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THE CHEMISTRY OF THE METAL CARBONATO COMPLEXES

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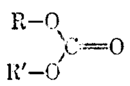
I. Introduction

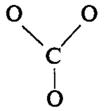
Carbonate is a fascinating ligand exhibiting both bidentate and monodentate characteristics in reactions and may be characterized as "quasi" bidentate. As a bidentate it is essentially *cis*-spanning.[2] The free *ionic* carbonate with equivalent oxygens belongs to the D_{3h} symmetry class, and a host of naturally occurring carbonate minerals appear as a family of anisodesmic oxy salts in which CO_3^{2-} maintains its fundamental covalency of carbon–oxygen bonds. However, the binding of the carbonate with numerous cations is essentially ionic.

Several organic carbonate esters corresponding to the general formula



and also the cyclic type are known in which one of the three oxygens of the carbonate happens to be a carbonyl oxygen and is distinctly different from the other two bound covalently to the R and R′ moieties. This is apparent in the change of symmetry from D_{3h} to C_{2v} type and has been amply supported by spectral studies.

If, however, the same carbonate is present as a bidentate ligand in certain metal carbonato complexes, for example, the $[Co(NH_3)_4CO_3]^+$ ion, it may be partially covalent and partially ionic. This difference in bonding in coordination compounds is known to reflect in reactions involving the carbonate and has been ably demonstrated in several studies. The present review attempts to collect and evaluate all scattered material concerning the chemistry of the metal carbonato complexes with the hope that at least some aspects of the interconversion of initially nonlinear structure i to the linear



i

O—C—O

ii

structure ii might be further explored. The analytical, biochemical, physiological, geochemical, and theoretical significance of this conversion needs no special emphasis and a study of the ligand characteristics of carbonate perhaps will lead to a better understanding of the interconversion process. The literature survey pertaining to this review includes published work until June 1968.

II. Carbon Dioxide, Carbonic Acid, and the Carbonates

The occurrence of carbon dioxide in the atmosphere, hydrosphere, geosphere, and biosphere is well known,[3] and it is

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not the purpose of this review to dwell on this subject extensively except to comment critically on the various species: $CO_2(g)$, $CO_2(aq)$, $H_2CO_3(aq)$, $HCO_3^-(aq)$, and $CO_3^{2-}(aq)$ which occur along with metal ions in aqueous solutions.

The numerous complex problems associated with the hydration of CO_2 are recognized since 1912,[4] and these have been extensively reviewed.[5,6] The kinetics of the hydration of carbon dioxide and the dehydration of carbonic acid have been studied by a variety of techniques such as manometric and rapid mixing methods,[7-10] ^{14}C-tracer studies,[11] ^{18}O-isotope fractionations studies,[12] nmr studies,[13] hydration under conditions of enforced stationarity,[14] relaxation methods,[15] enzyme-catalyzed studies,[16,17] and other catalysis studies by inorganic ions[18-22] (see under section III.D).

Many of the simple carbonates are amorphous powders, the colors of which depend on the cation, and are generally insoluble in water. The solubility data are available for some carbonates, and the solubility product constants reported in literature differ widely for each metal carbonate and usually range from $\sim10^{-2}$ to $\sim10^{-30}$ for most carbonates. All carbonates, both naturally occurring and laboratory preparations, readily dissolve in acids with the evolution of CO_2 and in excess carbonate to form suitable carbonato complexes, some of which exhibit bewildering complexity. Not much is known concerning the mixed hydroxo carbonato complexes of even the most common metals. The solubility characteristics of the carbonates in excess carbonate are therefore of particular interest to the geochemist specializing in sediments as carbonate rocks represent nearly 20% of all sedimentary matter.[23]

Among the more common naturally occurring carbonates are[24] $CaCO_3$ (calcite, aragonite), $MgCO_3$ (magnesite), and $CaMg(CO_3)_2$ (dolomite). Of commercial interest are several anhydrous normal carbonate minerals: $FeCO_3$ (siderite), $MnCO_3$ (rhodochrosite), $CoCO_3$ (cobalto-calcite), $ZnCO_3$ (smithsonite), $CdCO_3$ (otavite), $SrCO_3$ (strontianite), $BaCO_3$ (witherite), and $PbCO_3$ (cerussite). In addition are the acid carbonates and the hydrated normal carbonates like $NaHCO_3$ (nacholite), $KHCO_3$ (kalcinite), $(NH_4)HCO_3$ (teschemacherite), $Na_3H(CO_3)_2\cdot 2H_2O$ (trona), $Na_2CO_3\cdot H_2O$ (thermonatrite), $MgCO_3\cdot 3H_2O$ (nesquehonite), and $Na_2CO_3\cdot 10H_2O$ (natron). To this list also belong several hydrated normal carbonates that contain U along with Na, Mg, Ca, and other metals. Schroeckingerite has an interesting composition: $NaCa_3(UO_2)(CO_3)_3SO_4F\cdot 10H_2O$. Several basic carbonates are known to contain OH^- and in certain special minerals F^-, Cl^-, and SO_4^{2-} as well: $Zn_5(CO_3)_2(OH)_6$ (hydrozincite), $Cu_2(CO_3)\cdot(OH)_2$ (malachite), $Cu_3(CO_3)_2(OH)_2$ (azurite), $Mg_4(CO_3)_3(OH)_2\cdot 3H_2O$ (hydromagnesite), and $Pb_2(CO_3)Cl_2$ (phosgenite).

III. Carbonato Complexes

A. GENERAL CLASSIFICATION

A convenient classification for the study of metal complexes based on the number of ligand groups coordinated to the central metal ion has been found useful in the case of oxalates.[25] However, a clear-cut classification based on the number of carbonate groups coordinated can only have limited usefulness in view of the quasi-bidentate nature of the ligand itself as also the not-so-well understood aquocarbonato complexes containing one or more carbonate groups. One such example is that of nesquehonite: $MgCO_3\cdot 3H_2O$ or $Mg(OH)(HCO_3)\cdot 2H_2O$ (see under thermal decomposition studies). Although only a very small number of carbonato complexes are prepared with ease in the solid state by dissolving the carbonate in excess alkali carbonates, for example, $Na_3Co(CO_3)_3\cdot 3H_2O$,[26] a great majority of mixed ligand monocarbonato complexes can be obtained more readily from the *cis*-dichloro compound by a reaction with slurried Ag_2CO_3. Tables I, II, and III[27-94] show respectively the classification

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Table I

Ion-Pair and Chelated-Type Carbonato Complexes

Class	*Species*	*Metal complex and references*	
Ia	$MHCO_3^+$	$MgHCO_3^+$ (27–30)	$MnHCO_3^+$ (31)
		$CaHCO_3^+$ (27, 28)	$NaHCO_3^0$ (27, 28)
			$Ca(HCO_3)_2^0$ (27, 28, 33)
Ib	MCO_3^0	$MgCO_3^0$ (27, 28)	$CuCO_3^0$ (32)
		$CaCO_3^0$ (27, 28)	
Ic	MCO_3^-	$NaCO_3^-$ (27, 28)	
		$PuCO_3^{2+}$ (34, 35)	
IIa	$M(CO_3)_2^-$	$Ce(CO_3)_2^-$ (36)	$Sc(CO_3)_2^-$ (37)
IIb	$M(CO_3)_2^{2-}$	$Be(CO_3)_2^{2-}$ (38)	$ZrO(CO_3)_2^{2-}$ (41)
		$Cu(CO_3)_2^{2-}$ (39)	$UO_2(CO_3)_2^{2-}$ (42, 43)
		$Pb(CO_3)_2^{2-}$ (39, 40)	$PuO_2(CO_3)_2^{2-}$ (44)
IIc	$M(CO_3)_2^{3-}$		
IIIa	$M(CO_3)_3^{2-}$		
IIIb	$M(CO_3)_3^{3-}$	$Co(CO_3)_3^{3-}$ (45)	
IIIc	$M(CO_3)_3^{4-}$	$Cd(CO_3)_3^{4-}$ (46)	$UO_2(CO_3)_3^{4-}$ (47)
			$PuO_2(CO_3)_3^{4-}$ (48, 49)
IIId	$M(CO_3)_3^{5-}$	$AmO_2(CO_3)_3^{5-}$ (48, 49)	
IVa	$M(CO_3)_4^{4-}$	$Ce(CO_3)_4^{4-}$ (50)	$Th(CO_3)_4^{4-}$ (51)
			$Pu(CO_3)_4^{4-}$ (52)
IVb	$M(CO_3)_4^{5-}$	$Sc(CO_3)_4^{5-}$ (37, 53)	$Ce(CO_3)_4^{5-}$ (54)
			$Pr(CO_3)_4^{5-}$ (55)
			$Nd(CO_3)_4^{5-}$ (55)
			$Pm(CO_3)_4^{5-}$ (55, 56)
			$Sm(CO_3)_4^{5-}$ (55, 57)
			$Eu(CO_3)_4^{5-}$ (55, 57)
			$Er(CO_3)_4^{5-}$ (58)
V	$M(CO_3)_5^{6-}$	$Mo(CO_3)_5^{6-}$ (59)	$Th(CO_3)_5^{6-}$ (60–62)
			$Pu(CO_3)_5^{6-}$ (63)
VI	$M(CO_3)_6^{8-}$	$Ce(CO_3)_6^{8-}$ (64)	$Be_4O(CO_3)_6^{2-}$ (65)
	$M(CO_3)_8^{12-}$	$Th(CO_3)_8^{12-}$ (48)	
		$Pu(CO_3)_8^{12-}$ (63)	

Table II

Mixed-Ligand-Type Complexes[a]

Species	*Ref*	*Species*	*Ref*
$Co(NH_3)_4CO_3^+$	66	$Co(NO_2)_4CO_3^{3-}$	86
$Co(NH_3)_5CO_3^+$	67–69	$Co(NH_3)(NO_2)_3CO_3^{2-}$	87
$Co(en)_2CO_3^+$	70	$Co(NH_3)(CH_3COO)_3CO_3^{2-}$	87
$Co(pn)_2CO_3^+$	71	$Co(en)(CO_3)_2^-$	88
$Co(tn)_2CO_3^+$	73	$Pu(CO_3)_2C_2O_4^{2-}$	48
$Co(trien)CO_3^+$	74–78	$Pu(CO_3)_2(C_2O_4)_2^{4-}$	48
$Co(dan)_2CO_3^+$	79	$Pu(CO_3)_3C_2O_4^{4-}$	48
$Co(dipy)_2CO_3^+$	80	$Pu(CO_3)_3(C_2O_4)_2^{6-}$	48
$Co(o\text{-phen})_2CO_3^+$	81	$Pu(CO_3)_4(C_2O_4)_3^{10-}$	48
$Co(C_{16}H_{32}N_4)CO_3^+$	82, 83	$PuCO_3(C_2O_4)_7^{12-}$	48
$Co(NH_3)_2(NO_2)_2CO_3^-$	84	$Sc_2(CO_3)_4(C_2O_4)_3^{8-}$	53
$Co(en)(NH_3)_2CO_3^+$	85		

[a] Mixed-ligand-type carbonato complexes of metals containing OH and H_2O are known and are discussed in detail in the appropriate sections of this review. Abbreviations: en, ethylenediamine; pn, propylenediamine; tn, trimethylenediamine; trien, triethylenetetramine; dan, neopentanediamine (2,2-dimethyltrimethylenediamine); dipy, 2,2′-dipyridyl; *o*-phen, 1,10-*o*-phenanthroline; $C_{16}H_{32}N_4$, 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene (Schiff base).

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Table III

Addition Complexes

Complex	*Ref*	*Complex*	*Ref*
$(CH_3)_3SbCO_3$	89	$SnCl_4 \cdot 2C_2H_4CO_3$	92
$(CH_3)_2SnCO_3$	90	$SnCl_4 \cdot (C_2H_5)_2CO_3$	93
$(C_6H_5)_5CrCO_3H \cdot 3H_2O$	91	$SnCl_4 \cdot 2(C_2H_5)_2CO_3$	92
$[(C_6H_5)_5Cr]_2CO_3 \cdot 6H_2O$	91	$SbCl_5 \cdot (CH_3)_2CO_3$	94
$TiCl_4 \cdot 2C_2H_4CO_3$	92	$SbCl_5 \cdot (C_2H_5)_2CO_3$	94

as (a) ion-pair and chelated carbonato complexes, (b) mixed ligand type carbonato complexes, and (c) addition complexes.

B. STRUCTURE

Because of the unique nature of the carbonate ligand several ingenious methods have been reported for the elucidation of the structure of the carbonato complexes. Manometric measurement of liberated CO_2 offers a method in itself for establishing the stoichiometry of the complex. Among the many physico-chemical methods employed in the study of these coordination compounds are electrical conductance measurement, potentiometry, polarography, ion-exchange, elution chromatography, radioisotope techniques, electrophoresis, absorption spectroscopy, magnetic susceptibility measurements, X-ray crystallography, reaction kinetics, isotope exchange, and thermogravimetric analysis.

1. Preparative Chemistry

Although identification and characterization of several carbonato complexes reported in Table I have been done routinely by one or more methods that are usually complimentary, isolation in solid form is always desirable from the standpoint of structural investigations. Table IV[95–101] shows the reported compounds. It can be seen that the great majority of the carbonato complexes have been isolated as the sodium or potassium salts, and in special cases recourse is made to certain organic ions like the guanidinium ion ($CH_5N_3H^+$) and complex ions like $Co(NH_3)_6^{3+}$. Whether these cations impart additional stability to the carbonato complex ion or simply affect the solubility properties is not fully understood.

The reported occurrence of a large number of cobalt(III) complexes, both the cationic and the anionic type (see Tables II and III) in solution and in solid state is indicative of the extent of interest on the carbonato complexes in general. Some of these are used as starting materials in preparative chemistry for the synthesis of exotic coordination compounds. The reaction scheme shown in Figure 1 illustrates the many applications of the intermediate: $Co(CO_3)_3^{3-}$.

Cobalt(II) solutions on treatment with excess HCO_3^- and H_2O_2 yield a green solution indicating the presence of a carbonato complex. Various unrelated formulas have been suggested since early 1900, for example, K_3CoO_3,[102] $(KCO_2\text{–}O)_2\text{-}Co\text{–}O\text{–}Co(O\text{–}CO_2K)_2$,[103] $Co(OH)_4(COOH)_2$,[104] and $Co[Co(CO_3)_3]$.[105] The absorption maxima of the green solution were found to be at 260 and 440 mμ, the latter being weak. An analytical method for determining cobalt makes use of the uv maximum.[106]

Although $Co(CO_3)_3^{3-}$ was postulated earlier[107,108] than the isolation of $[Co(NH_3)_6][Co(CO_3)_3]$[45] in the solid form, the bidentate character of carbonate ligand attracted much attention and other preparations followed: $K_3[Co(CO_3)_3] \cdot 3H_2O$,[109] $Na_3[Co(CO_3)_3] \cdot 3H_2O$.[26] Furthermore the ability of the compound, $[Co(NH_3)_5CO_3]NO_3 \cdot H_2O$,[109] to lose water without disruption of the structure also gave impetus to the synthesis of several cobalt mixed ligand type complexes (see Tables II and IV). Spectral studies and kinetic studies soon followed to confirm the presence of chelated coordinated carbonate in several cobalt amine complexes, and these are discussed in this review at the appropriate place.

The reaction between Co(II), HCO_3^-, and H_2O_2 giving the green colored solution is known as the *Field–Durant reaction*.[103,110] Figure 1 illustrates the application of the green solution for a variety of syntheses. An extension of the method using a solution of $K_3Co(CO_3)_3$ as starting material yielded the following compounds: potassium carbonatoammoniatriacetatocobaltate(III),[111] potassium carbonatoethylenediaminediacetatocobaltate(III),[112] potassium tungstoco-

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Table IV

Metal Carbonato Complexes Isolated in Solid Form

Complex	*Remarks*	*Ref*
$Na_6[Be_4O(CO_3)_6]\cdot 5H_2O$	White, crystalline	95
$K_6[Be_4O(CO_3)_6]$	White, crystalline	95
$[Co(NH_3)_6][Be_4O(CO_3)_6]\cdot 10$ or $11H_2O$	Orange, crystalline	95
$NH_4[Sc(CO_3)_2]\cdot H_2O$ (1.5–2.0 H_2O)	Sparingly soluble	96
$(CH_5N_3H)_5[Sc(CO_3)_4]\cdot 5H_2O$	Hydrolyzes readily	53
$K_8[Sc_2(CO_3)_4(C_2O_4)_3]\cdot 6H_2O$	White, noncrystalline	53
$Na_8[Sc_2(CO_3)_4(C_2O_4)_3]\cdot 8H_2O$	White, noncrystalline	53
$(CH_5N_3H)_2[Sc_2(CO_3)(C_2O_4)_3]\cdot 3H_2O$	Hydrolyzes readily	53
$(CH_5N_3H)_2[Sc_2(CO_3)_2(C_2O_4)_3]\cdot H_2O$	Hydrolyzes readily	53
$K_6Mo(CO_3)_5\cdot 2H_2O$	White ppt	59
$(NH_4)_2[ZrO(CO_3)_2]\cdot 3H_2O$	White ppt	41
$Na_2[Cu(CO_3)_2]\cdot 3H_2O$		97
$K_2[Co(CO_3)_2]\cdot 4H_2O$		97
$Na[Ce(CO_3)_2]\cdot 2H_2O$	White ppt	54
$NH_4[Ce(CO_3)_2]\cdot 3H_2O$	White ppt	54
$(CH_5N_3H)[Ce(CO_3)_2]\cdot 2H_2O$	Insoluble	54
$(CH_5N_3H)_5[Ce(CO_3)_4]\cdot 2H_2O$	Dark red rods	54
$[Co(NH_3)_6]_5[Ce(CO_3)_4]\cdot 15H_2O$	Orange crystalline	54
$(NH_4)_5[Co(NH_3)_6]_3[Ce(CO_3)_5]_2\cdot 12H_2O$	Orange crystals	54
$(CH_5N_3H)_5[Co(NH_3)_6]_3[Ce(CO_3)_5]_2\cdot 12H_2O$	Orange crystals	54
$(CH_5N_3H)_4[Ce(CO_3)_4(H_2O)_2]\cdot 4H_2O$	Yellow needles	98
$(NH_4)_2(CH_5N_3H)_2[Ce(CO_3)_4(H_2O)_2]$		98
$Na_6[Ce(CO_3)_5H_2O]\cdot 11H_2O$	Bright yellow crystals	98
$K_6[Ce(CO_3)_5H_2O]\cdot H_2O$	Fine yellow crystals	98
$[Co(NH_3)_6]_2[Ce(CO_3)_5H_2O]\cdot 5H_2O$	Also tetrahydrate	98
$(CH_5N_3H)_6[Ce(CO_3)_5H_2O]\cdot H_2O$	Yellow plates	98
$(NH_4)(CH_5N_3H)_5[Ce(CO_3)_5H_2O]\cdot 4H_2O$		98
$(NH_4)_2[Co(NH_3)_6]_2[Ce(CO_3)_6]\cdot 4H_2O$	Rhombic crystals	98
$Na_5[Er(CO_3)_4]\cdot 18H_2O$		99
$[Co(o\text{-phen})_2CO_3]Cl\cdot 5H_2O$	Dark red crystals	81
$[Co(o\text{-phen})_2CO_3]Br\cdot 4H_2O$	Red crystalline	81
$[Co(o\text{-phen})_2CO_3]I$	Orange needles	81
$[Co(o\text{-phen})_2CO_3]NCS\cdot 3H_2O$	Brick-red ppt	81
$[Co(o\text{-phen})_2CO_3]NO_3\cdot 3H_2O$	Brick-red crystals	81
$[Co(o\text{-phen})_2CO_3]NO_2\cdot 4H_2O$	Red-brown crystalline	81
$[Co(o\text{-phen})_2CO_3]ClO_3$	Brownish red crystals	81
$[Co(o\text{-phen})_2CO_3]ClO_4$	Orange-red crystalline	81
$[Co(o\text{-phen})_2CO_3]BrO_3$	Red crystals	81
$[Co(o\text{-phen})_2CO_3]IO_4$	Pink crystalline	81
$[Co(o\text{-phen})_2CO_3]_2S_2O_6\cdot 7H_2O$	Red crystals	81
$[Co(o\text{-phen})_2CO_3]_2S_2O_8\cdot 5H_2O$	Red crystals	81
$[Co(dipy)_2CO_3]_2CO_3$		80
$Na_3[Co(NO_2)_4CO_3]\cdot 6H_2O$	Dark yellow crystalline	86
$[Co(NH_3)_6][Co(NO_2)_4CO_3]$	Orange crystalline	86
$[Co(NH_3)_6][Co(NO_2)_2(CO_3)_2]\cdot 2H_2O$	Dark red crystals	86
$Na_3[Co(NO_2)_2(CO_3)_2]\cdot 4H_2O$	Dark red crystals	86
$[Co(en)_3][Co(NO_2)_2(CO_3)_2]\cdot 3H_2O$	Dark red crystals	86
$K_3[Co(CO_3)_3]\cdot 3H_2O$	Green crystals	100
$Na_3[Co(CO_3)_3]\cdot 3H_2O$	Green crystals	26
$[Co(NH_3)_6][Co(CO_3)_3]$	Dark green needles	45, 86
$[Co(NH_3)_6]_2[Co_2(NO_2)_6(CO_3)_3]\cdot 3H_2O$	Dark yellow crystals	86
$[Co(en)_3]_2[Co_2(NO_2)_6(CO_3)_3]\cdot 5H_2O$	Dark red plates	86
$Cs_6[Co_2(NO_2)_6(CO_3)_3]\cdot 5H_2O$	Orange crystalline	86
$[Co(trien)CO_3](C_6H_5)_4B$	Orange precipitate	73
$K[Co(NH_3)_2(NO_2)_2CO_3]\cdot 2H_2O$	Dark red crystals	101
$(CH_5N_3H)[Co(NH_3)_2(NO_2)_2CO_3]$	Orange needles	101
$[Co(NH_3)_6][Co(NH_3)_2(NO_2)_2CO_3]_3\cdot 3H_2O$	Orange crystals	101
$[Co(en)_3][Co(NH_3)_2(NO_2)_2CO_3]_3\cdot 6H_2O$	Dark red crystals	101

baltate(III),[113] a series of cobalt(III) complexes with the general formula $[Co(NO_2)_n(NH_3)_{6-n}]^{3-n}$ (n = 1-5),[114] and another series of the type, $[Co(CN)_n(NH_3)_{6-n}]^{3-n}$.[114] An interesting compound, $K_2[CoNH_3(NO_2)_3CO_3]\cdot H_2O$, was one

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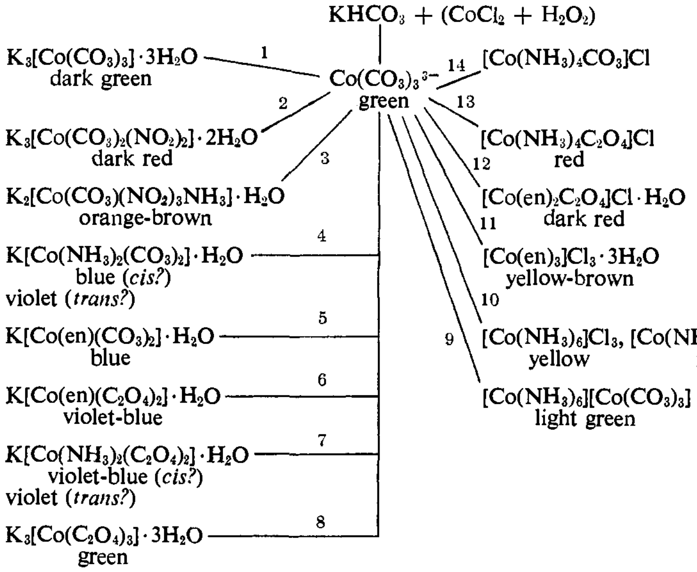

Figure 1. Synthetic applications of the $Co(CO_3)_3^{3-}$ ion. Reagents used and references (in parentheses): 1, crystallization (100); 2, KNO_2 (141); 3, $NH_4Cl + NaNO_2 + HC_2H_3O_2$ (114); 4, $(NH_4)_2CO_3$ (100); 5, enH_2CO_3 (100), 6, $enH_2CO_3 + K_2C_2O_4$ (100); 7, $(NH_4)_2C_2O_4$ (100); 8, $H_2C_2O_4$ (100); 9, $Co(NH_3)_6^{3+}$ (100); 10, $NH_3 + NH_4Cl$ (100); 11, en + KCl (100); 12, $enH_2C_2O_4$ + KCl (100); 13, $NH_3 + (NH_4)_2C_2O_4$ (100); 14, $NH_4Cl + NaHCO_3$ (100).

of the products obtained in the series studied, and this occurs in several isomeric structures.

The sodium salt, $Na_3[Co(CO_3)_3]\cdot 3H_2O$, has certain advantages over the potassium salt in that it is more insoluble and easier to purify it from bicarbonate ion contamination. In any case both are useful synthetic intermediates. The following compounds have been prepared in good yields, shown in parentheses, starting from $Na_3[Co(CO_3)_3].3H_2O$ and by simple reaction sequence:[26] (a) tris(ethylenediamine)cobalt(III) chloride (91%); (b) tris(acetylacetonato)cobalt(III) (95%); (c) tris(benzoylacetonato)cobalt(III) (81%); (d) tris-(1,3-diamino-2-propanol)cobalt(III) nitrate (79%); (e) tris-(*o*-aminophenol)cobalt(III) (88%); (f) sodium tris(mercaptoacetato)cobaltate(III) (85%); (g) tris(ethylenediamine)cobalt(III) tris(salicylato)cobaltate(III) (15%); and (h) sodium tris-(ethylenediamine)mercaptocobaltate(III) (95%). Recently an interesting mixed ligand type complex containing a macrocyclic Schiff base has been prepared by the following reaction.

$$Na_3[Co(CO_3)_3]\cdot 3H_2O + C_{16}H_{32}N_4\cdot 2HClO_4 \longrightarrow$$

$$\text{(macrocyclic Schiff base)} \quad [Co(C_{16}H_{32}N_4)CO_3]ClO_4$$

$$\text{(large red crystals)}$$

The mixed ligand type carbonato complexes of cobalt(III) are useful as synthetic intermediates in developing new reagents for use in biological chemistry,[115] for example, β-$[Co(trien)CO_3]^+$,[116] in the preparation of β-$[Co(trien)(A)]^{2+}$, where A = glycine, *l*-alanine, *l*-phenylalanine, *l*-leucine, *l*-isoleucine, *l*-hydroxyproline, and *l*-valine.[115] Other mixed ligand type complexes such as tetracidomonocarbonato- and diacidomonocarbonatodiammine are potential synthetic intermediates. By treating Erdmann's salt, $NH_4[Co(NH_3)_2(NO_2)_4]$,[117] with aqueous saturated $KHCO_3$ solution an interesting compound, $K[Co(NH_3)_2(NO_2)_2CO_3]\cdot 2H_2O$, has been prepared.[118] This is illustrative of a replacement reaction in which a four-membered chelate ring is made from initially all monodentate complex by a simple method. It can also be explained in terms of the *trans*-effect in view of NH_3 groups present *trans* to each other in Erdmann's salt.

The simplest beryllium carbonato complex, $Be(CO_3)_2^{2-}$, analogous to the alkaline earth carbonato complexes has never been isolated in the solid form although from ion-exchange experiments it is reported to occur in 0.1 *M* $(NH_4)_2CO_3$ solutions.[38] In carbonate solutions $Be(OH)_2$ dissolves to give a variety of basic beryllium carbonates, $3K_2Be(CO_3)_2\cdot Be(OH)_2$,[119] $3(NH_4)_2Be(CO_3)_2\cdot Be(OH)_2$,[119] $2(NH_4)_2Be(CO_3)_2\cdot Be(OH)_2$,[120] which are not well characterized. Conductometric titration studies made recently[95] support the equilibrium

$$4Be(CO_3)_2^{2-} + H_2O = [Be_4O(CO_3)_6]^{2-} + 2HCO_3^-$$

The corresponding sodium and potassium salts, $Na_6[Be_4O(CO_3)_6]\cdot 5H_2O$ and $K_6[Be_4O(CO_3)_6]$, have been isolated although the ammonium salt was found to be too unstable. A closely related compound, $[Co(NH_3)_6][(H_2O)_2Be_2(CO_3)_2(OH)_3]\cdot 3H_2O$, offers itself as a method for the gravimetric determination of Be(II).[121-123]

Scandium hydroxide dissolves in $(NH_4)_2CO_3$ to yield a stable crystalline complex, $(NH_4)Sc(CO_3)_2\cdot 1.5H_2O$.[96] At higher solution temperatures and increased ammonium carbonate concentrations, the product obtained is a dihydrate which is amorphous and less stable than the sesquihydrate. Several mixed carbonato-oxalato scandium complexes have been prepared recently for the first time,[53] and they are shown in Table IV.

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Tetranuclear complexes of the type $[Fe_4O_3(CO_3)_6]^{6-}$ account for the solubility of Fe(III) salts in excess carbonate solutions. The following compounds have been isolated in the solid state: $H_6[Fe_4O_3(CO_3)_6]$, $(NH_4)_6[Fe_4O_3(CO_3)_6] \cdot 4H_2O$, $[(NH_2)_2C{=}NH_2]_6[Fe_4O_3(CO_3)_6] \cdot 2H_2O$, $[Co(NH_3)_6]_2[Fe_4O_3(CO_3)_6](aq)$. Although Cr(III) salts dissolve in excess carbonate, no carbonato chromium complex is known. On prolonged standing the blue-violet solutions of Cr(III) carbonate become turbid blue gels prior to losing water. Mixtures of Fe(III) and Cr(III) carbonate, however, yield fine bluish-gray precipitates of constant Fe:Cr composition close to 1 : 0.2, an observation that needs further study.[124]

No carbonato complex of rhodium(III) has been prepared although the synthesis of several compounds containing the $Rh(A_m)Cl_2^+$, where A = NH_3·ethylenediamine, *meso*-butylenediamine, *dl*-butylenediamine, tetramethylenediamine, β,β',β''-triaminoethylamine, and triethylenetetramine, has been reported recently.[125] Attempts to prepare $Rh(en)_2CO_3^+$ starting from *cis*-$Rh(en)_2Cl_2^+$ and Ag_2CO_3 were unsuccessful.[126]

Several nonstoichiometric zirconium-carbonato complexes[127,128] are known to occur when precipitated basic zirconium carbonate is dissolved in excess carbonate. The solubility of the zirconium basic carbonates has been interpreted in terms of coordination by the carbonate ligand and in terms of a stable ionic dimeric species, $Zr_2O_3^{2+}$, occurring in solution.[129] Hydrous zirconia absorbs CO_2 to yield a material that exhibits cation-exchange properties[130] and a carbonato complex of the type $Na[Zr(OH)_3CO_3]$ seem to account for the observed ion exchange behavior.[131] However, a stable carbonate complex, $(NH_4)_2[ZrO(CO_3)_2] \cdot 3H_2O$,[41] has been reported recently.

The rare earth carbonates and their solubility in excess alkali carbonates were recognized since early 1800, and until today it is still a matter of conjecture as to the exact nature of the species present in aqueous solutions. The case of cerium is even more confusing with conflicting reports appearing in literature.[54,98,132,133] However, the various compounds listed in Table IV have been prepared and characterized in the solid state. Recent work from one of our laboratories[134] using elution chromatography and radiotracer methods indicates rare earth (RE) complexes of the form, $[RE(CO_3)_4]^{5-}$, except in the case of cerium. The rare earths studied were Pr(III), Nd(III), Pm(III), Sm(III), and Eu(III). There is experimental evidence to show that Ce is in the +4 oxidation state in the cerium complex when one uses alkali carbonates in forming the carbonato complex. However, guanidinium salts of the formulas, $(CH_5N_3H)_5[Ce(CO_3)_4] \cdot 2H_2O$ and $(CH_5N_3H)_4[Ce(CO_3)_4(H_2O)_4] \cdot 4H_2O$, are prepared and characterized[98] in support of both Ce(III) and Ce(IV) carbonato complexes. These compounds provide interesting examples for studying the unusual coordination number of cerium and the possibility of isomerism.

Spectrophotometric investigations[56] also support the formation of carbonato complexes of the type $M(CO_3)_4^{5-}$ for most of the rare earths: Nd(III), Pr(III), Sm(III), Er(III), Ho(III), and Eu(III). Additional evidence derives from polarographic studies for Eu(III).[58] A solid with the composition $Na_5Er(CO_3)_4 \cdot 18H_2O$ has been isolated.[56]

The carbonato complexes of the actinide elements show some unusual aspects of coordination chemistry. Coordination numbers of 5, 8, or even higher may be possible. Thorium(IV) forms mostly pentacarbonate hydrates, $M_6Th(CO_3)_5 \cdot xH_2O$, and attempts to prepare the hexacarbonatothorates have not been successful.[62] Extensive literature on the carbonato complexes of U(VI) is available,[49,135–139] parts of which are discussed under determination of stability constants. The complex ions $UO_2(CO_3)_2(H_2O)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$ are well characterized and widely used in technology and in analysis.

Several tetra-, penta-, and octacarbonato complexes of plutonium are known, and the general area of the complex compounds of the transuranium elements is reviewed in a recent monograph.[48] There is strong indication that the coordination number of the +4 state of Th, U, Np, and Pu in the carbonato as well as the oxalato complexes is 8. Mixed oxalato-carbonato complexes of Pu(IV) and Pu(VI) are known and are discussed under replacement reactions.

Americium(III), -(V), and -(VI) and Cm(III) are also known to form carbonato complexes and some of them serve as methods of separation from each other.[140]

2. *Isomerism*

The coordination capacity of the carbonate ion in a given complex compound imposes certain restrictions regarding its stereochemistry. The quasi-bidentate nature of the carbonate ligand is apparent in the case of certain cerium(IV) complexes[64] illustrated in Figure 2. Accordingly, *cis–trans* and

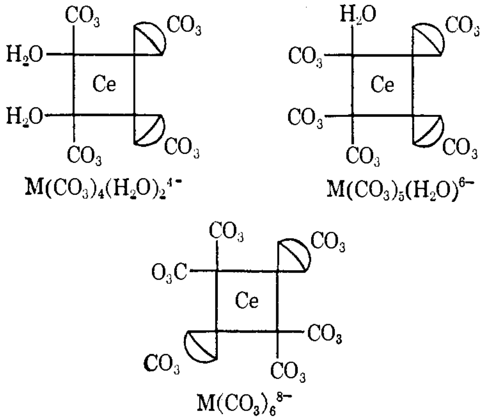

Figure 2. Quasi-bidentate carbonate ligand.

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optical isomerism are possible from a theoretical standpoint in several carbonato complexes. In practice, however, since most of the carbonates are synthesized under fairly alkaline conditions (unlike the related oxalato complexes), there is always the possibility of contamination by the aquo and the hydroxo species in addition to the carbonato compound, making separation and isolation not an easy task. Hence studies on *cis–trans* isomerism are limited in their scope.

a. *cis–trans* Isomerism

The *cis*-dinitrobiscarbonatocobaltate(III) ion has been isolated in the solid state as the following compounds:[86] $Na_3[Co(NO_2)_2(CO_3)_2]\cdot 4H_2O$, $[Co(NH_3)_6][Co(NO_2)_2(CO_3)_2]\cdot 2H_2O$, and $[Co(en)_3][Co(NO_2)_2(CO_3)_2]\cdot 3H_2O$. Evidence for the corresponding *trans* compound derives mostly from preparative chemistry.[141] Figure 3 illustrates the *cis–trans* isomerism in a typical biscarbonato complex and Figure 4 shows a flow diagram for the complete synthesis of a typical mixed ligand type *trans*- and *cis*-carbonato complex starting from $CoCl_2\cdot 6H_2O$.[142] The *cis* isomer has a higher absorbance than the *trans* in keeping with the earlier observations on the spectral characteristics of *cis–trans* isomers of a number of cobalt(III) complexes.[143] Table V shows the optical properties of *cis–trans* isomers of two selected carbonato complexes. Among the cobalt(III) amine biscarbonato complexes the blue salt is usually the *cis* variety, whereas the violet salt obtained from the *cis* isomer is the *trans* compound. Figure 5 illustrates the application of preparative chemistry in the elucidation of *trans–cis* isomerism in the carbonato complexes.

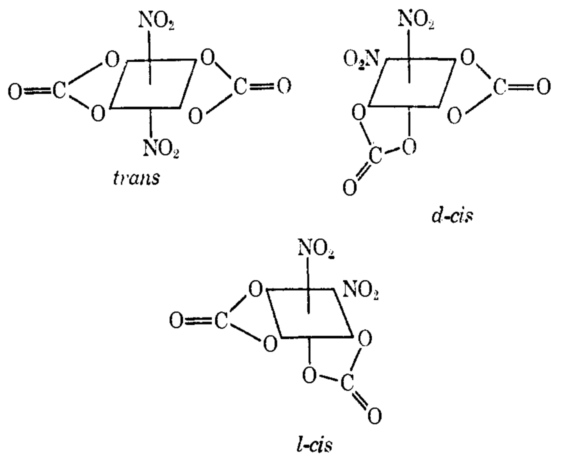

Figure 3. *cis–trans* isomerism in bis-carbonato complexes.

Table V

Optical Properties of *cis–trans* Isomers

Species	*Wavelength* λ_{max}, $m\mu$	*Absorbance*, a_m	*Ref*
cis-$[Co(NH_3)_2enCO_3]^+$	504	125	142
	347	148	
trans-$[Co(NH_3)_2enCO_3]^+$	512	95	142
	356	103	
cis-$[Co(NH_3)_2(CO_3)_2]^-$	575	138	88
	390	251	
trans-$[Co(NH_3)_2(CO_3)_2]^-$	540	63	88
	374	111	

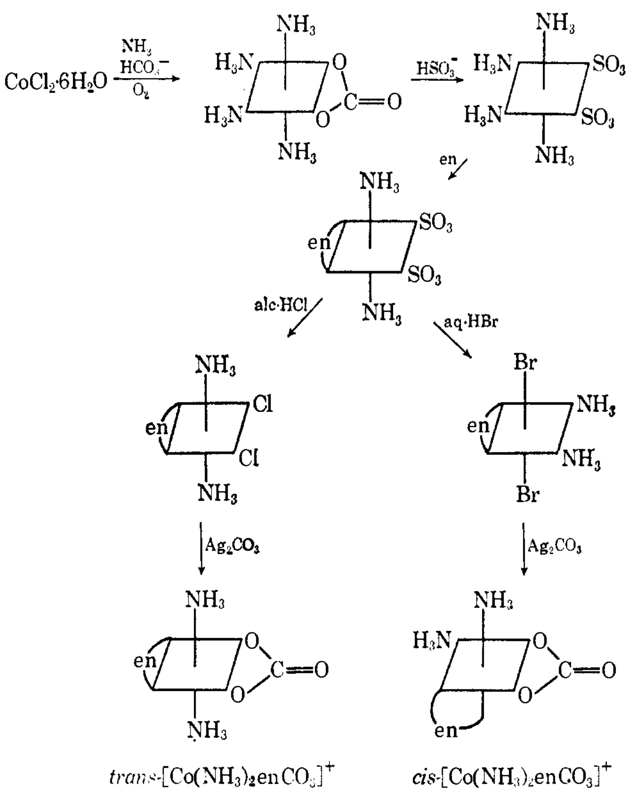

Figure 4. Synthesis of *cis*- and *trans*-carbonato complexes.

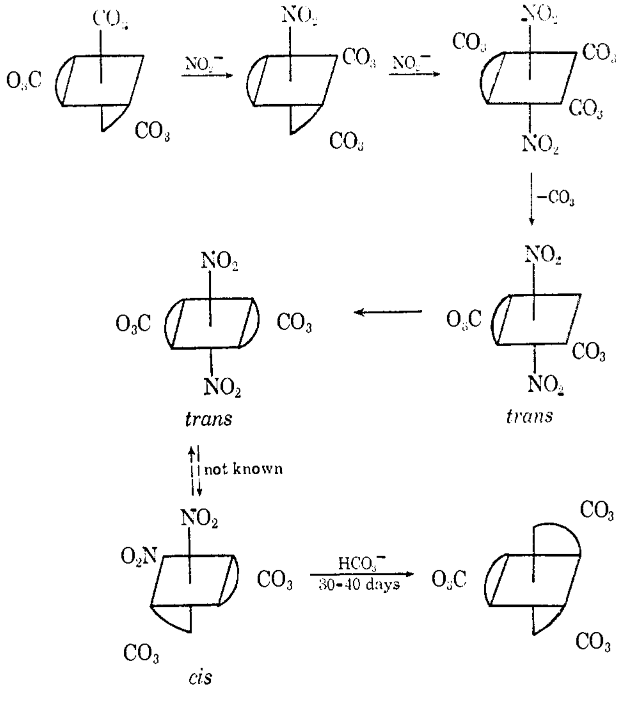

Figure 5. Reaction between $Co(CO_3)_3^{3-}$ and NO_2^- ions.

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Table VI

Ultraviolet Absorption Spectra of Metal Carbonato Complexes

Carbonato complex	λ_{max},[a] $m\mu$	a_m	*Ref*
HCO_3^-	210–230	Weak	159, 160
Na_2CO_3 (aq)	220 (sh)	~10–100	159, 160
Ethylene carbonate	270 (sh)		161
Propylene carbonate	270 (sh)		161
Propylene carbonate (aq soln)	223 (sh)		161
Propylene carbonate (ethanolic solution)	270 (sh)		161
$[Co(en)_2CO_3]^+$	238		161
	250 (s)		
$[Co(pn)_2CO_3]^+$	238		161
	248 (s)		
$[Co(tn)_2CO_3]^+$	238		161
	250 (s)		
$[Co(NH_3)_4CO_3]^+$	238		161
	258 (s)		
$[Co(NH_3)_5CO_3]^+$	233 (sh)		
	250–280 (s) (sh)		161
$[Co(o\text{-phen})_2CO_3]^+$	274	$\sim 6.3 \times 10^4$	81
$[Co(dipy)_2CO_3]^+$	...	...	80
cis-$[Co(NH_3)_2(CO_3)_2]^-$	220	1.38×10^4	100
trans-$[Co(NH_3)_2(CO_3)_2]^-$	234	2.00×10^4	100
cis-$[Co(NH_3)_2enCO_3]^-$	243	1.66×10^4	162
trans-$[Co(NH_3)_2enCO_3]^+$	235	1.41×10^4	162
$[Co(CO_3)_3]^{3-}$	260	$\sim 10^6$	100, 106
$[Co(NH_3)(NO_2)_3CO_3]^{2-}$	259	2.57×10^4	114
α-$[Co(trien)CO_3]^+$	250	$\sim 1.2 \times 10^4$	116
β-$[Co(trien)CO_3]^+$	250	$\sim 1.2 \times 10^4$	116
cis-$[Co(en)(CO_3)_2]^-$	239	2.88×10^4	88
trans-$[Co(en)(CO_3)_2]^-$	231	1.95×10^4	88
$[CoACo_3]^+$	243	1.6×10^4	82
$(A = C_{16}H_{32}N_4)$	192	$\sim 10^4$	

[a] s = solid; sh = shoulder.

Table VII

Visible Absorption Spectra of Metal Carbonato Complexes

Carbonato complex	λ_{max}, $m\mu$	a_m	*Ref*
$[Co(CO_3)_3]^{3-}$	440	166	100
	635	154	
$[Co(en)_2CO_3]^+$	358	120	163
	512	127	
$[Co(pn)_2CO_3]^+$	357	122	163
	515	133	
$[Co(tn)_2CO_3]^+$	360	128	163
	520	109	
		(α) (β)	
$[Co(trien)CO_3]^+$	360	112 140	116
(α, β forms)	510	140 180	
$[Co(o\text{-phen})_2CO_3]^+$	350	2000	81
	510	100	
$[Co(dipy)_2CO_3]^+$	...	...	80
$[Co(NH_3)_5CO_3]^+$	(348)	(160)	161
	505	94	164
$[Co(NH_3)_4CO_3]^+$	362	122	142
	522	104	
	520	105	164a
cis-$[Co(NH_3)_2(CO_3)_2]^-$	390	251	88
	575	138	
trans-$[Co(NH_3)_2(CO_3)_2]^-$	374	110	88
	540	63	
cis-$[Co(NH_3)_2enCO_3]^+$	347	148	142
	504	125	
trans-$[Co(NH_3)_2enCO_3]^+$	356	103	142
	512	95	
$[Co(NH_3)(NO_2)_3CO_3]^{2-}$	347	7413	114
	472	219	
cis-$[Co(en)(CO_3)_2]^-$	390	214	88
	570	148	
trans-$[Co(en)(CO_3)_2]^-$	388	204	88
	559	87	
$[CoACO_3]^+$	350	135	82
$(A = C_{16}H_{32}N_4)$	500	121	

b. Optical Isomerism

Additional structural evidence derives from the following: (i) resolution of optically active carbonato complexes, (ii) Walden inversion studies, (iii) optical rotary dispersion (ORD), and (iv) circular dichroism (CD) studies. Since the pioneer investigations by Bailar and coworkers[144–149] in this field, several cobalt(III) mixed ligand type carbonato complexes have been studied from this standpoint.

The stereospecific preparation of L-carbonatobis(1-propylenediamine)cobalt(III) iodide reported recently[150] makes use of the lower solubility of the levo rotatory isomer in aqueous acetone. ORD studies on (+)-D-$[Co(en)_2CO_3Cl]$[151] and D-$[Co(en)_2CO_3]ClO_4 \cdot 0.5H_2O$[152] provide valuable data on their structures. With the availability of commercial instruments for measuring both ORD and CD, structural information concerning absolute configuration and conformation of dissymmetric mixed ligand type carbonato complexes might be expected in the future. For a recent review on this see Kirschner.[153]

3. Spectroscopic Data

Metal carbonato complexes provide an interesting series of compounds for detailed spectral studies of the metal–oxygen (M–O) bond, of the environmental effects on the C=O stretching frequency, of the nature of the transitions in the absorption spectra of transitional metal complexes, and of the position of the carbonate ligand in the spectrochemical series. Although some of these topics have been discussed in depth in recent literature,[97,154–158] no collective study on the metal carbonato complexes is currently available. Tables VI, VII,

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Table VIII

Infrared Absorption Spectra of Metal Carbonato Complexes[a]

Carbonato complex	ν_1	ν_5	ν_2	ν_8	ν_3	*Ref*
$Na_2[Cu(CO_3)_2]\cdot 3H_2O$	1529	1326	1066 1050	850	755	97
$K_2[Co(CO_3)_2]\cdot 4H_2O$	. . .	1338	1082 1049	884	799 766	97
$K_3[Co(CO_3)_3]\cdot 3H_2O$	1527	1330	1080 1037	851	809	97
$[Co(NH_3)_6][Co(CO_3)_3]$	1523	1285	1073 1031	889	738	97
	1590	1287	1033	831	742	155
$K[Co(NH_3)_2(CO_3)_2]$	1623 1597	1265	1026	839	763 744	155
$K[Co(ND_3)_2(CO_3)_2]$	1639 1607	1260	1026	836	762 742	155
$[Co(en)_2CO_3]ClO_4$	1643	1267 1285	. . .	833	757	155
$[Co(enD)_2CO_3]ClO_4$	1615 1603	1275 1288	. . .	823	762	155
$[Co(en)_2CO_3]Cl$	1577	1281 1272	1059 1035	830	754	97
$[Co(en)_2CO_3]Br$	1575	1282 1276	1059 1038	825	757	97
	1628 1615	1276	. . .	827	759	155
$[Co(enD)_2CO_3]Br$	1618	1285	. . .	821	768	155
$[Co(en)_2CO_3]I$	1565	1290 1278	1055 1034	824	756	97
$[Co(pn)_2CO_3]X$	1565–1572	1260–1273	1050–1059	826–830	750–754	161
$[Co(tn)_2CO_3]X$	1565–1572	1280–1284	1030–1035	826–830	750–754	161
$[Co(trien)_2CO_3](C_6H_5)_4B$	1574	1261	1030	844	748	73
$[Co(dipy)_2CO_3]_2CO_3$	1610					80
$[CoA(CO_3)]ClO_4$ ($A = C_{16}H_{32}N_4$)	1660 1630	1220		820	750	82
$[Co(NH_3)_4CO_3]ClO_4$	1602	1284	. . .	836	762	155
$[Co(ND_3)_4CO_3]ClO_4$	1603	1292	. . .	835	765	155
$[Co(NH_3)_4CO_3]Cl$	1593	1265	1030	834	760	155
	1604	1268		832	768	156
$[Co(ND_3)_4CO_3]Cl$	1635 1607	(1268)	(1031)	832	753	155
$[Co(NH_3)_4CO_3]_2SO_4\cdot 3H_2O$	. . .[b]	1260	. . .	856	756	97
$[Co(NH_3)_2enCO_3]Cl\cdot 0.5H_2O$ (*cis*)	1630	1260	1021 1054	830	762	162
$[Co(NH_3)_2enCO_3]Cl\cdot H_2O$ (*trans*)	1640	1260	1055	830	759	162

[a] Values in cm^{-1}. The frequency notation used for ν_1, ν_5, ν_2, ν_8, ν_3, is the same as in Fujita, Martell, and Nakamoto.[155] Only carbonate ligand frequencies are shown here. [b] Band reported to be obscured by NH_3 and H_2O bands in the spectral region 1640–1550 cm^{-1}.

VIII, and IX[159–167] show the ultraviolet, visible, and infrared absorption spectral data on these complexes as also the organic carbonate esters in which the ligand is known to be essentially covalently bound. Much of the published work centers around cobalt(III) complexes of the mixed ligand type which show two characteristic strong absorption bands in the visible and one intense band in the ultraviolet.

The ultraviolet absorption spectrum of aqueous carbonate ion (10^{-2} *M* Na_2CO_3) shows a steep shoulder in the region 230–210 mμ with no maximum. Under similar conditions

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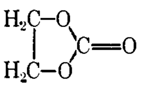
both aqueous bicarbonate ion (10^{-2} *M* $NaHCO_3$) and $CO_2\cdot$(aq), however, exhibit extremely weak absorption, also with no maximum. This difference in the ultraviolet absorption spectra has been utilized in developing a spectrophotometric titration method[160] for the analytical determination of carbonate–bicarbonate and carbonate–hydroxide mixtures.

The ultraviolet absorption spectra of a great majority of the carbonato complexes, mostly cobalt(III) mixed ligand types, show intense absorption ($a_M \simeq 10^4$) in the region 220–270 mμ. The pentaammine–carbonato complex, $[Co(NH_3)_5CO_3]^+$, has a broad band between 250 and 280 mμ in the solid state whereas in aqueous solution only a shoulder at 233 mμ. The tetraammine–carbonato complex, $[Co(NH_3)_4CO_3]^+$, exhibits a *blue shift* of nearly 20 mμ in solution compared to the ultraviolet maximum in the solid state. The organic carbonates (ethylene carbonate[168])



also show significant solvent effects, and the ultraviolet absorption band may be identified with the ligand carbonate, most likely due to transitions of the π electrons of the >C=O group.[159,169]

The visible as well as the ultraviolet absorption spectra of $[Co(en)_2L]Br$, where L is a bidentate acido ligand (carbonato, oxalato, malonato, succinato, maleato, and phthalato rings), provide interesting correlations between band width and chelate ring size.[170] The mixed ligand type carbonato complexes of cobalt(III) exhibit two strong absorption bands in the region 470–650 and 340–440 mμ, confirming the well-characterized spin-allowed transitions.[171–173]

By successive replacement of the carbonate in $Co(CO)_3{}^{3-}$ with other ligands three series of cobalt(III) complexes have been synthesized and their absorption spectra reveal interesting details concerning stereochemistry. One such series is[88]

blue $K[Co(en)(CO_3)_2]\cdot H_2O$
violet $K[Co(en)(CO_3)_2]\cdot H_2O$

The blue variety is reported to be the *cis* form and the violet one, the *trans* form. Both the blue and the violet forms are known in complexes where no carbonate ligand is present, for example, $K[Co(NH_3)_2(C_2O_4)_2]\cdot H_2O$ and $K[Co(en)(C_2O_4)_2]\cdot H_2O$. The authors[88] themselves recommend further studies on this intriguing type of *blue–violet* stereoisomerism as it is contrary to our current beliefs concerning the steric capability of en, CO_3, and C_2O_4 to span *trans* positions in an octahedral complex. All our experience has been in favor of *cis*-spanning only for these ligands, and it would indeed be interesting to notice an exception.

Changes in the position and intensity of the absorption maximum of several rare earth element tripositive ions upon addition of excess carbonate ion have been interpreted in terms of the carbonato complex formation.[99] Of the rare earths studied (Nd, Pr, Sm, Er, Ho, and Eu) neodymium(III) seems to offer evidence for a carbonate complex equilibrium

$$Nd^{3+} + 4CO_3{}^{2-} = Nd(CO_3)_4{}^{5-}$$

The formation constant $K \simeq 12$ has been reported for $Nd(CO_3)_4{}^{5-}$ at a constant ionic strength 5.35 and Nd(III) = 0.0298 *M*.

The infrared absorption spectra of numerous simple ionic carbonates both of laboratory and mineral origin (Li_2CO_3, Na_2CO_3, K_2CO_3, $(NH_4)_2CO_3$, $MgCO_3$, $3MgCO_3\cdot Mg(OH)_2\cdot 3H_2O$, $CaCO_3$ (calcite, aragonite), $SrCO_3$ (strontianite), $BaCO_3$ (witherite), $MnCO_3$ (rhodochrosite), $FeCO_3$ (siderite), $CoCO_3$, Ag_2CO_3, $CdCO_3$, $PbCO_3$ (cerrusite), $NaHCO_3$, $KHCO_3$, and NH_4HCO_3) are known.[174–176] As a result the free carbonate ion has been the subject of intensive spectral investigations both by infrared and Raman methods.[177–181]

Recent interest in the use of infrared spectral data for elucidating the structure of coordination compounds[97] prompted an extensive experimental and theoretical study of the carbonate ion (D_{3h} symmetry) as a potential ligand. The calculated frequencies obtained from a normal coordinate treatment of carbonate as unidentate (C_s symmetry) and bidentate (C_{2v} symmetry) models[155,182,183] have been compared with the experimental frequencies of cobalt(III) mixed ligand carbonato complexes. The good agreement reported confirms earlier observations on the M–O bond in carbonato complexes and the degree of covalency of the bound carbonate.

A covalently bound carbonate, as in organic carbonate esters whose infrared spectral data appear in Table IX, gives rise to absorption in the region 1720–1760 cm^{-1} characteristic of >C=O stretching frequency and ionic carbonates (*cf.* Na_2CO_3) at 1410–1450 cm^{-1}. The infrared absorption spectra of various metal–carbonato complexes show a very strong absorption in the neighborhood of 1600 cm^{-1}, indicating a certain degree of covalent character of the bound carbonate in the complex (see ν_1 in Table VIII). It can be shown in the following carbonate complexes that there is nearly 40–45% covalent character: $Co(NH_3)_4CO_3{}^+$, $Co(en)_2CO_3{}^+$, $Co(pn)_2CO_3{}^+$, $Co(tn)_2CO_3{}^+$, $Co(trien)CO_3{}^+$, $[Co(NH_3)_2(CO_3)_2]^-$, $Co(CO_3)_3{}^{3-}$. Similar estimate show ~50% or even higher covalent character[25,184] for the trisoxalato complexes of Fe(III), Al(III), Cr(III), and Co(III). This might mean at least qualitatively that the M–O bond in metal–carbonato complexes is less covalent than the M–O bond in metal–oxalato complexes, a plausible reason for the nonexistence of $Cr(CO_3)_3{}^{3-}$ as opposed to the extraordinarily stable $Cr(C_2O_4)_3{}^{3-}$ ion.

The proton magnetic resonance spectra of *cis*- and *trans*-$[Co(NH_3)_2enCO_3]^+$ show interesting structural details concerning the C–H protons in two different environments.[142]

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Table IX

Infrared Absorption Spectra of Covalent Carbonates

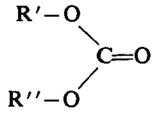
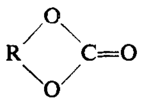
R'	*R''*	$\nu_{C=O}$, *cm*$^{-1}$	ν_{C-O}, *cm*$^{-1}$	*Medium*[a]	*Ref*
	Covalent Carbonate				
CH_3	CH_3	1755	1280	C	165
		1748	1280	L	165
		1760	1280	N	97
		1760		E	166
C_2H_5	C_2H_5	1750		E	166
		1750	1262	N	97
		1739	1262	C	165
		1748		C	167
		1745		E	166
		1748 1730		M	167
n-C_3H_7	n-C_3H_7	1775		E	166
n-C_4H_9	n-C_4H_9	1745		C	167
		1745 1727		M	167
t-C_4H_9	t-C_4H_9	1739		C	167
		1739 1712		M	167
n-C_5H_{11}	n-C_5H_{11}	1773		E	166
n-C_6H_{13}	n-C_6H_{11}	1738		E	166
CH_3	t-C_4H_9O	1795 1764		C	167
		1795 1776		M	167
CCl_3	CCl_3	1832	1178	C	165
CCl_3	C_2H_5	1780	~1235	L	165
CH_2CH_2Cl	CH_2CH_2Cl	1750	1246	C	165
$CHClCCl_3$	$CHClCCl_3$	1794	1240	C	165
$CH(CH_3)CH_2Cl$	$CH(CH_3)CH_2Cl$	1743	1256	L	165
$CH(CH_3)CH(CH_3)Cl$	$CH(CH_3)CH(CH_3)Cl$	1743	1268	L	165
$CH(CH_2Cl)_2$	$CH(CH_2Cl)_2$	1741	1254	C	165
$CH(C_6H_5)CH_2Cl$	$CH(C_6H_5)CH_2Cl$	1751	1226	N	165
C_2H_5	$C_6H_4OCO_2C_2H_5$	1756	1234	L	165
Bis(2-chlorocyclohexyl)[b]		1743		N	165
		1746		N	165
Diphenyl		1760		E	166
		1775	1227	S	165
		1779	1260	N	97
Di-*p*-tolyl		1770		N	166
Di-*m*-tolyl		1775		N	166
		1783		N	167
		1783 1761		M	166
Di-*o*-tolyl		1765		N	166
		1779		C	167
		1779 1757		M	167
Bis(*o*-methoxy)phenyl		1770		N	166
Methylphenyl		1755	1262	L	165
		1755	1262	N	97
Ethylphenyl		1757	1252	L	165
		1757	1252	N	97
	Cyclic Carbonates				
$-CH_2CH_2-$		1818		C	167
		1870	1162	L	97
		1810	1163	Solid	97

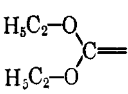
Table IX (Continued)

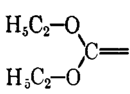
R	$\nu_{C=O}$, *cm*$^{-1}$	ν_{C-O}, *cm*$^{-1}$	*Medium*[a]	*Ref*
Cyclic Carbonates				
$-CH_2CH_2-$	1805 1779		M	167
	1817 1763	1138 sh,w	C, S	165
	1795 1770	 sh,w	L	165
	1788 1762	sh,w	F	165
$-CH{=}CH-$	1833 ~1770	1160 w	C	165
	1830 1801	 sh, w	L	165
	1822 1796	 s	F	165
$[-CH—CH-]_n$	1833	1162	N	165
$-CH(CH_3)CH_2-$	1809	1171	C	165
	1792		L	165
$-CHClCHCl-$	1852 1794	1115 sh, m	L	165
$-CHClCH_2-$	1828 1797	1151 sh, m	L	165
$-CH(CH_2Cl)CH_2-$	1803	1165	L	165
$-CH(C_6H_5)CH_2-$	1816		C	165
	1770	1164	KCl disk	165
	1832 ~1770	 w	S	165
$(CH_3)_3SbCO_3$	1730	s	1280 s	89

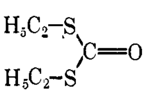
[a] C = carbon tetrachloride, L = liquid, N = Nujol, E = neat, M = methanol, S = carbon disulfide, F = thin film, s = strong, m = medium, w = weak. [b] Two values are for stereoisomers.

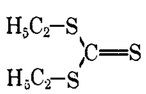
The C–H groups in the *trans* isomer (*cf.* Figure 4) are equivalent whereas in the *cis* isomer they are not. Similar comparison of the ammonias and the amine group is complicated by the quadrupole relaxation of the N^{14} nucleus and the rapid exchange of protons on these groups with solvent D_2O.[185]

Interesting possibilities exist if electronically similar sulfur atoms are substituted for oxygen atoms in the carbonate ligand. The following covalent thiocarbonates are known.[186]


(colorless)


(yellow)


(colorless)


(deep reddish orange)

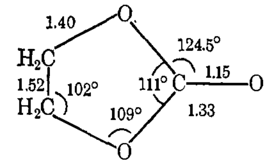
The only metal thiocarbonato complex[187] is that of Ni(II) with CS_3^{2-}.

$$Ni^{2+} + 2CS_3^{2-} = Ni(CS_3)_2^{2-} \qquad \log K_f = 8.8$$
$$(a_M = 1600 \text{ at } 510\ m\mu)$$

4. Crystal Structure

Since carbonic acid has never been isolated, no crystal-structure information is available for H_2CO_3. However, several simple ionic carbonates, basic carbonates of mineral origin (*cf.* azurite[188,189] and malachite[190]), and two mixed ligand type carbonato complexes of cobalt(III) have been investigated, one of which, $[Co(NH_3)_5CO_3]Br \cdot H_2O$, by a mistaken identity.[191] Reported crystallographic data are presented in Table X.

Of the covalent carbonates, ethylene carbonate has been thoroughly investigated,[192] and the following interatomic distances show normal C–C (aliphatic) and C–O bond lengths



of 1.54 and 1.42 Å, respectively, in the ethylenic part of the molecule. However, as compared to the C–O bond length in an ionic carbonate like $CaCO_3$ (calcite) which is about 1.24 Å (three equivalent oxygens), ethylene carbonate does reveal nonequivalence of one oxygen from the other two. Also this study indicates ethylene carbonate is not planar, the atoms of CO_3 being in one plane and the ethylenic carbons in a different plane making a 20° angle. In a subsequent study[168] on the infrared spectrum of ethylene carbonate in the solid, liquid, vapor, and dissolved states (3600–400 cm^{-1}) along with the Raman spectrum in solution, it has been found that the symmetry of the molecule is altered from C_2 in the solid state to C_{2v} in the other states resulting in a planar configuration. This

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Table X

Crystallographic Data on Carbonates

Compound	*Symmetry classification*	*Space group*	*a, Å*	*b, Å*	*c, Å*	*β*	*Ref*
$NaHCO_3$	Monoclinic	$P(2_1)/c\text{-}C_{2h}^5$	3.51	9.71	8.05	111° 51′	196, 197
$KHCO_3$	Monoclinic	$P(2_1)/c\text{-}C_{2h}^6$	15.11	5.67	3.71	103° 45′	198
NH_4HCO_3	Monoclinic						199
$Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$	Monoclinic	C(2)/c	20.41	3.49	10.31	106° 20′	200
$KAgCO_3$	Orthorhombic	$IbcA\text{-}D_{2h}^{27}$	20.23	5.75	5.95		201
Ag_2CO_3	Monoclinic	$P(2_1)\text{-}C_2^2$	4.83	9.52	3.23	92° 42′	202
$[Co(NH_3)_4CO_3]Br$	Orthorhombic	P(cmn)	6.76	7.629	16.886		194
$[Co(NH_3)_5CO_3]Br \cdot H_2O$	Orthorhombic	$P(2_1)/na$	12.37	12.14	6.43		191
$[Co(NH_3)_4CO_3]_2SO_4 \cdot 3H_2O$	Monoclinic	C_s'	11.80	10.60	7.42	98° 39′	193
Ethylene carbonate	Monoclinic	C(2)/c	8.92	6.25	6.94	100° 30′	192

has particular significance in the solution and solid-state properties of several carbonato complexes.

The crystal structure of $[Co(NH_3)_4CO_3]^+$ has been studied by several workers[193–195] to learn if carbonate chelation would result in a four-membered ring structure. The observed O–C–O bond angle in the complex was 110° and the C–O–Co bond angle 90°, which indicate highly strained four-membered ring formation. Additional evidence comes from the O–Co–O bond angle of 70° which is drastically different from the usual 90° found in regular octahedral structures. The crystal structure of $[Co(NH_3)_5CO_3]^+$ confirms carbonate acting as a monodentate ligand and internal hydrogen bonding between ammine nitrogen and the carbonate[191] in the solid state.

5. *Miscellaneous Structural Evidence*

The molar electrical conductance of $K_3[Co(NO_2)_2(CO_3)_2] \cdot 2H_2O$ corresponds to a four-ion electrolyte and is confirmed by cryoscopic measurements.[141] Similar observation on a related binuclear compound, $K_8[Co_2(NO_2)_8(CO_3)_3] \cdot 2H_2O$, confirms its structure in the same study. Conductance measurements also offer supporting evidence for the following compounds: $K[Co(NH_3)_2(CO_3)_2]$,[203] $Na_3[Co(NO_3)_4CO_3]$,[86] $Cs_6[Co_2(NO_2)_6(CO_3)_3]$,[86] $Na_3[Co(NO_2)_2(CO_3)_2]$,[86] $Co(NH_3)_6[Co(NH_3)_2(NO_2)_2CO_3]_3$,[101] $Co(en)_3[Co(NH_3)_2(NO_2)_2CO_3]_3$,[101] and $K[Co(NH_3)_2(NO_2)_2CO_3]$.[101]

Hydrazine hydrate and CO_2 react with $[Co(NH_3)_4CO_3]^+$ ion to form a new coordination compound having the formula, $(N_2H_3COO)_2Co(N_2H_5)_2CO_3$, which is stable in air and soluble in water and dilute HCl. The magnetic moment of 4.92 BM suggests cobalt in the +2 state.[204]

C. STABILITY

Several methods are known for the detection of complexes in solution and for the determination of their stability constants.[205–212] In this section an attempt will be made to discuss the various methods employed in the detection of carbonato complexes in aqueous solutions and in systems amenable to quantitative study, the determination of their stability constants.

1. *Stability Constant Data*

Stability constant data including those of the ion-pair carbonate complexes are presented in Table XI, and widely scattered experimental evidence for carbonate complexing in systems containing metal ions and carbonate–bicarbonate ions is shown in Table XII. Although excellent compilation of stability constant data on the carbonate ligand was first published in 1957[213] and later revised in 1961,[214] during the past decade several new systems have been explored, some with quantitative interest.

2. *Methods of Determination*

a. Spectrophotometric Method

Detailed studies on the absorption spectra of $Co(NH_3)_6{}^{3+}$ and $Co(en)_3{}^{3+}$ ions in carbonate solutions (0.01–1.0 *M*) and a comparison of the resulting spectra with that of $[Co(NH_3)_5CO_3{}^+]$ ion confirm that the intense band in the ultraviolet region experiences systematic shifts in the wavelength of absorption due to the formation of ion pairs of the type $[Co(NH_3)_6{}^{3+} \cdot$

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Table XI

Stability Constants on Carbonato Complexes[a]

Complex	*Log K*	*Temp, °C*	*Conditions, μ*	*Method*	*Ref*
$[CaHCO_3]^+$	1.26	25	$\longrightarrow 0$	Potentiometry	27, 28
$[MgHCO_3]^+$	1.16	25	$\longrightarrow 0$	Potentiometry	27, 28
$[MnHCO_3]^+$	1.80	25	$\longrightarrow 0$	Solubility	223
$[NaHCO_3]^0$	−0.25	25	$\longrightarrow 0$	Potentiometry	28
$[NPO_2HCO_3]^0$	2.43	...	$\longrightarrow 0$		244
$[Cu(HCO_3)_4]^{2-}$	11.52	25	1 M KNO_3	Polarography	233
$[Pu(CO_3)]^{2+}$	46.96	20	7.0	Solubility	221
$[Co(NH_3)_6{}^{3+} \cdot CO_3{}^{2-}]$	1.73	18–20	...	Spectrophotometry	215, 216
$[Co(en)_3{}^{3+} \cdot CO_3{}^{2-}]$	1.95	18–20	...	Spectrophotometry	215, 216
$[MgCO_3]^0$	3.4	25	$\longrightarrow 0$	Potentiometry	29
$[CaCO_3]^0$	3.2	25	$\longrightarrow 0$	Potentiometry	28
$[Cd(Moen)_2CO_3]^0$	6.92	25	0.1–1.0 M Na_2CO_3	Polarography	234
$[Cd(Dien)_2CO_3]^0$	6.02	25	0.1–1.0 M Na_2CO_3	Polarography	234
$[Zn(Moen)_2CO_3]^0$	9.78	25	0.1–1.0 M Na_2CO_3	Polarography	235
$[NaCO_3]^-$	1.27	25	$\longrightarrow 0$	Potentiometry	29
$[PuO_2(CO_3)(OH)]^-$	23.85	20	$\longrightarrow 0$	Solubility potentiometry	48
$[PuO_2(CO_3)(OH)_2]^{2-}$	23.0	20	$\longrightarrow 0$	Solubility glass electrode	48
$[Pu(CO_3)_3]^{2-}$	2.09	20	$\longrightarrow 0$	Solubility potentiometry	48
$[UO_2(CO_3)_2]^{2-}$	14.57	25	0.2	Solubility	42
$[Pb(CO_3)_2]^{2-}$	8.2	18	1.7 M KNO_3	Polarography	39
$[Cu(CO_3)_2]^{2-}$	8.6	18	1.7 M KNO_3	Polarography	39
	10.01	25	$\longrightarrow 0$	Solubility potentiometry	32
$[UO_2(CO_3)_3]^{4-}$	20.7	25	0.2	Solubility	42
	22.8	25	1.0	Solubility	222
$[Cd(CO_3)_3]^{4-}$	6.24	25	$\longrightarrow 0$	Solubility polarography	46
$[Cu(CO_3)_3]^{4-}$	−7.2	25	...	Polarography	233
$[Nd(CO_3)_4]^{5-}$	1.08	...	5.35	Spectrophotometry	56

[a] μ = ionic strength; $\longrightarrow 0$ = approaching zero μ; K refers to cumulative or gross stability constant, $M + nL = ML_n$.

$CO_3{}^{2-}$]. Calculations on the degree of ion-pair formation show greater than 40% in a 0.01 M Na_2CO_3 and a tenfold increase in carbonate concentration results in nearly 70% ion pairs.[215,216] Such ion-pair formation is well known in coordination chemistry.[217]

The absorption spectra of the carbonato complexes of Pr(III), Nd(III), Sm(III), Eu(III), Ho(III), and Er(III) show appreciable bathochromic shifts in the region 240–1000 mμ compared to those of the corresponding rare earth chloride solutions.[56] Neodymium(III) shows an exceptionally large shift accompanied by an increased intensity in absorption, whereas Dy(III), Yb(III), and Tm(III) differ little from those of their chlorides. Graphical evaluation[56] of the Nd(III)–$CO_3{}^{2-}$ spectral data gives the composition and the dissociation constant for $Nd(CO_3)_4{}^{5-}$ ($K_{diss} = 0.0863$, $K_{formation} \simeq 12.0$). An independent ion-exchange study followed by thermodynamic analysis[134] of the anion-exchange behavior of Nd(III) in K_2CO_3 solutions confirms the presence of $Nd(CO_3)_4{}^{5-}$ among several other complexes.

Job's method of continuous variation[218] has been used in the study of uranium(VI)–carbonato complexes,[219] and the following complexes, $[UO_2(CO_3)_3]^{4-}$, $[UO_2(CO_3)_2]^{2-}$, and $[U_2O_5(OH)(HCO_3)]^0$, are reported to occur at pH 11.2, 7.7, and 5.7, respectively. Conductometric studies[137] show discontinuities at U:CO_3 ratios 1:3 and 1:2 suggesting the existence of $[UO_2(CO_3)_3]^{4-}$ and $[UO_2(CO_3)_2]^{2-}$ ions in equilibrium.

$$[UO_2(CO_3)_3]^{4-} = [UO_2(CO_3)_2]^{2-} + CO_3{}^{2-}$$
$$K = 1.7 \times 10^{-4}\ (25°,\ \mu \longrightarrow 0)$$

Spectrophotometric and potentiometric methods have been used in conjunction to study the equilibria[148]

$$UO_3 \cdot 2H_2O(s) + CO_2(g) = UO_2CO_3(s) + 2H_2O \qquad K_1 \simeq 10^4$$
$$UO_2CO_3(s) + 2HCO_3{}^- + H_2O = [UO_2(CO_3)_2(H_2O)_2]^{2-} + CO_2(g) \qquad K_2 \simeq 26$$

In addition carbonato complexes of uranium(IV) of the composition $Na_6U(CO_3)_5 \cdot 11H_2O$ and the ion $U(CO_3)_5{}^{6-}$ have been characterized.

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Table XII

Evidence for Carbonato Complex Ion Formation

Complex	*Temp, °C*	*Conditions*	*Method*	*Ref*
$[Eu(HCO_3)_2]^+$	25	$KHCO_3$	Ion exchange	55
$[Nd(HCO_3)_2]^+$	25	$KHCO_3$	Ion exchange	55
$[Eu(HCO_3)_4]^-$	25	$KHCO_3$	Ion exchange	55
$[Nd(HCO_3)_4]^-$	25	$KHCO_3$	Ion exchange	55
$[Nd(HCO_3)_6]^{3-}$	25	$KHCO_3$	Ion exchange	55
$[Eu(HCO_3)_7]^{4-}$	25	$KHCO_3$	Ion exchange	55
$[Eu(HCO_3)_5]^{2-}$	25	$KHCO_3$	Ion exchange	55
$[Nd(HCO_3)_5]^{2-}$	25	$KHCO_3$	Ion exchange	55
$[Fe(Dien)_2CO_3]^+$	25	Na_2CO_3	Polarography	238
$[Fe(Dien)_2CO_3]^0$	25	Na_2CO_3	Polarography	238
$[Fe(trien)CO_3]^0$	25	Na_2CO_3	Polarography	238
$[Co(Dien)_2CO_3]^0$	25	Na_2CO_3	Polarography	236
$[Co(Moen)_2CO_3]^0$	25	Na_2CO_3	Polarography	236
$[Ni(Moen)_4CO_3]^0$	25	Na_2CO_3	Polarography	237
$[Ni(Moen)_3CO_3]^0$	25	Na_2CO_3	Polarography	237
$[Ni(Moen)_2CO_3]^0$	25	Na_2CO_3	Polarography	237
$[Ni(Dien)CO_3]^0$	25	Na_2CO_3	Polarography	237
$[Sc(CO_3)_2]^-$	0–50	Excess CO_3^{2-}	Solubility, preparative	96
Y(III) anionic complex	25	Excess CO_3^{2-}	Ion exchange	37
$[Eu(CO_3)_2]^-$	25	K_2CO_3	Ion exchange	55
$[Nd(CO_3)_2]^-$	25	K_2CO_3	Ion exchange	55
$[Ce(CO_3)_2]^-$	...	Excess CO_3	Polarography	239
$[Be(CO_3)_2]^-$	...	0.1 M $(NH_4)_2CO_3$	Ion exchange	38
$[M(CO_3)_2]^-$	...	Excess CO_3^{2-}	Preparative	57
(M = rare earth element)			Solubility	222
			Ion exchange	55
$[Fe_2(OH)_3(CO_3)_3]^{3-}$	...	Saturated $(NH_4)_2CO_3$	Preparative	124
			Solubility	
$[Co(CO_3)_3]^{3-}$	...	Excess CO_3^{2-}	Preparative	45
			Ion exchange	100
$[Ce(CO_3)_4]^{4-}$	...	Excess CO_3^{2-}	Preparative	50
			Ion exchange	134
$[Th(CO_3)_4]^{4-}$	...	Excess CO_3^{2-}	High-frequency Titration	51
$[U(CO_3)_4]^{4-}$	...	Excess CO_3^{2-}	Preparative	64
$[UO_2(CO_3)_2(OH)_2]^{4-}$	25	Na_2CO_3 $NaHCO_3$	Polarography	241
$[Pu(CO_3)_4]^{4-}$	...	Excess CO_3^{2-}	Preparative	48
			Conductance	
			Solubility	52
			Freezing point	
$[PuO_2(CO_3)_3]^{4-}$	...	45% K_2CO_3	Solubility	49
$[Pr(CO_3)_4]^{5-}$	25	Excess K_2CO_3	Ion exchange	134
$[Sm(CO_3)_4]^{5-}$	25	Excess K_2CO_3	Ion exchange	57, 134
$[Eu(CO_3)_4]^{5-}$	25	Excess K_2CO_3	Ion exchange	134
$[Nd(CO_3)_4]^{5-}$	25	Excess K_2CO_3	Ion exchange	134
$[Th(CO_3)_3(OH)_3]^{5-}$	...	...	Preparative	60
$[U(CO_3)_3(OH)_3]^{5-}$	...	Excess CO_3^{2-}	Preparative	60
			Solubility	
$[Be_4O(CO_3)_6]^{6-}$	...	...	Preparative	95, 248
$[Eu(OH)(CO_3)_4]^{6-}$	25	K_2CO_3	Ion exchange	55
$[Nd(OH)(CO_3)_4]^{6-}$	25	K_2CO_3	Ion exchange	55
$[Ce(CO_3)_5]^{6-}$	...	Excess K_2CO_3	Polarography	239
			Preparative	
$[Th(CO_3)_5]^{6-}$	...	Excess Na_2CO_3	Solubility	245
			Preparative	246
			Potentiometric	61
			Freezing point	60
trans-$[Th(CO_3)_4(OH)_2]^{6-}$	...	...	Spectrophotometry	242
$[Mo(CO_3)_5(H_2O)_2]^{6-}$	...	Excess CO_3^{2-}	Preparative	59
			Conductance	
$[U(CO_3)_5]^{6-}$	...	Excess CO_3^{2-}	Preparative	60
			Solubility	43
			Spectrophotometry	64
			Polarography	241

Table XII (Continued)

Complex	*Temp, °C*	*Conditions*	*Method*	*Ref*
$[U(CO_3)_4(OH)_2]^{6-}$	...	Excess HCO_3^- and CO_3^{2-}	Polarography	241
$[Pu(CO_3)_5]^{6-}$	...	Excess CO_3^{2-}	Preparative Solubility	48
$[Fe_4O_3(CO_3)_6]^{6-}$	...	Saturated $(NH_4)_2CO_3$	Preparative Solubility	124
$[Ce(CO_3)_6]^{8-}$	...	Excess CO_3^{2-}	Preparative	50
$[Pu(CO_3)_8]^{12-}$	...	...	Preparative, solubility	48
Zr(IV) anionic complex	...	Excess $(NH_4)_2CO_3$	Ion exchange	227
V(IV) complex	...	Excess Na_2CO_3	Ion exchange	228
Pu(III) complex	...	Excess K_2CO_3	Spectrophotometry	48, 49
Pu(IV) complex	...	Excess K_2CO_3	Spectrophotometry Polarography	49
Am(III) complex	...	Excess K_2CO_3	Transference number	247
			Solubility, ion-exchange	49
			Spectrophotometry	220
Am(VI) complex	...	Excess Na_2CO_3	Solubility Spectrophotometry	49
Cm(III) complex	...	Excess CO_3^{2-}	Solubility	49
Ga(III) anionic complex	...	Excess $(NH_4)_2CO_3$	Ion exchange	229
In(III) anionic complex	...	Excess $(NH_4)_2CO_3$	Ion exchange	230

Based on the absorption spectrum of americium(VI) in 0.1 M Na_2CO_3 and its distribution on Dowex-1 resin, a reddish brown carbonato complex has been reported.[220] The infrared spectra of solid americium(VI) carbonates confirm the presence of the O–Am–O group, and further studies may be needed to determine the exact composition of the Am(VI)–carbonato complex.

Spectral evidence also suggests the formation of anionic complexes in the plutonium(III)–carbonate system.[48] The absorption spectra of plutonium(IV) in carbonate solutions (35–45% K_2CO_3) in the range 400–1100 mμ show evidence for the complexes $Pu(CO_3)_2^0$, $Pu(CO_3)_3^{2-}$, $Pu(CO_3)_4^{4-}$, and $Pu(CO_3)_5^{6-}$. At lower carbonate concentration, however, there is evidence for $PuCO_3^{2+}$ ($K_{inst} = 1.5 \times 10^{-47}$) which undergoes partial decomposition at elevated pH's (>11.3) according to the reaction[221]

$$PuCO_3^{2+} + 4OH^- = Pu(OH)_4 + CO_3^{2-}$$

Plutonium(VI) forms several sparingly soluble carbonates and carbonato complexes of which $[PuO_2(CO_3)_2]^{2-}$ ($K_{inst} = 1 \times 10^{-15}$) is well known[48] and is analogous to $[UO_2(CO_3)_2]^{2-}$ ($K_{inst} = 3 \times 10^{-15}$). Interestingly plutonium in various oxidation states shows the following order, $Pu^{4+} > Pu^{3+}$, $PuO_2^{2+} > PuO_2^+$, toward complexing, and this order more or less parallels their ionic potential (e/r). In the absence of reliable data on the Pu–CO_3 systems, this might be illustrated with the well-known oxalato complexes.

Oxidation state	+4		+3		+6		+5
Oxalate complex	$Pu(C_2O_4)_2^0$		$Pu(C_2O_4)_2^-$		$PuO_2(C_2O_4)_2^{2-}$		...
pK	16.9	>	9.3	~	11.4		...
Crystal radius, Å	0.99		1.03		0.81		0.87
Charge/radius	4.44	>	2.91	~	2.47	>	1.15
Carbonate complex	$PuCO_3^{2+}$		...		$PuO_2(CO_3)_2^{2-}$		...
pK	46.8	>	...		15.0		...

The carbonate ligand seems to be favored by Pu(IV) or Pu(VI) over other ligands, and a number of substitution reactions yield the compounds that contain both oxalate and carbonate.[48]

$$K_2[Pu(CO_3)_2C_2O_4]\cdot 1.5H_2O$$
$$Na_4[Pu(CO_3)_2(C_2O_4)_2]\cdot 3H_2O$$
$$K_4[Pu(CO_3)_3C_2O_4]\cdot nH_2O$$
$$K_6[Pu(CO_3)_3(C_2O_4)_2]\cdot nH_2O$$
$$K_{10}[Pu(CO_3)_4(C_2O_4)_3]\cdot nH_2O$$
$$K_{12}[Pu(CO_3)(C_2O_4)_7]\cdot nH_2O$$
$$K_{12}[Pu(C_2O_4)_8]\cdot nH_2O \quad (?)$$

Electrical conductivity data and cryoscopic measurements support these formulas. In aqueous solution, however, the following replacement reaction would be of kinetic and thermodynamic interest in view of the different types of oxygen atoms present in the system.

$$PuO_2(C_2O_4)_2^{2-} + 2CO_3^{2-} = PuO_2(CO_3)_2^{2-} + 2C_2O_4^{2-} \qquad K \sim 10^{3.5}$$

b. Solubility Method

Most metals form sparingly soluble carbonates whose solubility in excess carbonate could be appreciable as a result of carbonate complexing. The solubility of $UO_2(OH)_2$ ($K_{sp} = 1.8 \times 10^{-22}$) in aqueous carbonate solutions at pH 7.0–9.0 has been accounted in terms of the well-known complexes[42] $UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$. The respective stability constants are shown in Table XI. A related investigation[222] on the solubility of uranyl 8-hydroxyquinolinate in 1.3 M $(NH_4)_2CO_3$ and 2 M NH_4Cl gives a value for the dissociation constant of $UO_2(CO_3)_3^{4-}$, $K_{diss} = 1.7 \times 10^{-23}$ (25°, $\mu \rightarrow 1.0$). The solubility of $Pu(OH)_4$ in K_2CO_3 at a high ionic strength of 10.0 has been measured as a function of pH and CO_3^{2-} ion concentration.[221] The reported value for K_{inst} for $PuCO_3^{2+}$ is 1.1×10^{-47}. Solubility studies also indicate several complexes

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of the types $[Pu(CO_3)(OH)_2(H_2O)]^0$, $[Pu(CO_3)(OH)_3(H_2O)_3]^-$, and $[PuCO_3(OH)_4(H_2O)_2]^{2-}$.

The role of manganese(II)–carbonate complex in water-supply chemistry and in natural waters has been elucidated through solubility studies.[223] Solubility of $MnCO_3(s)$ in water at 25° in a solution saturated with CO_2 was studied by analyzing the equilibrium concentrations of Mn(II) and HCO_3^- ions by periodate and potentiometric titrations, respectively. The thermodynamic activities, $a_{MnHCO_3^+}$, $a_{Mn^{2+}}$, and $a_{HCO_3^-}$, were computed from concentration data using the Debye–Hückel relation. An average value of 63 has been reported for the equilibrium constant for

$$Mn^{2+} + HCO_3^- = MnHCO_3^+$$

which gives the free energy of formation of the ion-pair complex, $\Delta F = -197$ kcal/mole.

Studies on Sc(III),[96] Ce(III),[133] Fe(III),[124] Am(III),[49] Cm(III),[49] Th(IV),[60–62] U(IV),[60] Pu(IV),[63] Pu(VI),[49] and Am(VI)[49] give qualitative evidence for various types of carbonato complexes (*cf.* Table XII).

c. Ion-Exchange Method

The method of studying metal complexes in solution by ion exchange is described in detail in the literature.[224–226] Excellent studies have been made on the carbonato and bicarbonato complexes of the lanthanide elements[55,134] using radioisotopes, ^{141}Ce, ^{143}Pr, ^{147}Nd, ^{147}Pm, ^{153}Sm, and $^{152,154}Eu$, and Dowex-1 resin in its carbonate form. By elution chromatography the distribution coefficients were measured over a concentration range 0.37–2.6 *m* K_2CO_3. Graphical evaluation of the data not only gives evidence for $M(CO_3)_4^{5-}$ type species in solution but also confirms solubility studies[50] on Ce(IV).

Detailed thermodynamic analysis of Eu(III)–Nd(III)–carbonate–bicarbonate systems suggests the presence of $[M(OH)(CO_3)_4]^{6-}$ and $M(CO_3)_2^-$ complex ions at high and low concentrations of the ligand, respectively. The various equilibria are as follows.

Carbonate system

$$[M(CO_3)_2]^- + CO_3^{2-} = [M(CO_3)_3]^{3-}$$
$$K_3 = 87.8 \text{ (Eu)}$$

$$[M(CO_3)_3]^{3-} + CO_3^{2-} + OH^- = [M(CO_3)_4(OH)]^{6-}$$
$$K_4K_5 = 56.2 \text{ (Eu)}$$
$$= 47.8 \text{ (Nd)}$$

Bicarbonate system

$$[Nd(HCO_3)_2]^+ + HCO_3^- = [Nd(HCO_3)_3]^0 \quad K_3 = 510$$
$$[Nd(HCO_3)_3]^0 + HCO_3^- = [Nd(HCO_3)_4]^- \quad K_4 = 62.7$$
$$[Nd(HCO_3)_4]^- + 2HCO_3^- = [Nd(HCO_3)_6]^{3-} \quad K_5K_6 = 481$$
$$[Eu(HCO_3)_2]^+ + 2HCO_3^- = [Eu(HCO_3)_4]^- \quad K_3K_4 = 3.52 \times 10^4$$
$$[Eu(HCO_3)_4]^- + HCO_3^- = [Eu(HCO_3)_5]^{2-} \quad K_5 = 17.3$$
$$[Eu(HCO_3)_5]^- + 2HCO_3^- = [Eu(HCO_3)_7]^{4-} \quad K_6K_7 = 101$$

Studies[38] on the absorption of Be(II), Ce(IV), Th(IV), and U(VI) in $(NH_4)_2CO_3$ solutions using batch equilibration technique as a function of ligand concentration in 0–1.2 *M* $(NH_4)_2CO_3$ proved the formation of $[Be(CO_3)_2]^-$ complex and complexes of Ce(IV) and Th(IV) with charges of −6 and −8. These might very well be hydroxy carbonato complexes. The differences in the distribution behavior of U(VI) and Th(IV) as carbonato complexes form the basis of a method of separation of one from the other by ion exchange.

Carbonato complexes have been detected by ion-exchange technique in the case of Y(III),[37] Zr(IV),[227] V(IV),[228] Am(III),[220] Co(III),[45] Ga(III),[229] and In(III).[230]

d. Polarographic Method

The theoretical principles and the methodology involved in the determination of the composition and stability of complex ions by polarography are well known.[231,232] The half-wave potential, $E_{1/2}$, of a metal ion is generally shifted to more negative values due to complexation. By measuring $E_{1/2}$ as a function of ligand concentration, it is possible to obtain both the composition and stability constant of the complex ion in question. One of the chief requisites for the application of this method is that the reduction of the metal complex at the dropping mercury electrode be reversible.

Polarographic studies on copper(II) in carbonate medium establishes the presence of $Cu(CO_3)_2^{2-}$ and $Cu(CO_3)_3^{4-}$ ions.[39,233] The drastic change in the value of the stability constant in going from $Cu(CO_3)_2^{2-}$ to $Cu(CO_3)_3^{4-}$ is in keeping with the general behavior of copper(II) complexes. Amperometric titration of copper(II) solutions with 1.0 *M* $KHCO_3$ confirms the presence of $Cu(HCO_3)_4^{2-}$ complex. At higher bicarbonate ion concentration there is evidence for the equilibrium

$$Cu(HCO_3)_4^{2-} + HCO_3^- = Cu(HCO_3)_5^{3-}$$
$$K = 1.05 \times 10^{-2} \ (25°, \mu = 1)$$

(Evidence for a hexacoordinated copper(II) of the formula $Cu(HC_2O_4)_6^{4-}$, stable on the resin phase, is available.[25])

Lead(II) resembles[39] copper(II) in forming a complex ion, $Pb(CO_3)_2^{2-}$. Investigation on the nature of cadmium(II) in carbonate medium[46] proves the existence of $Cd(CO_3)_3^{4-}$ since a plot of $E_{1/2}$ *vs.* log $a_\pm$ for carbonate ion gives a slope of −0.092 in agreement with the theoretical value of −0.090 for the complex. Formation of mixed ligand type amine carbonato complexes of cadmium(II),[234] zinc(II),[235] cobalt(II),[236] nickel(II),[237] iron(II),[238] and iron(III)[238] has been reported in a series of papers. They have the general formulas, $[M(Moen)CO_3]^0$, $[M(Dien)CO_3]^0$, $[M(Trien)CO_3]^0$, and $[M(Amine)(CO_3)_x]^{(2-2x)-}$, where M is a bipositive metal, Moen = monoethanolamine, Dien = diethanolamine, and Trien = triethanolamine.

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(238) R. S. Subrahmanya, *ibid.,* **43,** 133 (1956).

Polarographic investigations on cerium(IV),[239] uranium(IV) and -(VI),[240,241] plutonium(IV),[49] and europium(III)[58] suggest the occurrence of several anionic carbonato complexes.

e. Potentiometric Method

The principles and details of this method have been discussed in several books on coordination chemistry.[205] The ion-pair complexes of magnesium(II) and carbonate–bicarbonate and the corresponding calcium(II) complexes are of great interest in the study of natural waters and in developing a chemical model for sea water.[28] The potentiometric method has been successfully applied in the detection and determination of the ion-pair dissociation constants of magnesium(II) complexes.[29] It is based on the titration of a solution equimolal in carbonate and bicarbonate ions with $MgCl_2$ and measuring the accompanying changes in pH at various stages of the titration. Deviation of the activity coefficients of CO_3^{2-} and HCO_3^- in $MgCl_2$, NaCl–$MgCl_2$, and NaCl solutions can be attributed to the formation of complexes of the types $MgCO_3^0$, $MgHCO_3^+$, and $NaCO_3^-$ (*cf.* Table XI).

The carbonato complexes of copper(II)[32] and plutonium(VI)[48] and the bicarbonato complexes of calcium(II)[27] have been examined potentiometrically. On the basis of potentiometric and thermometric titration studies of $Th(NO_3)_4$ and $[Th_4(OH)_8](NO_3)_8$ in KOH and $KHCO_3$ medium with HNO_3, evidence has been presented for the equilibria[61]

$$Th^{4+} + 5CO_3^{2-} = [Th(CO_3)_5]^{6-}$$

$$[Th_4(OH)_8]^{8+} + 20CO_3^{2-} = 4[Th(CO_3)_5]^{6-} + 8OH^-$$

ruling out the following species reported earlier.[242,243]

$$[Th(CO_3)_4]^{4-},\ [Th(CO_3)_4(OH)_2]^{6-},\ [Th(CO_3)_4]_2^{8-}$$

f. Other Methods

Preparative chemistry has been helpful in establishing the composition of a large number of carbonato complexes of metals like Be, Sc, Ce, Th, U, Pu, Fe, Co, and Mo (*cf.* Table IV). Cryoscopic titration technique gives experimental evidence for several thorium(IV), uranium(VI), and plutonium(IV) carbonato complexes, and some of these observations have been confirmed by conductometric titration, high-frequency titration, and transference number measurements. Several applications of carbonate equilibria in nature and in the laboratory require precise data on the stability constants of the carbonato complexes, and it is highly desirable if a redetermination of the stability constants by more than one procedure is possible.

D. REACTIONS AND REACTION KINETICS

1. Racemization

Preparation of optically active forms of chelated carbonato complexes has been accomplished by Werner and several later investigators (see section III.B). The only kinetic study of the racemization of such compounds is that of Holden and Harris,[72] who examined the species $Co(en)_2CO_3^+$ in the neighborhood of pH ~9. They concluded that the racemization reaction bore no kinetic relationship to the much more rapid carbonate exchange process, indicating that the diacido ligand replacement could occur with complete retention of configuration. In the presence of added carbonate, the racemization is inhibited and appears to be a very complex process, with several alternative paths available. In absence of added carbonate, the rate law simplifies to the expression

$$R = k[(H^+)(Co(en)_2CO_3^+)]^{1/2} \qquad (1)$$

The suggested mechanism for this consisted of the equilibrations

$$d\text{-}Co(en)_2CO_3^+ + H_3O^+ + H_2O \rightleftarrows d\text{-}cis\text{-}Co(en)_2(H_2O)_2^{3+} + HCO_3^- \qquad (2)$$

$$d\text{-}cis\text{-}Co(en)_2(H_2O)_2^{3+} \rightleftarrows l\text{-}cis\text{-}Co(en)_2(H_2O)_2^{3+} \qquad (3)$$

with reaction 3 being rate-determining. However, at pH ~9, hydroxo forms of the aquated species predominate, and several other paths for loss of optical activity exist. These include not only racemization but *cis–trans* isomerization of each of the species *d-cis*-$Co(en)_2(H_2O)_2^{3+}$, *d-cis*-$Co(en)_2(OH)(H_2O)^{2+}$, and *d-cis*-$Co(en)_2(OH)_2^{2+}$. Much more information is also needed concerning various other equilibration of the type of reaction 2, including

$$d\text{-}cis\text{-}Co(en)_2CO_3^+ + 2H_2O \rightleftarrows d\text{-}cis\text{-}Co(en)_2(OH)(H_2O)^{2+} + HCO_3^- \qquad (4)$$

$$d\text{-}cis\text{-}Co(en)_2CO_3^+ + OH^- + H_2O \rightleftarrows d\text{-}cis\text{-}Co(en)_2(OH)_2^+ + HCO_3^- \qquad (5)$$

Clearly much more work needs to be done on this system before a thorough understanding of the nature of this type of racemization reaction becomes possible.

2. Ligand Substitution and Isotope Exchange

The earliest studies of carbonate replacement in carbonato complexes were concerned with acid hydrolysis (aquation). For the nonchelated species, $Co(NH_3)_5CO_3^+$ (the only one of this type which has been studied), the picture is now quite complete. Lamb and coworkers[109,249] showed that the hydrolysis had an acid dependence, which they ascribed to the equilibrium

$$Co(NH_3)_5CO_3^+ + H_3O^+ \rightleftarrows Co(NH_3)_5CO_3H^{2+} + H_2O \qquad 1/K \qquad (6)$$

followed by substitution of water for the protonated carbonate

$$Co(NH_3)_5CO_3H^{2+} + H_2O \longrightarrow Co(NH_3)_5OH_2^{3+} + HCO_3^- \qquad (7)$$

Later work utilizing oxygen-18 labeling[250,251] has shown that

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the carbonate loss is by means of decarboxylation, since the metal–oxygen bond of the complex remains intact.[252]

$$\mathrm{Co(NH_3)_5{*}OCO_2H^{2+}} \longrightarrow \mathrm{Co(NH_3)_5{*}OH^{2+}} + \mathrm{CO_2} \qquad k_1 \quad (8)$$

(*It is of interest that carbonate removal by* Pb^{2+} *or* Hg^{2+} *in aqueous solution also occurs without Co–O bond fission, though the situation with respect to* Ba^{2+} *is not so clearly defined.*)

Recent kinetic studies[164] covering the wide acidity range $1 < \mathrm{pH} < 8$ have clarified existing disagreements[109,253,254] concerning the magnitudes of K (the acid dissociation constant of $\mathrm{Co(NH_3)_5CO_3H^{2+}}$) and k_1 (the rate constant of reaction 8). The former is now conclusively known to have a value of 6.4 at 25° and $\mu = 0.5\ M$. From eq 6 and 8, it is seen that the observed pseudo-first-order rate constant should satisfy the relation

$$k_{\mathrm{obsd}} = k_1(\mathrm{H^+})/[K + (\mathrm{H^+})] \qquad (9)$$

This is found to fit the experimental data admirably,[164] with $k_1 = 1.25\ \mathrm{sec^{-1}}$ at 25°, $\mu = 0.5\ M$. The temperature dependence parameters are $\Delta H^{\pm} = 17.0 \pm 0.5$ kcal/mole and $\Delta S^{\pm} = -0.5 \pm 1.0$ eu.

In strongly basic solution, a hydrolysis occurs[254] but is very much slower than the acid-catalyzed reaction and yields the hydroxo product

$$\mathrm{Co(NH_3)_5CO_3^+} + \mathrm{OH^-} \longrightarrow \mathrm{Co(NH_3)_5OH^{2+}} + \mathrm{CO_3^{2-}} \qquad k_2 \quad (10)$$

The rate law is of the normal second-order form for alkaline hydrolysis

$$R = k_2(\mathrm{complex})(\mathrm{OH^-}) \qquad (11)$$

The value of k_2 is $3.3 \times 10^{-6}\ M^{-1}\ \mathrm{sec^{-1}}$ at 25° and $\mu = 1.0\ M$, and its temperature dependence is described by the parameters $\Delta H^{\pm} = 30$ kcal/mole and $\Delta S^{\pm} = 18$ eu. There is no evidence for any appreciable contribution to the hydrolysis by a reaction of the type

$$\mathrm{Co(NH_3)_5CO_3^+} + \mathrm{H_2O} \longrightarrow \mathrm{Co(NH_3)_5OH^{2+}} + \mathrm{HCO_3^-} \quad (12)$$

Related studies[163,255] of the isotopic exchange reaction

$$\mathrm{Co(NH_3)_5CO_3^+} + \mathrm{H^{14}CO_3^-} \rightleftharpoons \mathrm{Co(NH_3)_5{}^{14}CO_3^+} + \mathrm{HCO_3^-} \quad (13)$$

have been made in the range $9 < \mathrm{pH} < 10$. Interpretation of the data in terms of acid hydrolysis and/or direct carbonate exchange[163,254,255] are probably in error. The rate-determining processes under the exchange conditions now appear[164] to be the ones by means of which carbon can exchange between $\mathrm{CO_2}$ and carbonate, namely

$$\mathrm{H_2CO_3} \rightleftharpoons \mathrm{H_2O} + \mathrm{CO_2} \qquad (14)$$

$$\mathrm{HCO_3^-} \rightleftharpoons \mathrm{OH^-} + \mathrm{CO_2} \qquad (15)$$

We turn now to consideration of the ligand replacement process with respect to chelated carbonato species of the general form $\mathrm{CoN_4CO_3^+}$ (where $\mathrm{N_4}$ represents $\mathrm{(NH_3)_4}$, $\mathrm{(NH_3)_2}$, en, $\mathrm{en_2}$, $\mathrm{pn_2}$, $\mathrm{tn_2}$, tren, α-trien, β-trien, etc.). In these compounds, there is good evidence that the bidentate carbonato attachment, though under great steric strain (see section III.B), is firm enough even in aqueous solution to cause it to behave as an extremely weak base. This contrasts sharply with the relatively high basicity of monodentate carbonate, as discussed above, and is paralleled by the behavior of the corresponding oxalato complexes.[256] The reactivity of the bidentate carbonato complexes is thus in a number of respects quite different from the monodentate species, both as regards hydrolysis reactions and carbonate exchange reactions.

The earliest kinetic work on this type of compound was Pedersen's study[257a] of the acid-catalyzed hydrolysis of the ion $\mathrm{CO(NH_3)_4CO_3^+}$ within the limited acidity range $3 < \mathrm{pH} < 4$ established by glycolate and acetate buffers. The rate law was shown to be of the form

$$k_{\mathrm{obs}} = k_0 + k_1(\mathrm{H^+}) \qquad (16)$$

and was explained in terms of a dual mechanism, with contributions from noncatalyzed aquation and specific hydrogen ion catalysis. Recently, this same reaction has been investigated[257b] over a much wider acidity range ($1 < \mathrm{pH} < 5$), in the absence of buffer at the lower pH's and with a phosphate–citrate buffer at the upper end of the scale. Pedersen's conclusions have been confirmed and expanded into a detailed mechanism on the basis of data obtained both by acidometric and spectrophotometric techniques. All the observations are consistent with a successive ring-opening–decarboxylation mechanism, as follows.

$$\mathrm{Co(NH_3)_4CO_3^+} + \mathrm{H_2O} \longrightarrow \mathrm{Co(NH_3)_4(OH)(CO_3H)^+} \qquad k_0 \quad (17)$$

$$\mathrm{Co(NH_3)_4CO_3^+} + \mathrm{H_3O^+} \longrightarrow \mathrm{Co(NH_3)_4(OH_2)(CO_3H)^{2+}} \qquad k_1 \quad (18)$$

$$\mathrm{Co(NH_3)_4(OH_2)(CO_3H)^{2+}} \rightleftharpoons \mathrm{Co(NH_3)_4(OH)(CO_3H)^+} + \mathrm{H^+} \qquad K_1 \quad (19)$$

$$\mathrm{Co(NH_3)_4(OH_2)(CO_3H)^{2+}} \longrightarrow \mathrm{Co(NH_3)_4(OH)(OH_2)^{2+}} + \mathrm{CO_2} \qquad k_2 \quad (20)$$

$$\mathrm{Co(NH_3)_4(OH_2)_2^{3+}} \rightleftharpoons \mathrm{Co(NH_3)_4(OH)(OH_2)^{2+}} + \mathrm{H^+} \qquad K_2 \quad (21)$$

k_2 is known to be large by analogy to the decarboxylation of $\mathrm{Co(NH_3)_5CO_3H^+}$ as discussed above and also based on an estimate[258] of $k_1 \sim 2\ \mathrm{sec^{-1}}$ for $\mathrm{[Co(en)_2(OH_2)(CO_3H)]^{2+}}$ at 20°. K_1 and K_2 govern "instantaneous" proton-transfer equilibrations, so Pedersen's rate law (eq 16) is applicable. At 25° and $\mu = 0.5\ M$, $k_0 = 1.3 \times 10^{-4}\ \mathrm{sec^{-1}}$ and $k_1 = 1.5\ M^{-1}\ \mathrm{sec^{-1}}$, and the corresponding temperature dependence parameters are, for $\Delta H^{\pm}$, 12 ± 5 and 15.3 ± 1.0 kcal/mole, and for $\Delta S^{\pm}$, -37 ± 19 and -6.3 ± 3.8 eu. k_0 is essentially independent of ionic strength variation, while k_1 behaves in the manner expected for reaction between two unipositive ions. Posey and Taube[258a] have shown by means of oxygen-18 tracer studies that only one of the oxygens in the diaquo product comes from the solvent. The mechanistic formulation given above is completely consistent with this observation, since Co-O bond fission can occur in the rate-determining ring-opening reactions defined by k_0 and k_1, while one of the carbonato oxygens must remain attached to cobalt during decarboxylation. It is of interest that a polarographic study[258b]

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of the hydration of $Co(NH_3)_4CO_3^+$ at the two pH's (3.29 and 4.10) also yields values for k_0 and k_1 which agree very well with the values given above.

All other studies of the acid hydrolysis of the $CoN_4CO_3^+$ type of complex can be readily fitted into the outlined scheme. For $Co(en)_2CO_3^+$, the published[259,260] data are interpreted very satisfactorily by means of eq 16, with $k_0 = 1.3 \times 10^{-4}$ sec^{-1} and $k_1 = 0.52$ M^{-1} sec^{-1} at 25° and $\mu \sim 0.3$ M, values quite close to those for the tetraammine under these conditions.[257b] An additional term in the rate law previously proposed[260,261] for $Co(en)_2CO_3^+$ is probably in error, since it can contribute significantly only at pH >4, where the process becomes complicated by the fact that hydrolysis is no longer essentially complete. Studies of the pn_2 and tn_2 analogs[161] show that there are no great differences introduced by altering the nonlabile amine ligands, the only significant change being an increase in k_0 by a factor of about 3 for the tn_2 complex.

Base hydrolysis of $Co(en)_2CO_3^+$ has been studied by several workers[253,262–264] and appears to consist of a relatively slow hydroxide-catalyzed ring-opening reaction followed by an even slower displacement of the carbonate group. Also involved are a number of *cis–trans* equilibria so that the overall process becomes quite complex.

$$Co(en)_2CO_3^+ + OH^- \longrightarrow cis\text{-}Co(en)_2(OH)(CO_3) \qquad k_1 \quad (22)$$

$$cis\text{-}Co(en)(OH)(CO_3) + OH^- \longrightarrow cis\text{-}Co(en)_2(OH)_2^+ + CO_3^{2-} \qquad k_2 \quad (23)$$

$$cis\text{-}Co(en)_2(OH)(CO_3) \rightleftarrows trans\text{-}Co(en)_2(OH)(CO_3) \quad (24)$$

$$cis\text{-}Co(en)_2(OH)_2^+ \rightleftarrows trans\text{-}Co(en)_2(OH)_2^+ \quad (25)$$

At 25° and $\mu \sim 1$ M, $k_1 \sim 4 \times 10^{-3}$ M^{-1} sec^{-1} and $k_2 \sim 10^{-6}$ M^{-1} sec^{-1}. In strongly basic solution both reactions 22 and 23 go essentially to completion, and the rate of isomerization of *cis*-$Co(en)_2(OH)(CO_3)$ is much too slow[262] to require consideration in interpreting the successive reaction data. It is interesting to note that k_2 above corresponds to the k_2 of reaction 10 for $Co(NH_3)_5CO_3^+$, and that these two rate constants differ by only a small factor, if at all, at 25°.

Substitution of tren for $(en)_2$ has a relatively small effect on k_1, but prevents the occurrence of the *cis–trans* equilibria, thus simplifying the interpretation of data obtained at lower basicities.[253] For the complex $Co(tren)CO_3^+$ it has thus been possible to evaluate rate constants not only for the ring-opening process, k_1, but also for ring closure and for noncatalyzed hydrolysis of the ring-opened species.

$$Co(tren)CO_3^+ + OH^- \rightleftarrows Co(tren)(OH)(CO_3) \qquad k_1, k_1^* \quad (26)$$

$$Co(tren)(OH)(CO_3) + H_2O \rightleftarrows Co(tren)(OH)_2^+ + HCO_3^- \qquad k_3, k_3^* \quad (27)$$

At 20° and $\mu \sim 0.1$ M, $k_1 = 6.0 \times 10^{-3}$ M^{-1} sec^{-1}, $k_1^* = 6.5 \times 10^{-5}$ sec^{-1}, $k_3 = 4.5 \times 10^{-6}$ sec^{-1}, and $k_3^* = 2.3 \times 10^{-3}$ sec^{-1}. It is noteworthy that the latter figure is the only directly observed rate constant so far reported for a carbonate anation reaction. Data[254] on the acid hydrolysis of $Co(NH_3)_5CO_3^+$ (eq 8) do show that this reaction is also an equilibration in the range of 8.4 < pH < 9.4. However, the mechanism of the reverse process is not known so that any rate-constant estimation is without meaning at this stage.

We consider now in some detail a third type of carbonato ligand replacement reaction—one which can be investigated conveniently only in the range 7 < pH < 10, where net decomposition of carbonato complexes by acid or base hydrolysis is negligible. Here one may evaluate rates of ligand substitution by examination of its exchange with carbon-14-labeled "free" carbonate present in the same solution. For the pentaammine carbonato cobaltic complex, it is now evident[164] that the residual acid-catalyzed hydrolysis rate, which of course could provide an exchange path, is still much more rapid even at pH ~10 than the observed isotopic carbon interchange. As explained above, the rate-determining processes are therefore those by means of which carbon exchanges between CO_2 and carbonate (reactions 14 and 15). However, in the case of the tetramine series, $CoN_4CO_3^+$, the situation is quite different since ring opening of the chelated carbonato ligand is a necessary first step in the interchange process. Harris and coworkers have made a series of studies[72,168,265–267] of the complexes for which $N_4 = (NH_3)_4$, $(en)_2$, $(pn)_2$, and $(tn)_2$ and an additional study has been reported[85] where N_4 = *cis*-$(NH_3)_2$en. The significant experimental facts are that the exchange rate is accelerated in a more or less linear fashion by increase in (H^+) and that plots of the rate *vs.* "free" carbonate concentration at a fixed acidity are linear and have a positive slope and a nonzero intercept, and both slope and intercept are similarly pH dependent. All the data have been successfully rationalized[163] in terms of a multistep mechanism involving (a) aquo-dechelation to form a ring-opened aquocarbonato species, (b) various acid and base equilibria involving the ring-opened species, (c) exchange by complete aquation, and (d) exchange by direct carbonate-for-carbonate interchange. In recent years, much new quantitative data concerning the equilibrations involved have been reported,[253,257b,262] and it is now possible to confirm and reinforce several aspects of the proposed general mechanism.

The aquo-dechelation step was given[163] as[268]

$$CoN_4CO_3^+ + H_2O \rightleftarrows CoN_4(OH)(CO_3H)^+ \qquad K_1 \quad (28)$$

The forward rate of reaction 28 at 25° is now known to be about 10^{-4} sec^{-1} (see acid hydrolysis discussion above), faster by a factor of about 10 than is necessary to account for the rate of carbonate exchange. Since the equilibrium constant K_1 is known[262] to be close to 10^{-3}, the reverse process is much more rapid, and establishment of the aquodechelation equilibrium will thus be attained within an hour.[269] The rate-determining exchange steps must therefore succeed the aquodechelation, as previously assumed, and will involve various

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(259) J. Y. Tong, E. St. A. Kean, and B. B. Hall, *Inorg. Chem.*, 3, 1103 (1964).

(260) G. M. Harris and V. S. Sastri, *ibid.*, 4, 263 (1965).

(261) R. B. Jordan and D. J. Francis, *ibid.*, 6, 1605 (1967).

(262) H. Scheidegger and G. Schwarzenbach, *Chimia*, 19, 166 (1965).

(263) M. E. Fargo, *Coord. Chem. Rev.*, 1, 66 (1966).

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(266) D. R. Stranks, *ibid.*, 48, 911 (1952).

(267) J. E. Boyle and G. M. Harris, *J. Amer. Chem. Soc.*, 80, 782 (1958).

(268) The product was previously assumed[163,253,262] to be in the form $CoN_4(OH_2)(CO_3)^+$. However, recent data on the pK of the closely related complex $CoN_4(OH_2)(C_2O_4)^+$ (S. C. Chan, private communication) indicate that the water ligand must be much more acidic than the carbonato group. Presumably there is some degree of sharing of the proton by internal hydrogen bonding between the OH and CO_3 groups.

(269) Contributions to the dechelation by the acid- or base-catalyzed reactions 18 and 22 need not be considered since they are very slow throughout the pH range of the exchange studies.

possible reactions of the species in acid–base equilibrium, namely

$$\mathrm{CoN_4(H_2O)(CO_3H)^{2+} \rightleftarrows CoN_4(OH)(CO_3H)^+ + H^+} \qquad K_2 \quad (29)$$

$$\mathrm{CoN_4(OH)(CO_3H)^+ \rightleftarrows CoN_4(OH)(CO_3) + H^+} \qquad K_3 \quad (30)$$

The magnitudes of K_2 and K_3 are close to 5×10^{-6} and 2×10^{-9}, respectively, at room temperatures[262] and are not altered greatly by changes in the nature of N_4 even as drastic as substituting tren for en.[253] The considerable resistance of the neutral deprotonated product $\mathrm{CoN_4(OH)(CO_3)}$ either to hydrolysis or isomerization[262,263] suggests that it is probably inactive in the exchange process. However, $\mathrm{CoN_4(H_2O)(CO_3H)^{2+}}$ is known to decarboxylate rapidly (see discussion above regarding reaction 20) and $\mathrm{CoN_4(OH)(CO_3H)^+}$ may be similarly unstable, though probably much less so due to the possibility of internal bridging by the one remaining acidic proton.[268] One is therefore provided with two equilibrations to account for the "free"-carbonate-independent aquation exchange path

$$\mathrm{CoN_4(H_2O)(CO_3H)^{2+} \overset{k_1}{\rightleftarrows} CoN_4(OH)(OH_2)^{2+} + CO_2} \quad (31)$$

$$\mathrm{CoN_4(OH)(CO_3H)^+ \overset{k_2}{\rightleftarrows} CoN_4(OH)_2^+ + CO_2} \quad (32)$$

accompanied, of course, by additional "instantaneous" acid–base equilibrations analogous to reaction 21. The rate of carbonate exchange by this mechanism is thus given by the expression

$$R_A = k[\mathrm{CoN_4(H_2O)(CO_3H)^{2+}}] + k_2[\mathrm{CoN_4(OH)(CO_3H)^+}] \quad (33)$$

Symbolizing the total concentration of all forms of the carbonato complex, chelated or not, by a, and recalling that K_1 is very small, one may recast eq 33 in the form

$$R_A = k_1K_1(\mathrm{H^+})a/K_2 + k_2K_1a \quad (34)$$

Since all quantities are known except k_1 and k_2, one can evaluate the latter from the experimental observations at two or more acidities. This method of analysis has been applied to the data[163] with respect to the "free" carbonate-independent exchange rate of $(\mathrm{pn})_2$ and to some new data[142] on the ions *cis*- and *trans*-$\mathrm{Co(NH_3)_2enCO_3^+}$, where a wider pH range was covered than in any of the earlier work, enabling greater assurance concerning the interpretation. Using the values already mentioned for K_1 and K_2 at 25°, one derives $k_1 \sim 1$ sec^{-1} and $k_2 \sim 2 \times 10^{-3}$ sec^{-1} for both sets of data considered. The former value is of the order of magnitude expected (see discussion above of reaction 20), and k_2 exhibits the considerable decrease in decarboxylation reactivity one would predict for the half-protonated species.

The second-order "free"-carbonate-dependent direct exchange path may be interpreted in two main ways. The first adopts the conventional ion-pairing point of view of anation and relates the reaction to carbonate interchange within the ion pairs (all the free carbonate is assumed to be in the form $\mathrm{HCO_3^-}$, which is true within 5% in the range $7 < \mathrm{pH} < 9$), $\mathrm{CoN_4(OH_2)(CO_3H)^{2+} \cdot HCO_3^-}$ or $\mathrm{CoN_4(OH)(CO_3H)^+ \cdot HCO_3^-}$. Alternatively, one can visualize attack by "free" carbonate to displace $\mathrm{H_2O}$ or $\mathrm{OH^-}$ and form the unstable intermediate $\mathrm{CoN_4(CO_3H)_2^+}$ with subsequent ring closure completing the exchange, in the manner proposed for the exchange of glycine with triglycinatonickel(II).[270] Unfortunately, a clear-cut choice between the two mechanisms is not possible, since the study has not included high enough "free" carbonate concentrations to test for the curvature of the rate *vs.* carbonate concentration plot expected for the ion-pair concept. The data are therefore analyzed without definition of possible intermediates, according to the reactions

$$\mathrm{CoN_4(OH_2)(CO_3H)^{2+} + H{*}CO_3^- \overset{k_3}{\rightleftarrows} CoN_4(OH_2)({*}CO_3H)^{2+} + HCO_3^-} \quad (35)$$

$$\mathrm{CoN_4(OH)(CO_3H)^+ + H{*}CO_3^- \overset{k_4}{\rightleftarrows} CoN_4(OH)({*}CO_3H)^+ + HCO_3^-} \quad (36)$$

The rate of direct carbonate exchange is thus given by

$$R_B = k_3[\mathrm{CoN_4(OH_2)(CO_3H)^{2+}}][\mathrm{HCO_3^-}] + k_4[\mathrm{CoN_4(OH)(CO_3H)^+}][\mathrm{HCO_3^-}] \quad (37a)$$

which, using the symbolism of eq 34 with the definition b = [total free carbonate], yields the expression

$$R_B = k_3K_1(\mathrm{H^+})ab/K_2 + k_4K_1ab \quad (37b)$$

When applied to the experimental observations,[163,267] one obtains $k_3 \sim 100\ M^{-1}$ sec^{-1} and $k_4 \sim 0.3\ M^{-1}$ sec^{-1} at 25°, showing again the several hundred-fold factor noted for the k_1/k_2 ratio.

Mention should be made of the fact that, while the values of k_1, k_2, k_3, and k_4 do not deviate by more than a factor or 2 or 3 for the various N_4 species when N_4 is $(\mathrm{NH_3})_4$, $(\mathrm{en})_2$, $(\mathrm{pn})_2$, or $(\mathrm{NH_3})_2$en, the complex $\mathrm{Co(tn)_2CO_3^+}$ undergoes carbonate exchange with rate constants smaller by a factor of about an order of magnitude.[267] The ring-opened $(\mathrm{tn})_2$ species should not differ significantly from the others in the series. One therefore must ascribe its decreased reactivity to a decrease in K_1, the dechelation equilibrium constant. This perhaps is a result of tighter bonding of the carbonato in the chelate form due to increased steric hindrance by, or greater degree of hydrogen bonding to, the trimethylenediamine groups as compared to the other amine ligands.

Finally, there is one further type of isotopic exchange rate study which is relevant to work reviewed so far. This is the study of the exchange of oxygen atoms between $\mathrm{Co(NH_3)_4CO_3^+}$ ion and oxygen-18-labeled solvent water.[271] The rate constant observed at 25°, pH ~9, and low ionic strength is $k_{ex} = 1.7 \times 10^{-5}$ sec^{-1}, and was equated to the rate of the previously suggested ring-opening process of reaction 17. However, for this, $k_0 = 1.3 \times 10^{-4}$ sec^{-1}, as reported above. The oxygen-exchange rate constant is, in fact, rather close to the rate constant for limiting pseudo-first-order carbonate exchange by aquation, which is expressed by R_A/a, where R_A is defined in eq 34. For $\mathrm{Co(NH_3)_4CO_3^+}$, $R_A/a \sim 1.0 \times 10^{-5}$ sec^{-1} under the conditions specified for k_{ex}.[142] This near-equivalence of k_{ex} and R_A/a suggests that Odell, *et al.*,[271] may, in fact, have been really measuring the aquation portion of the carbonate exchange rate with the complex ion. This is possible since "free" carbonate equilibrates its oxygen atoms with the solvent water much more rapidly than the rate they reported, as they themselves showed. An alternative explanation follows from

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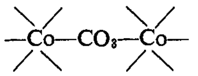
the fact that k_{ex} need not be as great as k_0 even if it results from the same process. The exchange mechanism is assumed to be

$$Co(NH_3)_4CO_3^+ + H_2O^* \rightleftharpoons Co(NH_3)_4(^*OH)(CO_3H)^+ \quad (38)$$

However, k_{ex} will be identical with k_0 of reaction 17 *only if every ring-opening-ring-closing event results in oxygen atom exchange between water and complex.* This clearly need not be so, since in the reverse of reaction 38 the labeled oxygen has at a maximum a one-third chance of remaining in the complex ion, and perhaps very much less than this. In fact, the studies by Taube and coworkers[250,257b] suggest that exchange of oxygen atoms does *not* occur between water and the carbonato moiety at all, at least in the complete decarboxylation reaction in strongly acid solution.

3. Addition and Polymerization

Partial hydrolysis of $Co(CO_3)_3^{3-}$ ion has been reported[141] to result in the formation of a *sesquicarbonato ion* corresponding to $[Co_2(NO_2)_8(CO_3)_3]^{8-}$. The presence of binuclear cobalt is confirmed by preparation and identification of $K_8[Co_2(NO_2)_8(CO_3)_3]\cdot 2H_2O$. The change in molar conductance and cryoscopic measurements of the mean ionic weight confirm the presence of nine ions, and a bridged structure



has been proposed to account for the presence of binuclear cobalt. On heating the compound loses water first and the anhydrous material decomposes to yield CO_2.

$$\underset{\text{(large dark red cubic crystals)}}{K_8[Co_2(NO_2)_8(CO_3)_3]} \longrightarrow 8KNO_2 + Co_2O_3 + 3CO_2$$

A binuclear sesquicarbonato anion, $[Co_2(NO_2)_6(CO_3)_3]^{6-}$, has been isolated as its cesium salt (orange microcrystalline pentahydrate) and as the hexaamminecobalt(III) salt (dark yellow microcrystalline trihydrate). Electrical conductance measurements, elemental analysis, crystallo-optic studies, and thermal decomposition studies confirm the above formula for the complex ion.

Several binuclear mixed ligand carbonato complexes of Ce(IV) and U(IV) of the types

$$(CHN_3H_5)_5NH_4[Ce_2(CO_3)_5F_4]$$
$$(CHN_3H_5)_8(NH_4)_2[U_2(CO_3)_8C_2O_4]\cdot 6H_2O$$

are known. Both complexes are unstable in aqueous solutions and the uranium(IV) carbonate oxidizes even in the dry state.[64]

The Be(II) polynuclear complex anion, $Be_4O(CO_3)_6^{6-}$, has been well characterized[65,95] and a related binuclear species, $[Be_2(H_2O)_2(CO_3)_2(OH)_3]^{3-}$, finds itself as a gravimetric reagent for the determination of Be(II)[121-123] as mentioned earlier. Very little is known concerning the polynuclear carbonato complexes of Fe(III) and Cr(III).

4. Heterogeneous Reactions

In the preparative methods described, several simple carbonato complexes are obtained by an elegant heterogeneous reaction using moist solid Ag_2CO_3 in the last stage of synthesis. A *cis*-dichloro complex is thus converted to a carbonato complex without contamination or serious disruption of the rest of the structure. Likewise Hg_2CO_3 has been used in place of Ag_2CO_3, and the accompanying racemization effects were well studied.[145] Guanidinium carbonate finds extensive application in the preparation and isolation of several carbonato complexes, for example[62]

$$Th(C_2O_4)_2\cdot 6H_2O(c) + 5(CHN_3H_5)_2CO_3 \longrightarrow (CHN_3H_5)_6Th(CO_3)_5\cdot 4H_2O + (CHN_3H_5)_2C_2O_4 + 2H_2O$$

Lead(II) and Hg^{2+} are reported to cause instantaneous precipitation of the carbonate in $Co(NH_3)_5CO_3^+$ ion, whereas the reaction with Ba^{2+} ion is 100 times slower.[252] From a study of oxygen-18 experiments, several observations have been made concerning the reaction

$$Co(NH_3)_5CO_3^+ + M^{2+} + H_2O \longrightarrow Co(NH_3)_5OH_2^{3+} + MCO_3$$

5. Thermal Decomposition

Extensive studies have been made on the thermal decomposition of simple carbonates and mixed carbonates both of natural and synthetic origin on account of their scientific interest and industrial value. An example of such studies[272] is the thermal decomposition of $MgCO_3\cdot 3H_2O$ (nesquehonite) and $MgCO_3\cdot(NH_4)_2CO_3\cdot 4H_2O$ using thermogravimetric analysis (TGA) and differential thermal analysis (DTA) and by optical microscopy. Interest in the study on magnesium compounds stems out of the fact "active" magnesia (MgO) is a good catalyst and can be prepared from any one of the following naturally occurring magnesium carbonates: magnesite, $MgCO_3$; nesquehonite, $MgCO_3\cdot 3H_2O$; lansfordite, $MgCO_3\cdot 5H_2O$; hydromagnesite, $4MgCO_3\cdot Mg(OH)_2\cdot 4H_2O$; and artinite, $MgCO_3\cdot Mg(OH)_2\cdot 3H_2O$.

The thermal behavior of the carbonato complexes of several types, however, received good attention in the hands of Russian workers,[50,54,98] and routine TGA and DTA studies have been reported as part of analytical characterization of newly isolated carbonato complexes in the solid form (see Table IV).

Ammonium scandium carbonate, $NH_4Sc(CO_3)_2\cdot 1.5H_2O$, decomposes in three stages,[96] first losing water at 120°, carbon dioxide at 140–190°, forming crystalline ScO(OH) at 280–305°, and finally Sc_2O_3 at 435–480°. Thermal studies indicate that one water is somehow most firmly held in $Na_6Th(CO_3)_5\cdot 12H_2O$ suggesting nonequivalence of water molecules in the hydrates.[273] The corresponding guanidiunium salt, $(CH_6N_3)_6Th(CO_3)_5\cdot nH_2O$, begins to lose all water at 50–80° and decomposes above 150°.[62] The crystals of $(NH_4)_2[ZrO(CO_3)_2]\cdot 3H_2O$ dehydrate readily and on further heating decompose to yield CO_2 and NH_3 and ZrO_2 at 600°.[41]

$$(NH_4)_2[ZrO(CO_3)_2] \longrightarrow ZrO_2 + 2NH_3(g) + 2CO_2(g) + H_2O(g)$$

The following pattern of decomposition is reported for a tetranuclear carbonato complex of Fe(III).[124]

$$(NH_4)_6[Fe_4O_3(CO_3)_6]\cdot 4H_2O \longrightarrow 2Fe_2O_3 + 7H_2O(g) + 6CO_2(g) + 6NH_3(g)$$

The thermal decomposition of several cobalt(III)–carbonato complexes ($K_3Co(CO_3)_3\cdot 3H_2O$,[100] $[Co(NH_3)_6][Co(CO_3)_3]$,[100] $K[Co(NH_3)_2(CO_3)_2]\cdot H_2O$,[100] $K_3[Co(CO_3)_2(NO_2)_2]$,[141] [Co-

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(272) R. M. Dell and S. W. Weller, *Trans. Faraday Soc.*, 55, 2203 (1959).

(273) I. I. Chernyaev, V. A. Golovnya, and A. K. Molodkin, *Russ. J. Inorg. Chem.*, 3, 117 (1958).

$(NH_3)_4CO_3]NO_3 \cdot 1.2H_2O$,[274] and $Co(NH_3)_4CO_3X$, where X = Cl, Br, I[274]) may be represented by the following equations.

$$2K_3Co(CO_3)_3 \longrightarrow 3K_2CO_3 + Co_2O_3 + 3CO_2(g)$$

$$[Co(NH_3)_6][Co(CO_3)_3] \longrightarrow Co_2O_3 + 6NH_3(g) + 3CO_2(g)$$

$$2K[Co(NH_3)_2(CO_3)_2] \longrightarrow K_2CO_3 + Co_2O_3 + 4NH_3(g) + 3CO_2(g)$$

$$2K_3[Co(CO_3)_3(NO_2)_2] \longrightarrow K_2CO_3 + Co_2O_3 + 4KNO_2 + CO_2(g)$$

$$6[Co(NH_3)_4CO_3]Cl \longrightarrow 3Co_2OCl_2 + N_2(g) + 22NH_3(g) + 3H_2O(g) + 6CO_2(g)$$

$$6[Co(NH_3)_4CO_3]Br \longrightarrow 3Co_2OBr_2 + N_2(g) + 22NH_3(g) + 3H_2O(g) + 6CO_2(g)$$

A recent development in thermal studies is the use of mass spectrometer with rapid scanning devices to identify the gaseous reaction products and to establish the right stoichiometry in conjunction with other analytical methods. In the thermal decomposition of $[Co(NH_3)_4CO_3]X$ type complexes, the exact nature of $Co_2OX_2(s)$ is not known. Also the iodide and nitrate complexes are reported to yield complex stoichiometric results with varying $NH_3(g)$/complex(s), $CO_2(g)$/complex(s) ratios as well as free iodine in the case of the iodide complex.[274] In an earlier TGA study[275] the anhydrous mixed ligand type carbonato complexes exhibited the following order of decreasing thermal stability: $[Co(en)_2CO_3]Cl > [Co(pn)_2CO_3]Cl > [Co(tn)_2CO_3Cl] > [CO(NH_3)_4CO_3]NO_3$ (explosively unstable). The dehydration endothermic peak maxima temperatures obtained in DTA, however, indicate the following order of stability for the corresponding hydrates: $[Co(pn)_2CO_3]Cl \cdot H_2O < [Co(NH_3)_4CO_3NO_3] \cdot H_2O < [Co(tn)_2CO_3]Cl \cdot H_2O < [Co(en)_2CO_3]Cl \cdot H_2O$.

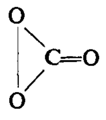
The pyrolysis of several covalently bound organic carbonates of the dialkyl, diaryl, and alkyl–aryl types has been the subject of extensive investigation both from a kinetic standpoint and mechanistic correlation standpoint.[276–278] Dimethyl carbonate vapor is reported to show extraordinary stability toward pyrolysis and photolysis even at temperatures as high at 350°.[279]

6. Mass Spectral Studies

Coordinated carbonate in complexes of the type $[Co(NH_3)_4CO_3]X$ decomposes on heating, and therefore direct introduction into a mass spectrometer would only result in analyzing gaseous CO_2, NH_3, and H_2O. Among the products of thermal dissociation small amounts of N_2 and NO have also been detected mass spectrally but not N_2O because of a masking CO_2 peak (*m*/*e* 44).[274]

Several covalently bound carbonates, primarily organic carbonate esters, have been studied with the following objectives: (i) to ascertain if a covalent carbonate is relatively stable under electron impact,[280] (ii) to study electron impact induced rearrangements,[280–282] (iii) to observe protonation of CO_3,[280, 281] and (iv) to collect pertinent evidence for the possible occurrence of CO_3 as a detectable species.[280] In all the 24 covalently bound carbonates studied mass spectrally it is interesting to note dimethyl carbonate is somewhat unique in that it does show a significant parent peak indicating its stability toward electron impact. Although no unequivocal evidence for the occurrence of CO_3^+ ion (*m*/*e* 60) as a distinguishable moiety in the mass fragments can be given, there is experimental evidence for the corresponding triply protonated species, $C(OH)_3^+$, observed in the mass spectra of several dialkyl carbonates in varying abundance. This is further supported by high resolution mass spectrometry.[281]

The special interest in the molecular species CO_3, carbon trioxide, has been reviewed recently by one of the authors (K. V. K.).[283] Subsequently additional experimental evidence for the related $C(OH)_3^+$ ion has been reported by an nmr study[284] which was directed toward a search for the trihydroxy carbonium ion. In an earlier study where CO_3 has been isolated for the first time in Dry Ice matrix by uv photolysis of CO_2,[285] several possible structures have been proposed. One of them is



suggesting nonequivalence of the oxygens in CO_3. The observed infrared absorption frequencies for normal CO_3 and the related isotopic species are shown in Table XIII along with the known vibrational frequencies of the *ionically*, *covalently*, and *coordinately* bound carbonate. The large number of observed bands in the infrared spectrum of CO_3 seem to indicate close similarity to the coordinated carbonate.

7. Photochemical Studies

Photochemical studies on gaseous carbon dioxide are too numerous to summarize here.[288–294] Several such studies[295–297] have been reported for carbonic acid and simple carbonates but none on carbonato complexes. The effect of iron(II) on the photoreduction of CO_2 in aqueous solution to form oxalic

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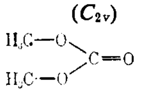
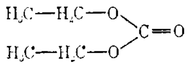
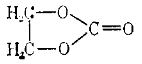
Table XIII

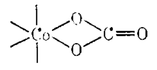
Vibrational Frequencies of Various Related "CO_3" Species

Carbon trioxide (C_{2v}?)	*Observed bands* (cm^{-1})[285]							
(a) $^{12}C^{16}O_3$	568	593	972	1073	1880	2045	3105	3922
(b) $^{13}C^{16}O_3$	565	592	947	1074	1835	1991	3050	
(c) $^{12}C^{18}O_3$	540	562	955	1015	1845	2008	3011	
	also 2140 in (a) and 2029 in (c)							

Carbonate: ionic (D_{3h})	*Frequency assignments* (cm^{-1})[286 a] ν_1	ν_3	ν_4	ν_2
$^{12}C^{16}O_3{}^{2-}$	1063	1415 (2)	680 (2)	879
$^{13}C^{16}O_3{}^{2-}$	1063	1376 (2)	677 (2)	851
$^{12}C^{18}O_3{}^{2-}$	1025	1416 (2)	674 (2)	868

ν_1: C–O symmetric stretching; ν_3: C–O asymmetric stretching; ν_4: in-plane deformation; ν_2: out-of-plane deformation.

Carbonate: covalent (C_{2v})	*Observed bands* (cm^{-1})[97 b]				
	1760	1280	793	969	914
	1750	1262	790	1021	858
	1870	1162	774	1074	974

Carbonate: coordinate (C_{2v})	*Calculated and observed bands for bidentate carbonate* (cm^{-1})[155 c]							
	1595	1038	771	370	1282	669	429	...[d]
$[Co(NH_3)_4CO_3]Cl$	1593	1030	760	395	1265	673	430	834

[a] Frequency data taken from ref 286; $^{12}C^{18}O_3{}^{2-}$ from Urey.[287] [b] See Gatehouse, Livingstone, and Nyholm.[97] [c] See Fujita, Martell, and Nakamoto.[155] [d] Calculated.

acid by ultraviolet radiation received recent attention.[298,299] The photolysis of dimethyl carbonate yields CO_2, dimethyl ether, and occasionally methanol, depending on imposed experimental conditions.[300]

8. Isotope Effects

Although deuterium,[163] carbon-14,[163,255] and oxygen-18[250–252,257] have been used as tracers for studying the kinetics and mechanism of isotopic exchange between free carbonate–bicarbonate ion and several cobalt(III) carbonato mixed ligand type complexes (see section III.D), only the following three reactions received attention from the standpoint of evaluating the equilibrium carbon isotope effects.

$$Co(NH_3)_4{}^{12}CO_3]^+ + \left\{\begin{matrix}H^{14}CO_3{}^- \\ {}^{14}CO_3{}^{2-}\end{matrix}\right. \rightleftarrows [Co(NH_3)_4{}^{14}CO_3]^+ + \left\{\begin{matrix}H^{12}CO_3{}^- \\ {}^{12}CO_3{}^{2-}\end{matrix}\right. \quad (39)$$

$$[Co(en)_2{}^{12}CO_3]^+ + \left\{\begin{matrix}H^{14}CO_3{}^- \\ {}^{14}CO_3{}^{2-}\end{matrix}\right. \rightleftarrows [Co(en)_2{}^{14}CO_3]^+ + \left\{\begin{matrix}H^{12}CO_3{}^- \\ {}^{14}CO_3{}^{2-}\end{matrix}\right. \quad (40)$$

$$[Co(en)_2{}^{12}CO_3]^+ + \left\{\begin{matrix}H^{13}CO_3{}^- \\ {}^{13}CO_3{}^{2-}\end{matrix}\right. \rightleftarrows [Co(en)_2{}^{13}CO_3]^+ + \left\{\begin{matrix}H^{12}CO_3{}^- \\ {}^{12}CO_3{}^{2-}\end{matrix}\right. \quad (41)$$

For reaction 39 the equilibrium isotope effect reported[301,302] is 0.875 at 0° and 0.900 at 30°, suggesting depletion of ^{14}C in the complex ion relative to free carbonate, the latter being the strongly bonded state of carbon. For reaction 40 the equilibrium isotope effect[303] is 0.990 ± 0.019 at 25° and for reaction 41[303] more or less the same, 0.991 ± 0.014 at 25°. All the three reactions, however, in a subsequent study[304] showed no true isotope effect, and the observed equilibrium constants have been explained in terms of a nonexchanging impurity,[305,306] the nature of which is still unknown. A recent explanation[307] takes into account that the isotope effect is indeed only apparent and might be due to colloidal decomposition products ($CoCO_3$) holding the $^*CO_3{}^{2-}$ in a nonexchangeable form.

The exchange equilibrium constants: $[Co(NH_3)_4{}^{12}CO_3]^+$—$H^{14}CO_3{}^-$, K_1, $[Co(NH_3)_4{}^{12}CO_3]^+$—$^{14}CO_3{}^{2-}$, K_2, and $[Co(NH_3)_4{}^{12}CO_3]^+$—$^{14}CO_2$, K_3, representing the respective equilibria have been calculated by the application of the theory of equilibrium isotope effects.[287] In the absence of experimental data on the fundamental vibrational frequencies of the complex ion $[Co(NH_3)_4CO_3]^+$, a substitute molecular species, $COCl_2$ (phosgene), has been used for evaluating the ratio partition functions: $f = Q_{^{14}COCl_2}/Q_{^{12}COCl_2}$. (For recent data on the fundamental vibrational frequencies of the normal ion see ref 155.) The calculated equilibrium constants at three different temperatures are shown below.[302] Knowledge of the partition function ratios is useful in predicting the exchange equilibrium constants but the paucity of spectroscopic data for both the normal and isotopically substituted molecules makes it a distant goal.

Temp, °K	K_1	K_2	K_3
273.16	0.858	0.876	1.116
293.16	0.871	0.887	1.106
313.16	0.882	0.897	1.098

Interest in the study of Mg^{2+} ion effect on the ^{13}C fractionation in the equilibrium

$$^{13}CO_2(g) + {}^{12}CO_3{}^{2-}(aq) = {}^{12}CO_2(g) + {}^{13}CO_3{}^{2-}(aq)$$

derives mainly from the fact that magnesium is the third major constituent among the various ionic species in sea water. It has been suggested[29] sea water contains nearly 67% of its total $CO_3{}^{2-}$ as $MgCO_3{}^0$ neutral complex, the actual structure of which, however, is conjectural at the present time although magnesium(II) is known[286] to exhibit hexacoordination in $Mg(H_2O)_6{}^{2+}$ and $Mg(C_2O_4)_2(H_2O)_2{}^{2-}$. If one assumes a coordination complex of the type $[Mg(H_2O)_4CO_3]^0$ in which carbonate acts as bidentate, then the symmetrical XY_3 form of free car-

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(307) S. Sheel and G. M. Harris, unpublished results quoted in ref 25 of Lapidus and Harris.[163]

bonate changes to what is in effect an XYZ_2 type of structure resulting in altered symmetry and perhaps changes in the characteristic vibrational frequencies. This would lead to preferential ^{13}C enrichment in $MgCO_3^0$ neutral complex according to the following equilibrium.

$$^{13}CO_2(g) + Mg^{12}CO_3^0(aq) = {}^{12}CO_2(g) + Mg^{13}CO_3^0(aq)$$

Experimentally it was found to be so as shown by the increased value of the equilibrium isotope effect in the presence of Mg^{2+} ions[286] in CO_2–CO_3^{2-} exchange ($K_{MgCO_3^0} > 1.012$). Frequency data are not available for $Mg^{12}CO_3^0$ and $Mg^{13}CO_3^0$ to calculate the theoretical equilibrium constant. However, by using a substitute like COF_2 (carbonyl fluoride) in place of the actual $MgCO_3^0$ complex, an inverse isotope effect (0.935) has been reported[286] stressing on the inadequacy of the COF_2 model. It would therefore be of interest to make the normal coordinate calculations for the $MgCO_3^0$ neutral complex and obtain frequency data that might permit evaluation of the partition function ratio, $Q_{Mg^{13}CO_3^0}/Q_{Mg^{12}CO_3^0}$, and calculation of the equilibrium constant. Equilibrium isotope effects will thus have diagnostic value in the detection of complexes, and it would seem a *metal ion–carbonate* ion system has certain experimental advantages over other ligand systems.

9. *Miscellaneous Rate Studies*

Both bicarbonate and carbonate ions are found to be unreactive[308] with the hydrated electron (e_{aq}^-) in a 10^{-3} M CH_3OH medium; the second-order rate constants were estimated as $<10^6$ M^{-1} sec^{-1}. No carbonato complex, however, has been studied.

Several kinetic studies[309–313] on the acid- and base-catalyzed hydrolysis of dialkyl, diaryl and cyclic carbonates have been reported in recent literature, and they might be of mechanistic value in kinetic investigations involving metal–carbonato complexes.

IV. Applications

A. ANALYTICAL APPLICATIONS

Although carbonate ion has been in use in analytical chemistry for either precipitating carbonates, hydroxides, or basic carbonates or for neutralizing acid solutions, there are only a few carbonato complexes of analytical interest. As has already been mentioned a spectrophotometric titration method for the analytical determination of carbonate–bicarbonate and carbonate–hydroxide mixture makes use of the ultraviolet absorption of the ligand.[160] An iodometric method for the determination of cobalt has been developed using $Co(CO_3)_3^{3-}$ ion as an intermediate[314] and a colorimetric method employing this green complex ion absorbing at 260 and 440 mμ.[106]

A procedure for the gravimetric determination of beryllium(II)[121–123] involves the sparingly soluble compound, $[Co(NH_3)_6][Be(H_2O)_2(CO_3)_2(OH)_3]\cdot 3H_2O$. Analytical separation of uranium(VI) from iron(III) and other elements has been accomplished by way of the carbonato complexes. Carbonate complexing is efficient in the separation of indium(III) from zinc(II), cadmium(II), and aluminum(III) by a combination of ion-exchange techniques using cation and anion exchangers[230] (KU-2 in NH_4 form and EDE-10P in CO_3 form). Separation of gallium(III) from large amounts of zinc(II) on EDE-10P resin was equally efficient as also small amounts of zinc(II) from large amounts of gallium(III) on KU-2 cation exchanger.[229]

B. INDUSTRIAL APPLICATIONS

Extensive literature is available on the leaching of uranium ores by soluble carbonates and the important role the carbonato complexes play in uranium metallurgy. Carbonate leaching of pitchblende[315] and the precipitation of uraninite from a solution containing the uranyl carbonato complexes[316] and recovery of uranium from carbonate leach solutions by solvent extraction[317] have received considerable attention in view of the importance of uranium as a nuclear material. The occurrence of $UO_2(CO_3)_2^{2-}$ at pH 4.5–6.5 and $UO_2(CO_3)_3^{4-}$ at pH 6.5–11.5, as observed in laboratory experiments, has been reported to be of mineralogical significance while considering the genesis of Colorado Plateau ores. Carbonate chelation is also useful in removing uranium contamination from clothing.[318]

In the rare earth industry carbonate complexing is used for the removal of thorium(IV). Manganese(II)–carbonato complexes seem to participate in the extraction of manganese from its minerals by $(NH_4)_2CO_3$ leaching.[319] In the hydrometallurgical processing of manganese carbonate ore, CO_2 at high pressure brings manganese into solution, perhaps as a complex, and reprecipitates $MnCO_3$ (also $FeCO_3$) while keeping $MgCO_3$ and $CaCO_3$ in solution when the pressure of CO_2 is released.[320] The ion-pair complex $MnHCO_3^+$ has been identified as one of the stable species that needs special attention in the purification of potable waters.[223] The rate of oxidation of Mn^{2+} in aerated water increases with increasing pH and markedly decreases if HCO_3^- ion is present.

The effect of adding several cobalt(III) and chromium(III) ammine compounds to the nickelation vats in the nickel electroplating industry has been studied.[321] Positive effect on luster formation in nickel plating was reported in the presence of $[Co(en)_2CO_3]Cl$ up to a concentration of 0.2 g/l. Other uses for the cobalt ammine compounds like $[Co(NH_3)_4CO_3]NO_3$ and $[Co(NH_3)_4CO_3]_2SO_4\cdot 3H_2O$ are as initiators in the photopolymerization of ethylenically unsaturated monomers.[322] Photopolymerization of acrylamide monomers is possible in about 30–35 min with the help of these two carbonato complexes.

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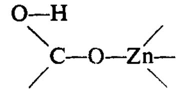
C. BIOLOGICAL APPLICATIONS

The transport of calcium(II) in the blood (pH 7.3) has been accounted for in terms of several bound-calcium species: Ca^{2+} ion (48%); Ca-phosphate complex (5%); $CaHCO_3^+$ (3%); Ca–citrate complex (3%); Ca-protein bound (41%). The less important ones are $Ca(HCO_3)_2^0$ or $CaCO_3^0$ ion-pair complexes.[33] The occurrence of zinc in the enzyme *carbonic anhydrase* naturally leads to the speculation if a carbonato complex of zinc(II) has any part in the overall hydration–dehydration equilibrium of CO_2 and H_2O. In an infrared spectral approach to this problem intended to elucidate the catalytic mechanism of carbonic anhydrase,[323] it has been found that a bicarbonate coordination with the zinc moiety can adequately explain the observed absorption bands. The carbonyl oxygen and the hydroxyl oxygen of the coordinated bicarbonate ion



are assumed to be held in the hydrophobic cavity of the enzyme in the hydration and O=C=O in the dehydration reactions.

Protonated carbonic acid, $C(OH)_3^+$, also called trihydroxy carbonium ion, found recently[283,284] might be of interest from a mechanistic point of view for the understanding of the various biological carboxylation processes. In an attempt to study the metal-complex catalyzed rearrangement of trimethylamine N-oxide, several metal ions and metal complexes have been found to be effective. However, $[Co(en)_2CO_3]^+$ ion is reported to have no catalytic effect[324] on the oxidative demethylation of $(CH_3)_3N$-O. While studying the fate of cobalt uptake, it has been found after subcutaneous injection of $[Co(NH_3)_4CO_3]Cl$; nearly 60% appeared in the urine in 3 hr and up to 80% in 24 hr.[325]

D. GEOCHEMICAL APPLICATIONS

Modern geochemistry dealing with the nature of the solute in various natural waters is primarily concerned with the problem of chemical speciation. The chemistry of CO_2 and certain metal ions in sea water is a good example. The occurrence of $UO_2(CO_3)_3^{4-}$ in sea water[326] and in hydrothermal solutions[327] has been reported with overwhelming supporting evidence not only for the complex-ion's ambient stability but also at elevated temperatures (150°) and pressures. Extensive studies on the stability relations among uranium compounds indicate that several carbonato complexes like UO_2CO_3, $UO_2(CO_3)_2(H_2O)_2^{2-}$, $UO_2(CO_3)_3^{4-}$ participate in the geochemistry of uranium.[32] From a study of the solubility of CuO in water as a function of pH under normal earth conditions corresponding to $p_{CO_2} = 10^{-3.52}$ atm, it was concluded[328] that sea water is saturated with respect to CuO and the dissolved species is $CuCO_3^0$, the neutral ion-pair complex at pH 8.1. However, at elevated pH's the occurrence of the anionic complex $Cu(CO_3)_2^{2-}$ is well known.

Several carbonato complexes of the ion-pair type have been reported to occur in small abundance[28] in a representative sample of sea water of 19% chlorinity, pH 8.1 at 25° and 1 atm total pressure. Of the total calcium(II) 91% is present as Ca^{2+} ion, 8% as $CaSO_4^0$ ion pair, 1% as $CaHCO_3^+$ ion pair, and 0.2% as $CaCO_3^0$ ion pair. Likewise, of the total magnesium(II), 87% is present as Mg^{2+} ion, 11% as $MgSO_4^0$ ion pair, 1% as $MgHCO_3^+$ ion pair, and 0.3% as $MgCO_3^0$ ion pair. The *Garrels–Thompson* model for sea water[28] thus demonstrates that of the total carbonate in sea water only 9% is present as free CO_3^{2-} ion, and the rest is attached to Ca(II) and Mg(II) (to a small degree to Na^+ ion) as the ion-pair complexes. It is interesting to note that a substantial fraction of the total carbonate in sea water, nearly 67%, is reported to occur as $MgCO_3^0$ neutral ion pair. This has numerous consequences in marine chemistry, marine biology, and algology. In concentrated brines it is even conceivable higher species such as $Ca(CO_3)_2^{2-}$ and $Ca(OH)_2(CO_3)_2^{4-}$ might occur.

In the study of equilibria among metal carbonates in water at 25° and 1 atm total pressure and in presence of CO_2, the stability of the following compounds has been reported:[32] $Pb_3(OH)_2(CO_3)_2$, hydrocerussite; $Cu_3(OH)_2(CO_3)_2$, azurite; and $Cu_2(OH)_2CO_3$, malachite. Malachite is stable relative to azurite under normal earth conditions ($p_{CO_2} = 10^{-3.52}$ atm); however, azurite can exist at higher p_{CO_2} and lower water activity obtainable in semiarid areas.

The list of applications is by no means exhaustive. The unique nature of carbonate ligand will be of multidisciplinary interest in areas of research that might appear totally unrelated at first glance.[329]

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