work on the triscarbonatocobaltate(III) system. Two recent reviews comment[2] on the problem and summarize most of the available information.

The salts of this green anion are well known, and are much used synthetically. The best characterized

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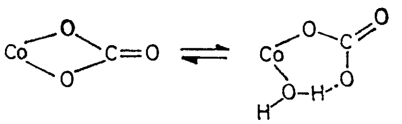
† Part XXVII, R. D. Gillard and A. Spencer, *J.C.S. Dalton*, 1972, 902.

[1] R. D. Gillard, S. H. Laurie, and P. R. Mitchell, *J. Chem. Soc.* (*A*), 1969, 3006.

[2] (*a*) C. R. Piriz Mac-Coll, *Co-ordination Chem. Rev.*, 1969, **4**, 147; (*b*) K. V. Krishnamurty, G. M. Harris, and V. S. Sastri, *Chem. Rev.*, 1970, **70**, 171.

solid compounds are[2] the hydrated alkali-metal salts, $M_3[Co(CO_3)_3],3H_2O$ (M = Na or K); the potassium salt decomposes rather readily on keeping, the sodium salt less readily. The anhydrous salt $[Co(NH_3)_6][Co(CO_3)_3]$ was made by McCutcheon and Schuele[3] and is much more stable.

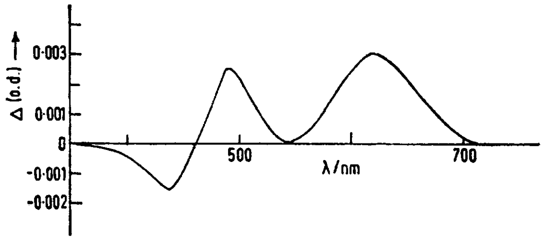
In the cases where carbonato-chelate rings are thought to exist in solid compounds, it is often said from kinetic experiments[2] that a pre-equilibration occurs on dissolution in aqueous media, whereby water inserts into the chelate ring as in (1).


(1)

We discuss our observations in terms of the successive equilibria of this type possible for $[Co(CO_3)_3]^{3-}$. We neglect here two features which would be considered in a more detailed study. These are (*a*) the geometric isomerism implicit in formulae (B), (C), and (D) and (*b*) the pH equilibria involving (B), (C), and (D).

$$\underset{(A)}{[Co(CO_3)_3]^{3-}} \rightleftharpoons \underset{(B)}{[Co(CO_3)_2(HCO_3)(OH)]^{3-}} \rightleftharpoons \underset{(C)}{[Co(CO_3)(HCO_3)_2(OH)_2]^{3-}} \rightleftharpoons \underset{(D)}{[Co(HCO_3)_3(OH)_3]^{3-}} \qquad (2)$$

Obviously, providing that the equilibria in (2) are established rapidly, the nature of the carbonato-anion in crystalline salts will be a function of the relative solubilities of the salts of the particular cation, and of the equilibrium constants linking (A) and (B), *etc.*



C.d. spectrum of $[(+)\text{-}Co(en)_3]^{3+}[Co(CO_3)_3]^{3-}$ in a KBr disc

Our experimental contributions toward establishing this are of two types. We have found that, on treating a cold neutral aqueous solution of potassium triscarbonatocobaltate(III) with (+)-trisethylenediaminecobalt(III) chloride, the diastereoisomer (+)$[Co(en)_3]$-(−)-$[Co(CO_3)_3]$ is obtained. Its properties in the solid state are recorded in the Figure. The filtrate shows no optical activity (*i.e.* racemization is fast) and so this experiment proves only that ' some ' (A) is present in neutral solution. Attempts to dissolve the diastereoisomer of course give solutions optically inactive in the 600 nm region.

If we assume that we can compare the helical chromophore CoO_6 in $[Co(CO_3)_3]^{3-}$ with the central CoO_6 chromophore containing four-membered rings in ' hexol ' $[\{(NH_3)_4Co(OH)_2\}_3Co]^{6+}$ which has been assigned[4] the D-configuration, our less soluble diastereoisomer is D-(+)$[Co(en)_3]$D(−)$[Co(CO_3)_3]$. It is at least interesting that previous resolutions of tris chelate anions using $[Co(en)_3]^{3+}$ to form diastereoisomers of the 3+ : 3− charge type have commonly given the less-soluble D-$[Co(en)_3]$-D[anion], *e.g.* [Co(D-cysteine-sulphinate)$_3]^{3-}$,[5] $[Co(C_2O_4)_3]^{3-}$.[6]

I.r. spectroscopy in the region 1250—1650 cm^{-1} provides[7] a convenient method of distinguishing between free carbonate ion, unidentate and bidentate ligand. The free ion (of D_{3h} symmetry) has its main band (ν_3) at *ca.* 1380 cm^{-1} in $[Co(NH_3)_6]Cl,CO_3$. In $[Co(NH_3)_5CO_3]Br$, where the carbonato-ligand is unidentate, this band is now split into two bands at 1450 and 1370 cm^{-1}, and in $[Co(NH_3)_4CO_3]Cl$, with bidentate carbonate, the splitting is further increased, with bands at 1592 and 1255 cm^{-1}. We have extended this work to D_2O solution, and also looked at the tricarbonatocobalt species. These tricarbonato-complexes can be divided into at least two types; those which are precipitated in an anhydrous form, *e.g.* $[Co(NH_3)_6][Co(CO_3)_3]$ and will not redissolve in water, and those which are water-soluble hydrates such as $K_3[Co(CO_3)_3],3H_2O$. The former seem indefinitely stable as solids while the latter tend to decompose even in the solid state. The solid-state i.r. spectra indicate that $[Co(NH_3)_6][Co(CO_3)_3]$ with bands at 1585 and 1280 cm^{-1} contains bidentate CO_3 groups, while $K_3[Co(CO_3)_3],3H_2O$ with bands at 1495 and 1335 cm^{-1}, and a weaker one at 1600 cm^{-1} may contain mainly unidentate CO_3 groups. In D_2O solution $Na_3[Co(CO_3)_3]$ shows two main bands at 1470 and 1345 cm^{-1} suggesting predominant species such as $[Co(OCO_2H)_3(OH)_3]^{3-}$ with unidentate bicarbonato-groups. Our spectroscopic results are collected in the Table. The solid-state i.r. spectrum of D-$[Co(en)_3]$D-$[Co(CO_3)_3]$ shows carbonato-bands at 1600 and 1300 cm^{-1} indicating the anticipated ring-closed form.

I.r. spectra of $[Co(NH_3)_5CO_3]NO_3$ and $[Co(NH_3)_4CO_3]NO_3$ dissolved in D_2O show bands at 1455 and 1610 cm^{-1} respectively (the lower-energy band is in the region of the strong NO_3^- band), suggesting that even in solution $[Co(NH_3)_4CO_3]NO_3$ may be present in the ring-closed form or possibly that water insertion has occurred to give a six-membered ring in neutral aqueous solution.

It is known from *X*-ray evidence[8] that in $[Co(NH_3)_4CO_3]Br$, the carbonate ligand forms a four-

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[3] T. P. McCutcheon and N. Schuele, *J. Amer. Chem. Soc.*, 1953, **75**, 1845.

[4] S. F. Mason and B. J. Norman, *Chem. Comm.*, 1966, 100.

[5] R. D. Gillard and R. Maskill, *Chem. Comm.*, 1968, 160.

[6] J. W. Vaughn, V. E. Magnuson, and G. J. Seiler, *Inorg. Chem.*, 1969, **8**, 1201.

[7] K. Nakamoto, J. Fujita, S. Tanaka, and M. Kobayashi, *J. Amer. Chem. Soc.*, 1957, **79**, 4906.

[8] G. A. Barclay and B. F. Hoskins, *J. Chem. Soc.*, 1962, 586.

membered chelate ring. We have further shown that the tris-chelated ion $[Co(CO_3)_3]^{3-}$ exists as such. However, in the latter case, solution i.r. spectra suggest that ring opening has occurred, and it seems likely that concentrations of species involving carbonato-chelate rings in solution will be low.

Summary of i.r. results on carbonato-complexes (for ν_3 of D_{3h} carbonate)

Compound	KBr disc	D_2O solution
Free CO_3^{2-}	1415[a]	
$KHCO_3$	1625, 1400	
$[Co(NH_3)_6]Cl,CO_3$	1390—1370[a]	
$[Co(NH_3)_5CO_3]Br$	1450,[a] 1370[a]	
$[Co(NH_3)_5CO_3]NO_3$	1470, 1360	1460, 1360
$[Co(NH_3)_4CO_3]Cl$	1592,[a] 1255[a]	
$[Co(NH_3)_4CO_3]NO_3$	1600, 1282	1610, 1355
$[Co(en)_2CO_3]Br$	1575, 1278	1610, 1350
$[Co(NH_3)_6][Co(CO_3)_3]$	1585, 1280	[c]
D-$[Co(en)_3]$D-$[Co(CO_3)_3]$	1600,[b] 1300	[c]
$K_3[Co(CO_3)_3],3H_2O$	1600, 1495, 1335	1600, 1470, 1345

[a] From ref. 7. [b] This region is complicated by the presence of absorptions from ethylenediamine. [c] Insoluble.

EXPERIMENTAL

I.r. spectra were obtained using a PE 225 instrument; spectra in D_2O were measured using silver chloride plates. Circular-dichroism spectra were obtained using a Jouan Dichrographe model B.

Resolution of the Triscarbonatocobaltate(III) *Ion.*—Cold (0°) saturated solutions of $K_3[Co(CO_3)_3],3H_2O$ and of $(+)[Co(en)_3]Cl_3$ (obtained by asymmetric synthesis [9]) were mixed and the mixture was stored at 0°. During a few hours, crystals of the diastereoisomer D-$(+)[Co(en)_3]$-D-$[Co(CO_3)_3]$ were formed. These were collected, dried, and their circular dichroism measured as a 1% KBr disc (see Figure).

We wish to thank the S.R.C. for a fellowship (M. G. P.).

[1/2053 *Received*, *4th November*, 1971]

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[9] J. A. Broomhead, F. P. Dwyer, and J. W. Hogarth, *Inorg. Synth.*, 1960, **6**, 186.