636. *The Infrared Spectra of Some Simple and Complex Carbonates.*

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The infrared spectra of some carbonato-metal complexes have been examined in the region between 4000 and 700 cm.$^{-1}$. The spectra have been compared with those of simple, acid, basic, and organic carbonates, and characteristic frequencies have been assigned for these compounds. Strong absorption bands, which are absent in the spectra of ionic carbonates, occur at 1577—1493, 1338—1272, and 1080—1020 cm.$^{-1}$ in those of the carbonato-complexes. The diagram below summarises the spectra.

The infrared spectra of dimethyl, diethyl, and diphenyl carbonate have also been recorded.

Earlier [1] we reported the infrared absorption spectra of some nitrato-metal complexes and assigned the bands corresponding to the vibrations ν_1, ν_2, ν_4, and ν_6 of the covalently bound nitrate group. In this investigation a number of carbonato-metal complexes have been examined in order to ascertain whether their spectra are related to the simple carbonates, in the same way as the spectra of nitrato-complexes are related to those of ionic nitrates, since the carbonate and nitrate ions are both planar XY_3 groups possessing D_{3h} symmetry.

The spectra of simple ionic carbonates fall generally into one of two groups according

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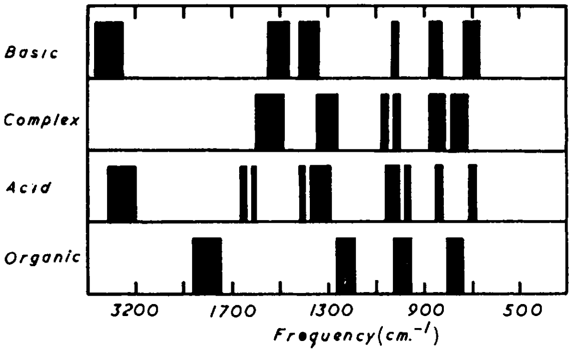
[1] Gatehouse, Livingstone, and Nyholm, *J.*, 1957, 4222.

to whether the compound is of the calcite or aragonite type. These compounds have been extensively examined [2,3,4,5] and the differences between the two groups arise mainly from intermolecular coupling of the out-of-plane bending mode (ν_2) and the lower symmetry in the crystal.[6]

Nakamoto *et al.*[7] recently reported the infrared absorption spectra of three carbonato-complexes of tervalent cobalt and made assignments with reference to the carbonate ion. They showed that co-ordination by the carbonato-group causes the appearance of a band which is inactive for the carbonate ion, and the splitting of the degenerate mode ν_3, owing to the lowering of symmetry of the ligand, as we demonstrated for the nitrato-complexes. Duval *et al.*[8] had earlier examined some carbonato-complexes of bi- and ter-valent cobalt and of bivalent copper, observing the appearance of a new absorption band, ν_2, in the vicinity of 1050 cm.$^{-1}$. However, these workers apparently did not resolve a broad absorption band in the region 1300—1500 cm.$^{-1}$.



Miller and Wilkins [2] reported the spectra of three hydrogen carbonates (NH_4^+, Na^+, and K^+) which are very similar to those of the complex carbonates and show the loss of degeneracy of ν_3, which results in the appearance of bands in the regions 1660—1620 (ν_4) and 1410—1295 cm.$^{-1}$ (ν_1).

The spectra of a number of basic carbonates have also been reported,[2,4] which show similarities to those of the complex carbonates. Apparently hydrogen bonding in these compounds causes a lowering of symmetry of the carbonato-group from D_{3h} to C_{2v}.

In addition to the carbonato-complexes we have examined three organic carbonates and the spectra of these are compared with the carbonates mentioned above.

EXPERIMENTAL

Absorption Measurements.—The infrared spectra were obtained with a Grubb-Parsons double-beam infrared spectrometer, equipped with an S3A monochromator and a rock-salt prism. The samples were ground in an agate vibration mill. The mulling agents used were Nujol, and hexachlorobutadiene for the region (6—8 μ) obscured by Nujol absorption bands. The samples were examined between rock-salt plates, coated with polystyrene, as described by one of us,[9] to ensure that there would be no replacement of the carbonato-group by chloride from the rock-salt plates.

Preparation of Compounds.—*Sodium carbonatocuprate*(II) *trihydrate.* This compound was

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[2] Miller and Wilkins, *Analyt. Chem.*, 1952, **24**, 1253.
[3] Loisfert and Pobeguin, *Compt. rend.*, 1952, **235**, 287.
[4] Hunt, Wisherd, and Bonham, *Analyt. Chem.*, 1950, **22**, 1478.
[5] Couture, *Ann. Phys.*, 1947, **2**, 5.
[6] Decius, *J. Chem. Phys.*, 1954, **22**, 1946; 1955, **23**, 1290.
[7] Nakamoto, Fujita, Tanaka, and Kobayashi, *J. Amer. Chem. Soc.*, 1957, **79**, 4904.
[8] Duval, Duval, and Lecomte, *Bull. Soc. chim. France*, 1943, **10**, 517.
[9] Gatehouse, *Chem. and Ind.*, 1957, 1351.

prepared by Applebey and Lane's method[10] (Found: Cu, 22·1; CO_3^{2-}, 42·6. Calc. for $C_2H_6O_9CuNa_2$: Cu, 22·4; CO_3^{2-}, 42·4%).

Potassium carbonatocobaltate(II) *tetrahydrate.* This was made similarly (Found: Co, 17·3; CO_3^{2-}, 36·1. Calc. for $C_2H_8O_{10}CoK_2$: Co, 17·9; CO_3^{2-}, 36·4%).

Potassium carbonatocobaltate(III) *trihydrate.* The method described by Mori *et al.*[11] was used (Found: Co, 16·0; CO_3^{2-}, 44·4. Calc. for $C_3H_6O_{12}CoK_3$: Co, 14·4; CO_3^{2-}, 43·9%). It seems impossible to obtain this compound quite pure, as seen from the analyses by Mori *et al.*[11] We prepared it a number of times and in each case the infrared absorption spectra were identical.

Hexamminocobalt(III) *carbonatocobaltate*(III). The method of preparation used was that of Mori *et al.*,[11] being more straightforward than that of McCutcheon and Schuele.[12] The product was dried *in vacuo* over phosphoric oxide (Found: Co, 29·6. Calc. for $C_3H_{18}O_9N_6Co_2$: Co, 29·5%).

Carbonatopentamminocobalt(III) *chloride.* The compound was prepared as described by Gmelin[13] (Found: Co, 24·8; Cl, 14·5. Calc. for $CH_{15}O_3N_5ClCo$: Co, 24·6; Cl, 14·8%).

Carbonatotetramminocobalt(III) *sulphate trihydrate.* The method quoted by Gmelin[14] was used (Found: Co, 22·9. Calc. for $C_2H_{30}O_{13}N_8SCo_2$: Co, 22·5%).

Carbonatobisethylenediaminecobalt(III) *chloride.* An aqueous solution of *trans*-dichlorobisethylenediaminecobalt(III) chloride was treated with the calculated quantity of sodium carbonate as described by Gmelin.[15] The carbonato-complex was dried at 100° (Found: Cl, 12·6. Calc. for $C_5H_{16}O_3N_4ClCo$: Cl, 12·9%).

Carbonatobisethylenediaminecobalt(III) *bromide.* The bromide was prepared in an analogous manner to the chloride from *trans*-dibromobisethylenediaminecobalt(III) bromide (Found: Br, 24·8. Calc. for $C_5H_{16}O_3N_4BrCo$: Br, 25·0%).

Carbonatobisethylenediaminecobalt(III) *iodide.* The iodide was prepared by treating a warm aqueous solution of the chloride with potassium iodide. On cooling, the solution deposited crystals of the iodide (Found: I, 34·1. Calc. for $C_5H_{16}O_3N_4ICo$: I, 34·6%).

Organic Carbonates.—The purity of the organic carbonates was checked by the measurement of the refractive index for the dimethyl and the diethyl ester and by a m. p. determination for the phenyl ester. The former were examined in the liquid state between rock-salt plates and the latter in the solid state in Nujol and hexachlorobutadiene mull.

Attempted Preparation of the Double Carbonate of Potassium and Nickel.—Attempts were made to prepare the double carbonate of potassium and nickel, reported by Deville.[16] The method used for the preparation of the copper and cobaltous complexes, described above, was tried, as well as Deville's method. Crystalline products were obtained with both procedures, but analysis showed that the products did not have the composition, $K_2CO_3,NiCO_3,4H_2O$, reported by Deville.

RESULTS AND DISCUSSION

The carbonate ion has D_{3h} symmetry, giving rise to four vibrations,[17] which are listed in Table 1. The absorption spectra of some alkali, alkaline-earth, and heavy-metal carbonates, reported by Miller and Wilkins,[2] display only two strong bands, at 1450—1410 and 880—840 cm.$^{-1}$ with, in some cases, a weak band at 715—685 cm.$^{-1}$. The

TABLE 1. *Fundamental frequencies of the carbonate ion.*[17]

Type[18]	Raman *	Infrared *	CO_3[11]	cm.$^{-2}$	Assignment
A_1'	a	ia	ν_1	1063	C–O sym. stretching
A_2''	ia	a	ν_2	879	CO_3 out-of-plane deformation
E'	a	a	ν_3	1415	C–O asymm. stretching
E'	a	a	ν_4	680	in-plane deformation (or rocking)

* a = active; ia = inactive.

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[10] Applebey and Lane, *J.*, 1918, **113**, 610.

[11] Mori, Shibata, Kyuono, and Adachi, *Bull. Chem. Soc. Japan*, 1956, **29**, 883.

[12] McCutcheon and Schuele, *J. Amer. Chem. Soc.*, 1953, **75**, 1845.

[13] Gmelin, " Handbuch der anorganische Chemie," Verlag Chemie, Berlin, 1930, **58**, *B*, 199.

[14] *Op. cit.*, p. 281.

[15] *Op. cit.*, p. 283.

[16] Deville, *Ann. Chim. Phys.*, 1851, **33**, 75.

[17] Herzberg, " Infrared and Raman Spectra of Polyatomic Molecules," van Nostrand, New York, 1945, p. 178.

[18] Meister, Cleveland, and Murray, Research Publications, Illinois Institute of Technology, Vol. 6, No. 1, Jan. 1948.

vibration, ν_1, gives rise to an absorption band only in simple carbonates of the aragonite type.

We have examined barium carbonate and found that it gives three strong absorption bands, 1420, 857, and 692 cm.$^{-1}$. Barium carbonate, containing ^{13}C was also examined,[19] and it was found that the band at 857 cm.$^{-1}$ is shifted to 832 cm.$^{-1}$, whereas the other bands are shifted only by a few cm.$^{-1}$. This identifies the band in the region of 850 cm.$^{-1}$ as the out-of-plane rocking vibration, ν_2, of the carbonate ion.

When the carbonate ion is covalently bound through one oxygen atom the symmetry is lowered and the carbonato-group belongs to the point group C_{2v}. If the carbonato-group is bidentate the symmetry is the same as of the monodentate ligand. Table 2 lists the vibration types and assignments of the carbonato-ligand.

TABLE 2. *Fundamental frequencies of the covalently bound carbonato-group.*

Type [18]	Raman	Infrared	Carbonato frequency	Assignment
A_1	a	a	ν_3	CO_2 bending
A_1	a	a	ν_1	CO_2 sym. stretch.
A_1	a	a	ν_2	CO stretch.
B_2	a	a	ν_6	Non-planar rock.
B_1	a	a	ν_4	Asym. stretch.
B_1	a	a	ν_5	Planar rock.

The principal absorption bands of the carbonato-complexes, examined in this investigation, are given in Table 3. By reference to the spectra of $[Co(NH_3)_6]Cl_3$ and *cis*-$[Co\ en_2Cl_2]Cl$, the bands due to co-ordinated ammonia and ethylenediamine have been identified in the spectra of the appropriate carbonato-complexes and are omitted in Table 3.

The vibration, ν_3, of the carbonate ion (see Table 1), being doubly degenerate, is split into two components when the carbonate ion is co-ordinated; these are now designated ν_4 and ν_1. A similar splitting occurs with basic, acid, and organic carbonates. The frequency ranges for these compounds are given in Table 5. The differences between the results reported here for $[Co(NH_3)_5CO_3]^+$ and those of Nakamoto *et al.*[7] could have arisen from confusion over ammonia and water absorption bands which occur in the same regions as ν_4 for the carbonate ligand or could have been due to the KBr disc technique used by the latter workers.

TABLE 3. *Infrared absorption bands of carbonato-complexes* (*cm.*$^{-1}$).

	ν_4	ν_1	ν_2	ν_6	ν_3 or ν_5
$Na_2[Cu(CO_3)_2],3H_2O$	1529 s	1326 s	1066 m 1050 m	850 s	755 s
$K_2[Co(CO_3)_2],4H_2O$	—	1338 m	1082 m 1049 m	884 m	799 s 766 m
$K_3[Co(CO_3)_3],3H_2O$	1527 s	1330 s	1080 w 1037 m	851 m	809 m
$[Co(NH_3)_6][Co(CO_3)_3]$	1523 s	1285 s	1073 w 1031 w	889 w	738 m
$[Co(NH_3)_5CO_3]Cl$	1493 s	1297 s	1057 m 1043 m	873 s 848 s	738 m
$[Co(NH_3)_4CO_3]_2SO_4,3H_2O$	*	1260 s	—	856 w	756 m
$[Co\ en_2CO_3]Cl$	1577 s	1281 s 1272 s	1021 m 1059 w 1035 w	830 s	754 m
$[Co\ en_2CO_3]Br$	1575 vs	1282 s 1276 s	1059 s 1038 s	825 s	757 s
$[Co\ en_2CO_3]I$	1565 m	1290 v.w.sh. 1278 s	1055 m 1034 m	824 s	756 m

w = weak; m = medium; s = strong; vs = very strong; sh = shoulder; en = ethylenediamine.

* Band here is obscured by NH_3 and H_2O bands in region 1640—1550 cm.$^{-1}$.

The hydrogen carbonates show a further splitting of ν_3 and ν_1, the bands being well

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[19] Comyns and Gatehouse, unpublished work.

defined. This effect probably arises from interaction between neighbouring HCO_3 groups. Zachariasen [20] described the crystal lattice of sodium hydrogen carbonate wherein two oxygens of each HCO_3 group are hydrogen-bonded to neighbouring HCO_3 groups and the third oxygen is " free." It is not unreasonable to expect a higher bond order for the " free " C–O bond, with which the appearance of an absorption in the 1660—1620 cm.$^{-1}$ region is consistent.

TABLE 4. *Infrared absorption bands of some organic carbonates.*

	ν_4 (cm.$^{-1}$)	ν_1	ν_6	Other bands ascribed to the carbonato-group	
Dimethyl carbonate	1760 s	1280 s	793 s	969 s	914 s
Diethyl carbonate	1750 s	1262 s	790 s	1021 s	858 s
Diphenyl carbonate [b]	1779 s	1260 s	790 s	1021 m	912 w, 874 w
Methyl phenyl carbonate [22]	1755 s	1262 s	a	a	
Ethyl phenyl carbonate [22]	1757 s	1252 s	a	a	
Ethylene carbonate (liquid) [23] ...	1870 s	1162 s	774 m	1074 s	974 s
(solid)	1810 s	1163 s	774 s	1078 s	972 s

[a] No bands are reported below 1060 cm.$^{-1}$. [b] The following bands were also obtained for diphenyl carbonate: 1599 m, 1500 s, 1188 s, 1162 s, 1073 m, 955 m, 764 m, 749 s, 712 w, 686 s.

The spectra of some organic carbonates are listed in Table 4 and are similar to the spectra of the complex carbonates. The absorption bands ν_4 and ν_1 occur in the ranges 1870—1750 and 1280—1162 cm.$^{-1}$ respectively. This greater difference in frequency between ν_4 and ν_1 is to be expected if we assume less ionic character in the organic carbonates than in the carbonato-complexes. The frequency of ν_4 in the organic carbonates corresponds to the C=O frequency found in a large number of carbonyl compounds.[21]

TABLE 5. *Frequency ranges of carbonate absorption bands (cm.$^{-1}$).*

Type of carbonate		ν_3	ν_1	ν_2		ν_4
Simple		1470—1420	1090—1020 w *	890—820		750—680
	OH	ν_4	ν_1	ν_2	ν_6	ν_3 or ν_5
Basic [2, 4]	3390—3270	1515—1470	1425—1325	1049—1047	877—835	712—686
Complex	—	1577—1493	1338—1260	1082—1055 1050—1021	889—824	809—738
Acid [2]	3300—3200	1660—1655 1630—1620	1410—1400 1370—1295	1050—1010 1000—990	840—830	705—698
Organic [22, 23]	—	1870—1750	1280—1252	1021—969(?)	793—774	—

* See p. 3140.

The normally forbidden absorption, ν_1, which appears weakly only in simple carbonates of the aragonite type, is active for the co-ordinated group (ν_2) and appears with medium intensity. This band is well defined only in the compounds not containing ethylenediamine, as the latter has a strong sharp band at 1053 cm.$^{-1}$, the carbonato-bands appearing on either side. It can be seen from Table 3 that there is little variation in ν_2 for the complexes, although the trend is similar to that observed for the nitrato-group,[1] with the more covalent compounds having the lower frequencies. A splitting of ν_2 is observed in the hydrogen carbonates and in the carbonato-complexes, and probably arises out of interaction of neighbouring groups; the possibility of its arising from Fermi resonance of ν_2 with $2\nu_5$ (or $2\nu_3$) where ν_5 (or ν_3) occurs at approximately 520—540 cm.$^{-1}$, must not be overlooked.*

The out-of-plane vibration, designated ν_2 for simple carbonates, becomes ν_6 for the carbonato-group, and apart from the organic carbonates does not differ greatly in frequency

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* The authors are grateful to the referees for this suggestion.

[20] Zachariasen, *J. Chem. Phys.*, 1933, **1**, 634.

[21] Hartwell, Richards, and Thompson, *J.*, 1948, 1436.

[22] Hales, Jones, and Kynaston, *J.*, 1957, 618.

[23] Angel, *Trans. Faraday Soc.*, 1956, **52**, 1178.

from that in the simple carbonates. The differences in this region between the calcite and aragonite type carbonates are discussed in detail by Decius.[6]

The carbonate-ion absorption ν_4 is doubly degenerate, giving rise to ν_3 and ν_5 for the complex carbonates. However, only one absorption band is observed below 800 cm.$^{-1}$ and its assignment would not be certain until the KBr region was examined.

The spectra are summarised in the diagram.

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