

THE CHEMISTRY OF THE METAL CARBONATO COMPLEXES

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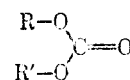
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I. Introduction

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

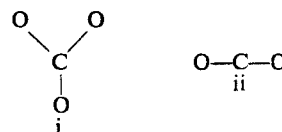
binding of the carbonate with numerous cations is essentially ionic.

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 carbonate complexes, for example, the $[\text{Co}(\text{NH}_3)_4\text{CO}_3]^+$ 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 carbonate complexes with the hope that at least some aspects of the interconversion of initially nonlinear structure i to the linear



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: $\text{CO}_2(\text{g})$, $\text{CO}_2(\text{aq})$, $\text{H}_2\text{CO}_3(\text{aq})$, $\text{HCO}_3^-(\text{aq})$, and $\text{CO}_3^{2-}(\text{aq})$ 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 ions¹⁸⁻²² (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 $\sim 10^{-2}$ to $\sim 10^{-30}$ 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 carbonate complexes, some of which exhibit bewildering complexity. Not much is known concerning the mixed hydroxo carbonate 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 are²⁴ CaCO_3 (calcite, aragonite), MgCO_3 (magnesite), and $\text{CaMg}(\text{CO}_3)_2$ (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

(nahcolite), KHCO_3 (kalcinite), $(\text{NH}_4)\text{HCO}_3$ (teschemacherite), $\text{Na}_3\text{H}(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O}$ (trona), $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ (thermonatrite), $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ (nesquehonite), and $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ (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: $\text{NaCa}_3(\text{UO}_2)(\text{CO}_3)_3\text{SO}_4\text{F} \cdot 10\text{H}_2\text{O}$. Several basic carbonates are known to contain OH^- and in certain special minerals F^- , Cl^- , and SO_4^{2-} as well: $\text{Zn}_3(\text{CO}_3)_2(\text{OH})_6$ (hydrozincite), $\text{Cu}_2(\text{CO}_3) \cdot (\text{OH})_2$ (malachite), $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$ (azurite), $\text{Mg}_4(\text{CO}_3)_3(\text{OH})_2 \cdot 3\text{H}_2\text{O}$ (hydromagnesite), and $\text{Pb}_2(\text{CO}_3)\text{Cl}_2$ (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: $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ or $\text{Mg}(\text{OH})(\text{HCO}_3) \cdot 2\text{H}_2\text{O}$ (see under thermal decomposition studies). Although only a very small number of carbonate complexes are prepared with ease in the solid state by dissolving the carbonate in excess alkali carbonates, for example, $\text{Na}_3\text{Co}(\text{CO}_3)_3 \cdot 3\text{H}_2\text{O}$,²⁶ a great majority of mixed ligand mono-carbonato complexes can be obtained more readily from the *cis*-dichloro compound by a reaction with slurried Ag_2CO_3 . Tables I, II, and III²⁷⁻⁹⁴ 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) CaHCO ₃ ⁺ (27, 28) | MnHCO ₃ ⁺ (31) NaHCO ₃ ⁰ (27, 28) Ca(HCO ₃) ₂ ⁰ (27, 28, 33) |
| Ib | MCO ₃ ⁰ | MgCO ₃ ⁰ (27, 28) CaCO ₃ ⁰ (27, 28) | CuCO ₃ ⁰ (32) |
| 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) Cu(CO ₃) ₂ ²⁻ (39) Pb(CO ₃) ₂ ²⁻ (39, 40) | ZrO(CO ₃) ₂ ²⁻ (41) UO ₂ (CO ₃) ₂ ²⁻ (42, 43) 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 ²⁻ (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) 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) |
| IVb | M(CO ₃) ₄ ⁵⁻ | Sc(CO ₃) ₄ ⁵⁻ (37, 53) | Th(CO ₃) ₅ ⁶⁻ (60-62) Pu(CO ₃) ₅ ⁶⁻ (63) Be ₄ O(CO ₃) ₆ ²⁻ (65) |
| V | M(CO ₃) ₅ ⁶⁻ | Mo(CO ₃) ₅ ⁶⁻ (59) | |
| VI | M(CO ₃) ₆ ⁸⁻ M(CO ₃) ₃ ¹²⁻ | Ce(CO ₃) ₆ ⁸⁻ (64) Th(CO ₃) ₆ ¹²⁻ (48) Pu(CO ₃) ₆ ¹²⁻ (63) | |

Table II
Mixed-Ligand-Type Complexes^a

| Species | Ref | Species | Ref |
|--|--------|---|-----|
| Co(NH ₃) ₄ CO ₃ ⁺ | 66 | Co(NO ₂) ₄ CO ₃ ³⁻ | 86 |
| Co(NH ₃) ₅ CO ₃ ⁺ | 67-69 | Co(NH ₃)(NO ₂) ₃ CO ₃ ²⁻ | 87 |
| Co(en) ₂ CO ₃ ⁺ | 70 | Co(NH ₃)(CH ₃ COO) ₃ CO ₃ ²⁻ | 87 |
| Co(pn) ₂ CO ₃ ⁺ | 71 | Co(en)(CO ₃) ₂ ⁻ | 88 |
| Co(tn) ₂ CO ₃ ⁺ | 73 | Pu(CO ₃) ₂ C ₂ O ₄ ²⁻ | 48 |
| Co(trien)CO ₃ ⁺ | 74-78 | Pu(CO ₃) ₂ (C ₂ O ₄) ₂ ⁴⁻ | 48 |
| Co(dan) ₂ CO ₃ ⁺ | 79 | Pu(CO ₃) ₂ C ₂ O ₄ ⁴⁻ | 48 |
| Co(dipy) ₂ CO ₃ ⁺ | 80 | Pu(CO ₃) ₃ (C ₂ O ₄) ₂ ⁶⁻ | 48 |
| Co(o-phen) ₂ CO ₃ ⁺ | 81 | Pu(CO ₃) ₄ (C ₂ O ₄) ₂ ¹⁰⁻ | 48 |
| Co(C ₁₈ H ₃₂ N ₄) ₂ CO ₃ ⁺ | 82, 83 | PuCO ₃ (C ₂ O ₄) ₂ ¹²⁻ | 48 |
| Co(NH ₃) ₂ (NO ₂) ₂ CO ₃ ⁻ | 84 | Sc ₂ (CO ₃) ₄ (C ₂ O ₄) ₃ ⁸⁻ | 53 |
| Co(en)(NH ₃) ₂ CO ₃ ⁺ | 85 | | |

^a Mixed-ligand-type carbonato complexes of metals containing OH and H₂O 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; C₁₈H₃₂N₄, 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 |
|--|-----|--|-----|
| $(\text{CH}_3)_3\text{SbCO}_3$ | 89 | $\text{SnCl}_4 \cdot 2\text{C}_2\text{H}_4\text{CO}_3$ | 92 |
| $(\text{CH}_3)_3\text{SnCO}_3$ | 90 | $\text{SnCl}_4 \cdot (\text{C}_2\text{H}_5)_2\text{CO}_3$ | 93 |
| $(\text{C}_6\text{H}_5)_3\text{CrCO}_2\text{H} \cdot 3\text{H}_2\text{O}$ | 91 | $\text{SnCl}_4 \cdot 2(\text{C}_2\text{H}_5)_2\text{CO}_3$ | 92 |
| $[(\text{C}_6\text{H}_5)_3\text{Cr}]_2\text{CO}_3 \cdot 6\text{H}_2\text{O}$ | 91 | $\text{SbCl}_5 \cdot (\text{CH}_3)_2\text{CO}_3$ | 94 |
| $\text{TiCl}_4 \cdot 2\text{C}_2\text{H}_4\text{CO}_3$ | 92 | $\text{SbCl}_5 \cdot (\text{C}_2\text{H}_5)_2\text{CO}_3$ | 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.

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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 IV⁹⁵⁻¹⁰¹ 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 $(\text{CH}_5\text{N}_2\text{H}^+)$ and complex ions like $\text{Co}(\text{NH}_3)_6^{3+}$. 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: $\text{Co}(\text{CO}_3)_3^{3-}$.

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 $(\text{KCO}_2\text{-O})_2\text{-Co-O-Co(O-CO}_2\text{K})_2$,¹⁰³ $\text{Co}(\text{OH})_4(\text{COOH})_2$,¹⁰⁴ and $\text{Co}[\text{Co}(\text{CO}_3)_3]$.¹⁰⁵ The absorption maxima of the green solution were found to be at 260 and 440 $\text{m}\mu$, the latter being weak. An analytical method for determining cobalt makes use of the uv maximum.¹⁰⁶

Although $\text{Co}(\text{CO}_3)_3^{3-}$ was postulated earlier^{107,108} than the isolation of $[\text{Co}(\text{NH}_3)_6][\text{Co}(\text{CO}_3)_3]^{45}$ in the solid form, the bidentate character of carbonate ligand attracted much attention and other preparations followed: $\text{K}_3[\text{Co}(\text{CO}_3)_3] \cdot 3\text{H}_2\text{O}$,¹⁰⁹ $\text{Na}_3[\text{Co}(\text{CO}_3)_3] \cdot 3\text{H}_2\text{O}$.²⁶ Furthermore the ability of the compound, $[\text{Co}(\text{NH}_3)_5\text{CO}_3]\text{NO}_3 \cdot \text{H}_2\text{O}$,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 $\text{Co}(\text{II})$, 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 $\text{K}_3\text{Co}(\text{CO}_3)_3$ 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 |
|--|-------------------------|--------|
| $\text{Na}_6[\text{Be}_2\text{O}(\text{CO}_3)_6] \cdot 5\text{H}_2\text{O}$ | White, crystalline | 95 |
| $\text{K}_6[\text{Be}_2\text{O}(\text{CO}_3)_6]$ | White, crystalline | 95 |
| $[\text{Co}(\text{NH}_3)_6][\text{Be}_2\text{O}(\text{CO}_3)_6] \cdot 10$ or $11\text{H}_2\text{O}$ | Orange, crystalline | 95 |
| $\text{NH}_4[\text{Sc}(\text{CO}_3)_2] \cdot \text{H}_2\text{O}$ (1.5–2.0 H_2O) | Sparingly soluble | 96 |
| $(\text{CH}_3\text{N}_3\text{H})_3[\text{Sc}(\text{CO}_3)_4] \cdot 5\text{H}_2\text{O}$ | Hydrolyzes readily | 53 |
| $\text{K}_6[\text{Sc}_2(\text{CO}_3)_4(\text{C}_2\text{O}_4)_2] \cdot 6\text{H}_2\text{O}$ | White, noncrystalline | 53 |
| $\text{Na}_4[\text{Sc}_2(\text{CO}_3)_4(\text{C}_2\text{O}_4)_2] \cdot 8\text{H}_2\text{O}$ | White, noncrystalline | 53 |
| $(\text{CH}_3\text{N}_3\text{H})_2[\text{Sc}_2(\text{CO}_3)_2(\text{C}_2\text{O}_4)_2] \cdot 3\text{H}_2\text{O}$ | Hydrolyzes readily | 53 |
| $(\text{CH}_3\text{N}_3\text{H})_2[\text{Sc}_2(\text{CO}_3)_2(\text{C}_2\text{O}_4)_2] \cdot \text{H}_2\text{O}$ | Hydrolyzes readily | 53 |
| $\text{K}_6\text{Mo}(\text{CO}_3)_5 \cdot 2\text{H}_2\text{O}$ | White ppt | 59 |
| $(\text{NH}_4)_2[\text{ZrO}(\text{CO}_3)_2] \cdot 3\text{H}_2\text{O}$ | White ppt | 41 |
| $\text{Na}_2[\text{Cu}(\text{CO}_3)_2] \cdot 3\text{H}_2\text{O}$ | | 97 |
| $\text{K}_2[\text{Co}(\text{CO}_3)_2] \cdot 4\text{H}_2\text{O}$ | | 97 |
| $\text{Na}[\text{Ce}(\text{CO}_3)_2] \cdot 2\text{H}_2\text{O}$ | White ppt | 54 |
| $\text{NH}_4[\text{Ce}(\text{CO}_3)_2] \cdot 3\text{H}_2\text{O}$ | White ppt | 54 |
| $(\text{CH}_3\text{N}_3\text{H})[\text{Ce}(\text{CO}_3)_2] \cdot 2\text{H}_2\text{O}$ | Insoluble | 54 |
| $(\text{CH}_3\text{N}_3\text{H})_3[\text{Ce}(\text{CO}_3)_4] \cdot 2\text{H}_2\text{O}$ | Dark red rods | 54 |
| $[\text{Co}(\text{NH}_3)_6][\text{Ce}(\text{CO}_3)_4] \cdot 15\text{H}_2\text{O}$ | Orange crystalline | 54 |
| $(\text{NH}_4)_3[\text{Co}(\text{NH}_3)_6][\text{Ce}(\text{CO}_3)_4] \cdot 12\text{H}_2\text{O}$ | Orange crystals | 54 |
| $(\text{CH}_3\text{N}_3\text{H})_3[\text{Co}(\text{NH}_3)_6][\text{Ce}(\text{CO}_3)_4] \cdot 12\text{H}_2\text{O}$ | Orange crystals | 54 |
| $(\text{CH}_3\text{N}_3\text{H})_4[\text{Ce}(\text{CO}_3)_4(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$ | Yellow needles | 98 |
| $(\text{NH}_4)_2(\text{CH}_3\text{N}_3\text{H})_2[\text{Ce}(\text{CO}_3)_4(\text{H}_2\text{O})_2]$ | | 98 |
| $\text{Na}_4[\text{Ce}(\text{CO}_3)_5\text{H}_2\text{O}] \cdot 11\text{H}_2\text{O}$ | Bright yellow crystals | 98 |
| $\text{K}_6[\text{Ce}(\text{CO}_3)_5\text{H}_2\text{O}] \cdot \text{H}_2\text{O}$ | Fine yellow crystals | 98 |
| $[\text{Co}(\text{NH}_3)_6][\text{Ce}(\text{CO}_3)_5\text{H}_2\text{O}] \cdot 5\text{H}_2\text{O}$ | Also tetrahydrate | 98 |
| $(\text{CH}_3\text{N}_3\text{H})_6[\text{Ce}(\text{CO}_3)_5\text{H}_2\text{O}] \cdot \text{H}_2\text{O}$ | Yellow plates | 98 |
| $(\text{NH}_4)(\text{CH}_3\text{N}_3\text{H})_5[\text{Ce}(\text{CO}_3)_5\text{H}_2\text{O}] \cdot 4\text{H}_2\text{O}$ | | 98 |
| $(\text{NH}_4)[\text{Co}(\text{NH}_3)_6][\text{Ce}(\text{CO}_3)_6] \cdot 4\text{H}_2\text{O}$ | Rhombic crystals | 98 |
| $\text{Na}_8[\text{Er}(\text{CO}_3)_4] \cdot 18\text{H}_2\text{O}$ | | 99 |
| $[\text{Co}(\textit{o}\text{-phen})_2\text{CO}_3]\text{Cl} \cdot 5\text{H}_2\text{O}$ | Dark red crystals | 81 |
| $[\text{Co}(\textit{o}\text{-phen})_2\text{CO}_3]\text{Br} \cdot 4\text{H}_2\text{O}$ | Red crystalline | 81 |
| $[\text{Co}(\textit{o}\text{-phen})_2\text{CO}_3]\text{I}$ | Orange needles | 81 |
| $[\text{Co}(\textit{o}\text{-phen})_2\text{CO}_3]\text{NCS} \cdot 3\text{H}_2\text{O}$ | Brick-red ppt | 81 |
| $[\text{Co}(\textit{o}\text{-phen})_2\text{CO}_3]\text{NO}_2 \cdot 3\text{H}_2\text{O}$ | Brick-red crystals | 81 |
| $[\text{Co}(\textit{o}\text{-phen})_2\text{CO}_3]\text{NO}_2 \cdot 4\text{H}_2\text{O}$ | Red-brown crystalline | 81 |
| $[\text{Co}(\textit{o}\text{-phen})_2\text{CO}_3]\text{ClO}_4$ | Brownish red crystals | 81 |
| $[\text{Co}(\textit{o}\text{-phen})_2\text{CO}_3]\text{ClO}_4$ | Orange-red crystalline | 81 |
| $[\text{Co}(\textit{o}\text{-phen})_2\text{CO}_3]\text{BrO}_3$ | Red crystals | 81 |
| $[\text{Co}(\textit{o}\text{-phen})_2\text{CO}_3]\text{IO}_4$ | Pink crystalline | 81 |
| $[\text{Co}(\textit{o}\text{-phen})_2\text{CO}_3]_2\text{S}_2\text{O}_8 \cdot 7\text{H}_2\text{O}$ | Red crystals | 81 |
| $[\text{Co}(\textit{o}\text{-phen})_2\text{CO}_3]_2\text{S}_2\text{O}_8 \cdot 5\text{H}_2\text{O}$ | Red crystals | 81 |
| $[\text{Co}(\textit{dipy})_2\text{CO}_3]_2\text{CO}_3$ | | 80 |
| $\text{Na}_3[\text{Co}(\text{NO}_2)_4\text{CO}_3] \cdot 6\text{H}_2\text{O}$ | Dark yellow crystalline | 86 |
| $[\text{Co}(\text{NH}_3)_6][\text{Co}(\text{NO}_2)_4\text{CO}_3]$ | Orange crystalline | 86 |
| $[\text{Co}(\text{NH}_3)_6][\text{Co}(\text{NO}_2)_2(\text{CO}_3)_2] \cdot 2\text{H}_2\text{O}$ | Dark red crystals | 86 |
| $\text{Na}_3[\text{Co}(\text{NO}_2)_2(\text{CO}_3)_2] \cdot 4\text{H}_2\text{O}$ | Dark red crystals | 86 |
| $[\text{Co}(\text{en})_3][\text{Co}(\text{NO}_2)_2(\text{CO}_3)_2] \cdot 3\text{H}_2\text{O}$ | Dark red crystals | 86 |
| $\text{K}_3[\text{Co}(\text{CO}_3)_3] \cdot 3\text{H}_2\text{O}$ | Green crystals | 100 |
| $\text{Na}_3[\text{Co}(\text{CO}_3)_3] \cdot 3\text{H}_2\text{O}$ | Green crystals | 26 |
| $[\text{Co}(\text{NH}_3)_6][\text{Co}(\text{CO}_3)_3]$ | Dark green needles | 45, 86 |
| $[\text{Co}(\text{NH}_3)_6][\text{Co}_2(\text{NO}_2)_6(\text{CO}_3)_2] \cdot 3\text{H}_2\text{O}$ | Dark yellow crystals | 86 |
| $[\text{Co}(\text{en})_3][\text{Co}_2(\text{NO}_2)_6(\text{CO}_3)_2] \cdot 5\text{H}_2\text{O}$ | Dark red plates | 86 |
| $\text{Cs}_6[\text{Co}_2(\text{NO}_2)_6(\text{CO}_3)_2] \cdot 5\text{H}_2\text{O}$ | Orange crystalline | 86 |
| $[\text{Co}(\text{trien})\text{CO}_3](\text{C}_6\text{H}_5)_4\text{B}$ | Orange precipitate | 73 |
| $\text{K}[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_2\text{CO}_3] \cdot 2\text{H}_2\text{O}$ | Dark red crystals | 101 |
| $(\text{CH}_3\text{N}_3\text{H})[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_2\text{CO}_3]$ | Orange needles | 101 |
| $[\text{Co}(\text{NH}_3)_6][\text{Co}(\text{NH}_3)_2(\text{NO}_2)_2\text{CO}_3]_3 \cdot 3\text{H}_2\text{O}$ | Orange crystals | 101 |
| $[\text{Co}(\text{en})_3][\text{Co}(\text{NH}_3)_2(\text{NO}_2)_2\text{CO}_3]_3 \cdot 6\text{H}_2\text{O}$ | Dark red crystals | 101 |

baltate(III),¹¹³ a series of cobalt(III) complexes with the general formula $[\text{Co}(\text{NO}_2)_n(\text{NH}_3)_{6-n}]^{3-n}$ ($n = 1-5$),¹¹⁴ and

another series of the type, $[\text{Co}(\text{CN})_n(\text{NH}_3)_{6-n}]^{3-n}$.¹¹⁴ An interesting compound, $\text{K}_2[\text{CoNH}_3(\text{NO}_2)_2\text{CO}_3] \cdot \text{H}_2\text{O}$, was one

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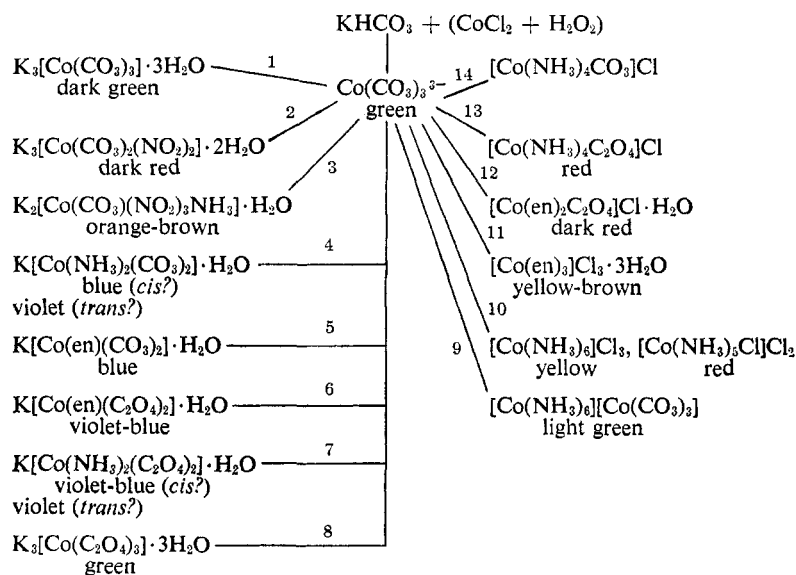
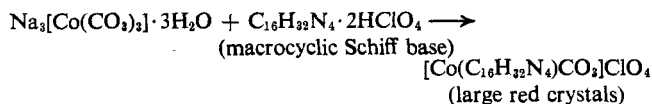


Figure 1. Synthetic applications of the Co(CO₃)₂²⁻ ion. Reagents used and references (in parentheses): 1, crystallization (100); 2, KNO₂ (141); 3, NH₄Cl + NaNO₂ + HC₂H₃O₂ (114); 4, (NH₄)₂CO₃ (100); 5, enH₂CO₃ (100); 6, enH₂CO₃ + K₂C₂O₄ (100); 7, (NH₄)₂C₂O₄ (100); 8, H₂C₂O₄ (100); 9, Co(NH₃)₆³⁺ (100); 10, NH₃ + NH₄Cl (100); 11, en + KCl (100); 12, enH₂C₂O₄ + KCl (100); 13, NH₃ + (NH₄)₂C₂O₄ (100); 14, NH₄Cl + NaHCO₃ (100).

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

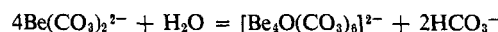
The sodium salt, Na₃[Co(CO₃)₃]·3H₂O, has certain advantages over the potassium salt in that it is more insoluble and easier to purify it from bicarbonate ion contamination. In any case both are useful synthetic intermediates. The following compounds have been prepared in good yields, shown in parentheses, starting from Na₃[Co(CO₃)₃]·3H₂O 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.



The mixed ligand type carbonate complexes of cobalt(III) are useful as synthetic intermediates in developing new reagents for use in biological chemistry,¹¹⁵ for example, β-[Co(trien)CO₃]⁺,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, NH₄[Co(NH₃)₂(NO₂)₂],¹¹⁷ with aqueous saturated KHCO₃ solution an in-

teresting compound, K[Co(NH₃)₂(NO₂)₂CO₃]·2H₂O, 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 NH₃ groups present *trans* to each other in Erdmann's salt.

The simplest beryllium carbonate complex, Be(CO₃)₂²⁻, analogous to the alkaline earth carbonate complexes has never been isolated in the solid form although from ion-exchange experiments it is reported to occur in 0.1 M (NH₄)₂CO₃ solutions.³⁸ In carbonate solutions Be(OH)₂ dissolves to give a variety of basic beryllium carbonates, 3K₂Be(CO₃)₂·Be(OH)₂,¹¹⁹ 3(NH₄)₂Be(CO₃)₂·Be(OH)₂,¹¹⁹ 2(NH₄)₂Be(CO₃)₂·Be(OH)₂,¹²⁰ which are not well characterized. Conductometric titration studies made recently⁹⁵ support the equilibrium



The corresponding sodium and potassium salts, Na₆[Be₄O(CO₃)₆]·5H₂O and K₆[Be₄O(CO₃)₆], have been isolated although the ammonium salt was found to be too unstable. A closely related compound, [Co(NH₃)₆][(H₂O)₂Be₂(CO₃)₂(OH)₃]·3H₂O, offers itself as a method for the gravimetric determination of Be(II).¹²¹⁻¹²³

Scandium hydroxide dissolves in (NH₄)₂CO₃ to yield a stable crystalline complex, (NH₄)Sc(CO₃)₂·1.5H₂O.⁹⁸ 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 carbonate-oxalato scandium complexes have been prepared recently for the first time,⁵³ and they are shown in Table IV.

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(115) D. A. Buckingham, J. P. Collman, D. A. R. Happer, and L. G. Marzilli, *J. Amer. Chem. Soc.*, **89**, 1082 (1967).

(116) A. M. Sargeson and G. H. Searle, *Inorg. Chem.*, **4**, 45 (1965).

(117) O. L. Erdman, *J. Prakt. Chem.*, **97**, 406 (1866).

Tetranuclear complexes of the type $[\text{Fe}_4\text{O}_3(\text{CO}_3)_6]^{6-}$ account for the solubility of Fe(III) salts in excess carbonate solutions. The following compounds have been isolated in the solid state: $\text{H}_6[\text{Fe}_4\text{O}_3(\text{CO}_3)_6]$, $(\text{NH}_4)_6[\text{Fe}_4\text{O}_3(\text{CO}_3)_6] \cdot 4\text{H}_2\text{O}$, $[(\text{NH}_2)_2\text{C}=\text{NH}]_6[\text{Fe}_4\text{O}_3(\text{CO}_3)_6] \cdot 2\text{H}_2\text{O}$, $[\text{Co}(\text{NH}_3)_6]_2[\text{Fe}_4\text{O}_3(\text{CO}_3)_6](\text{aq})$. Although Cr(III) salts dissolve in excess carbonate, no carbonate 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 carbonate complex of rhodium(III) has been prepared although the synthesis of several compounds containing the $\text{Rh}(\text{A}_m)\text{Cl}_2^+$, where $\text{A} = \text{NH}_3$, ethylenediamine, meso-butylenediamine, dl-butylenediamine, tetramethylenediamine, β, β', β'' -triaminoethylamine, and triethylenetetramine, has been reported recently.¹²⁵ Attempts to prepare $\text{Rh}(\text{en})_2\text{CO}_3^+$ starting from *cis*- $\text{Rh}(\text{en})_2\text{Cl}_2^+$ 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, $\text{Zr}_2\text{O}_3^{2+}$, occurring in solution.¹²⁹ Hydrous zirconia absorbs CO_2 to yield a material that exhibits cation-exchange properties¹³⁰ and a carbonate complex of the type $\text{Na}[\text{Zr}(\text{OH})_3\text{CO}_3]$ seem to account for the observed ion exchange behavior.¹³¹ However, a stable carbonate complex, $(\text{NH}_4)_4[\text{ZrO}(\text{CO}_3)_2] \cdot 3\text{H}_2\text{O}$,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 laboratories¹³⁴ using elution chromatography and radiotracer methods indicates rare earth (RE) complexes of the form, $[\text{RE}(\text{CO}_3)_4]^{5-}$, 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 carbonate complex. However, guanidinium salts of the formulas, $(\text{CH}_5\text{N}_3\text{H})_4[\text{Ce}(\text{CO}_3)_4] \cdot 2\text{H}_2\text{O}$ and $(\text{CH}_5\text{N}_3\text{H})_4[\text{Ce}(\text{CO}_3)_4(\text{H}_2\text{O})_4] \cdot 4\text{H}_2\text{O}$, are prepared and characterized⁹⁸ in support of both Ce(III) and Ce(IV) carbonate complexes. These com-

pounds provide interesting examples for studying the unusual coordination number of cerium and the possibility of isomerism.

Spectrophotometric investigations⁵⁶ also support the formation of carbonate complexes of the type $\text{M}(\text{CO}_3)_4^{5-}$ 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).⁵⁶ A solid with the composition $\text{Na}_3\text{Er}(\text{CO}_3)_4 \cdot 18\text{H}_2\text{O}$ has been isolated.⁵⁶

The carbonate 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, $\text{M}_6\text{Th}(\text{CO}_3)_5 \cdot x\text{H}_2\text{O}$, and attempts to prepare the hexacarbonatothorates have not been successful.⁶² Extensive literature on the carbonate complexes of U(VI) is available,^{49, 135-139} parts of which are discussed under determination of stability constants. The complex ions $\text{UO}_2(\text{CO}_3)_2(\text{H}_2\text{O})_2^{2-}$ and $\text{UO}_2(\text{CO}_3)_3^{4-}$ are well characterized and widely used in technology and in analysis.

Several tetra-, penta-, and octacarbonate 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 carbonate 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 carbonate 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) complexes⁶⁴ illustrated in Figure 2. Accordingly, *cis-trans* and

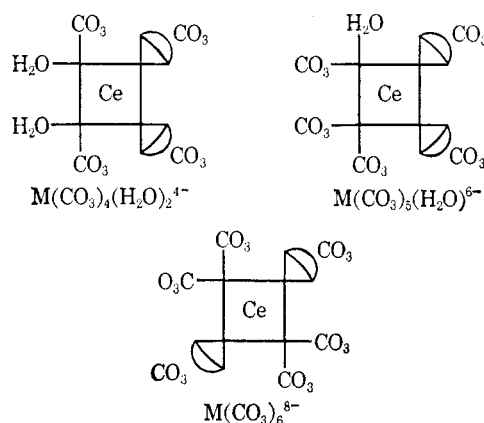


Figure 2. Quasi-bidentate carbonate ligand.

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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 $\text{Na}_3[\text{Co}(\text{NO}_2)_2(\text{CO}_3)_2] \cdot 4\text{H}_2\text{O}$, $[\text{Co}(\text{NH}_3)_6][\text{Co}(\text{NO}_2)_2(\text{CO}_3)_2] \cdot 2\text{H}_2\text{O}$, and $[\text{Co}(\text{en})_3][\text{Co}(\text{NO}_2)_2(\text{CO}_3)_2] \cdot 3\text{H}_2\text{O}$. Evidence for the corresponding *trans* compound derives mostly from preparative chemistry.¹⁴¹ Figure 3 illustrates the *cis-trans* isomerism in a

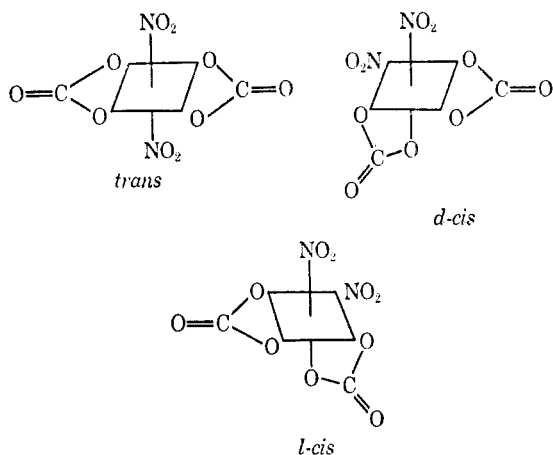


Figure 3. *cis-trans* isomerism in bis-carbonato complexes.

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 $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$.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*

Table V
Optical Properties of *cis-trans* Isomers

| Species | Wavelength λ_{max} , m μ | Absorbance, a_m | R_{el} |
|--|--|----------------------|-----------------|
| <i>cis</i> - $[\text{Co}(\text{NH}_3)_2\text{enCO}_3]^+$ | 504 | 125 | 142 |
| | 347 | 148 | |
| <i>trans</i> - $[\text{Co}(\text{NH}_3)_2\text{enCO}_3]^+$ | 512 | 95 | 142 |
| | 356 | 103 | |
| <i>cis</i> - $[\text{Co}(\text{NH}_3)_2(\text{CO}_3)_2]^-$ | 575 | 138 | 88 |
| | 390 | 251 | |
| <i>trans</i> - $[\text{Co}(\text{NH}_3)_2(\text{CO}_3)_2]^-$ | 540 | 63 | 88 |
| | 374 | 111 | |

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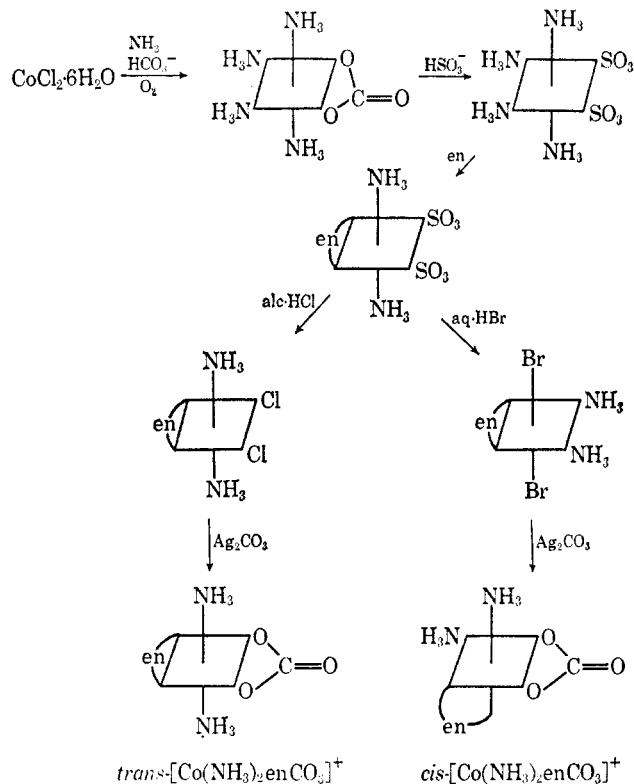


Figure 4. Synthesis of *cis*- and *trans*-carbonato complexes.

isomers of two selected carbonato complexes. Among the cobalt(III) ammine 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

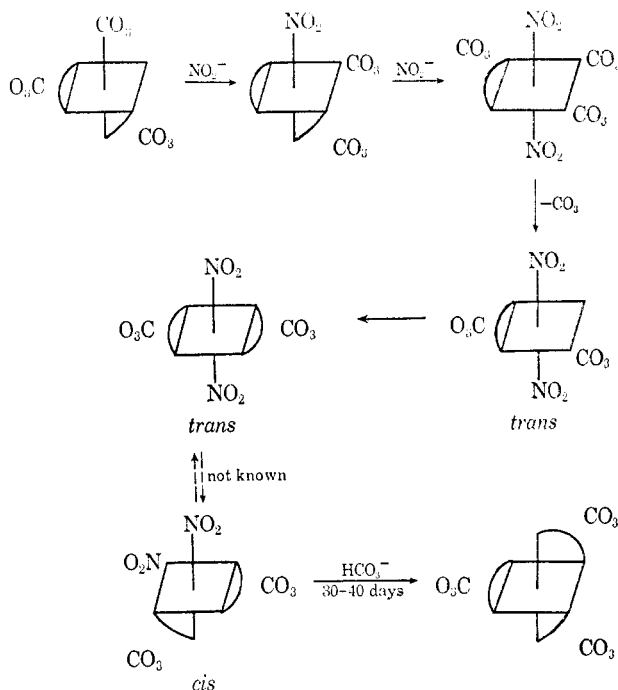


Figure 5. Reaction between $\text{Co}(\text{CO}_3)_3^{3-}$ and NO_2^- ions.

application of preparative chemistry in the elucidation of *trans-cis* isomerism in the carbonato complexes.

Table VI

| Ultraviolet Absorption Spectra of Metal Carbonato Complexes | | | |
|---|---------------------------|------------------------|----------|
| Carbonato complex | $\lambda_{max},^a$ $m\mu$ | a_m | Ref |
| HCO ₃ ⁻ | 210-230 | Weak | 159, 160 |
| Na ₂ CO 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) ₂ CO ₃] ⁺ | 238 | | 161 |
| | 250 (s) | | |
| [Co(pn) ₂ CO ₃] ⁺ | 238 | | 161 |
| | 248 (s) | | |
| [Co(tn) ₂ CO ₃] ⁺ | 238 | | 161 |
| | 250 (s) | | |
| [Co(NH ₃) ₄ CO ₃] ⁺ | 238 | | 161 |
| | 258 (s) | | |
| [Co(NH ₃) ₃ CO ₃] ⁺ | 233 (sh) | | |
| | 250-280 (s) | | 161 |
| | (sh) | | |
| [Co(o-phen) ₂ CO ₃] ⁺ | 274 | ~6.3 × 10 ⁴ | 81 |
| [Co(dipy) ₂ CO ₃] ⁺ | ... | ... | 80 |
| <i>cis</i> -[Co(NH ₃) ₂ (CO ₃) ₂] ⁻ | 220 | 1.38 × 10 ⁴ | 100 |
| <i>trans</i> -[Co(NH ₃) ₂ (CO ₃) ₂] ⁻ | 234 | 2.00 × 10 ⁴ | 100 |
| <i>cis</i> -[Co(NH ₃) ₂ enCO ₃] ⁻ | 243 | 1.66 × 10 ⁴ | 162 |
| <i>trans</i> -[Co(NH ₃) ₂ enCO ₃] ⁺ | 235 | 1.41 × 10 ⁴ | 162 |
| [Co(CO ₃) ₃] ²⁻ | 260 | ~10 ⁵ | 100, 106 |
| [Co(NH ₃)(NO ₂) ₂ CO ₃] ²⁻ | 259 | 2.57 × 10 ⁴ | 114 |
| α -[Co(trien)CO ₃] ⁺ | 250 | ~1.2 × 10 ⁴ | 116 |
| β -[Co(trien)CO ₃] ⁺ | 250 | ~1.2 × 10 ⁴ | 116 |
| <i>cis</i> -[Co(en)(CO ₃) ₂] ⁻ | 239 | 2.88 × 10 ⁴ | 88 |
| <i>trans</i> -[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 | ~10 ⁴ | |

^a s = solid; sh = shoulder.

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 coworkers¹⁴⁴⁻¹⁴⁹ 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 recently¹⁵⁰ makes use of the lower solubility of the levo rotatory isomer in aqueous acetone. ORD studies on (+)-D-[Co(en)₂CO₃Cl]¹⁵¹ and D-[Co(en)₂CO₃]ClO₄·0.5H₂O¹⁵² provide valuable data on their structures. With the availability of commercial in-

Table VII

| Visible Absorption Spectra of Metal Carbonato Complexes | | | |
|---|-------------------------|-------------|------|
| Carbonato complex | $\lambda_{max},$ $m\mu$ | a_m | Ref |
| [Co(CO ₃) ₃] ²⁻ | 440 | 166 | 100 |
| | 635 | 154 | |
| [Co(en) ₂ CO ₃] ⁺ | 358 | 120 | 163 |
| | 512 | 127 | |
| [Co(pn) ₂ CO ₃] ⁺ | 357 | 122 | 163 |
| | 515 | 133 | |
| [Co(tn) ₂ CO ₃] ⁺ | 360 | 128 | 163 |
| | 520 | 109 | |
| | (α) | (β) | |
| [Co(trien)CO ₃] ⁺ | 360 | 112 | 140 |
| (α , β forms) | 510 | 140 | 180 |
| [Co(o-phen) ₂ CO ₃] ⁺ | 350 | 2000 | 81 |
| | 510 | 100 | |
| [Co(dipy) ₂ CO ₃] ⁺ | ... | ... | 80 |
| [Co(NH ₃) ₃ CO ₃] ⁺ | (348) | (160) | 161 |
| | 505 | 94 | 164 |
| [Co(NH ₃) ₄ CO ₃] ⁺ | 362 | 122 | 142 |
| | 522 | 104 | |
| | 520 | 105 | 164a |
| <i>cis</i> -[Co(NH ₃) ₂ (CO ₃) ₂] ⁻ | 390 | 251 | 88 |
| | 575 | 138 | |
| <i>trans</i> -[Co(NH ₃) ₂ (CO ₃) ₂] ⁻ | 374 | 110 | 88 |
| | 540 | 63 | |
| <i>cis</i> -[Co(NH ₃) ₂ enCO ₃] ⁺ | 347 | 148 | 142 |
| | 504 | 125 | |
| <i>trans</i> -[Co(NH ₃) ₂ enCO ₃] ⁺ | 356 | 103 | 142 |
| | 512 | 95 | |
| [Co(NH ₃)(NO ₂) ₂ CO ₃] ²⁻ | 347 | 7413 | 114 |
| | 472 | 219 | |
| <i>cis</i> -[Co(en)(CO ₃) ₂] ⁻ | 390 | 214 | 88 |
| | 570 | 148 | |
| <i>trans</i> -[Co(en)(CO ₃) ₂] ⁻ | 388 | 204 | 88 |
| | 559 | 87 | |
| [CoACO ₃] ⁺ | 350 | 135 | 82 |
| (A = C ₁₆ H ₃₂ N ₄) | 500 | 121 | |

struments 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_6 | ν_2 | ν_8 | ν_3 | Ref |
|--|------------------|----------------|----------------|---------|--------------|-----|
| $\text{Na}_2[\text{Cu}(\text{CO}_3)_2] \cdot 3\text{H}_2\text{O}$ | 1529 | 1326 | { 1066 1050 | 850 | 755 | 97 |
| $\text{K}_2[\text{Co}(\text{CO}_3)_2] \cdot 4\text{H}_2\text{O}$ | ... | 1338 | { 1082 1049 | 884 | { 799 766 | 97 |
| $\text{K}_2[\text{Co}(\text{CO}_3)_2] \cdot 3\text{H}_2\text{O}$ | 1527 | 1330 | { 1080 1037 | 851 | 809 | 97 |
| $[\text{Co}(\text{NH}_3)_6][\text{Co}(\text{CO}_3)_2]$ | 1523 | 1285 | { 1073 1031 | 889 | 738 | 97 |
| $[\text{Co}(\text{NH}_3)_4(\text{CO}_3)_2]$ | 1590 | 1287 | 1033 | 831 | 742 | 155 |
| $[\text{Co}(\text{NH}_3)_2(\text{CO}_3)_2]$ | { 1623 1597 | 1265 | 1026 | 839 | { 763 744 | 155 |
| $[\text{Co}(\text{ND}_3)_2(\text{CO}_3)_2]$ | { 1639 1607 | 1260 | 1026 | 836 | { 762 742 | 155 |
| $[\text{Co}(\text{en})_2\text{CO}_3]\text{ClO}_4$ | 1643 | { 1267 1285 | ... | 833 | 757 | 155 |
| $[\text{Co}(\text{enD})_2\text{CO}_3]\text{ClO}_4$ | { 1615 1603 | { 1275 1288 | ... | 823 | 762 | 155 |
| $[\text{Co}(\text{en})_2\text{CO}_3]\text{Cl}$ | 1577 | { 1281 1272 | { 1059 1035 | 830 | 754 | 97 |
| $[\text{Co}(\text{en})_2\text{CO}_3]\text{Br}$ | 1575 | { 1282 1276 | { 1059 1038 | 825 | 757 | 97 |
| | { 1628 1615 | 1276 | ... | 827 | 759 | 155 |
| $[\text{Co}(\text{enD})_2\text{CO}_3]\text{Br}$ | 1618 | 1285 | ... | 821 | 768 | 155 |
| $[\text{Co}(\text{en})_2\text{CO}_3]\text{I}$ | 1565 | { 1290 1278 | { 1055 1034 | 824 | 756 | 97 |
| $[\text{Co}(\text{pn})_2\text{CO}_3]\text{X}$ | 1565- | 1260- | 1050- | 826- | 750- | 161 |
| | 1572 | 1273 | 1059 | 830 | 754 | |
| $[\text{Co}(\text{tn})_2\text{CO}_3]\text{X}$ | 1565- | 1280- | 1030- | 826- | 750- | 161 |
| | 1572 | 1284 | 1035 | 830 | 754 | |
| $[\text{Co}(\text{trien})_2\text{CO}_3](\text{C}_6\text{H}_5)_4\text{B}$ | 1574 | 1261 | 1030 | 844 | 748 | 73 |
| $[\text{Co}(\text{dipy})_2\text{CO}_3]_2\text{CO}_3$ | 1610 | | | | | 80 |
| $[\text{CoA}(\text{CO}_3)]\text{ClO}_4$ | { 1660 1630 | 1220 | | 820 | 750 | 82 |
| (A = $\text{C}_{16}\text{H}_{32}\text{N}_4$) | | | | | | |
| $[\text{Co}(\text{NH}_3)_4\text{CO}_3]\text{ClO}_4$ | 1602 | 1284 | ... | 836 | 762 | 155 |
| $[\text{Co}(\text{ND}_3)_4\text{CO}_3]\text{ClO}_4$ | 1603 | 1292 | ... | 835 | 765 | 155 |
| $[\text{Co}(\text{NH}_3)_4\text{CO}_3]\text{Cl}$ | 1593 | 1265 | 1030 | 834 | 760 | 155 |
| | 1604 | 1268 | | 832 | 768 | 156 |
| $[\text{Co}(\text{ND}_3)_4\text{CO}_3]\text{Cl}$ | { 1635 1607 | (1268) | (1031) | 832 | 753 | 155 |
| $[\text{Co}(\text{NH}_3)_4\text{CO}_3]_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$ | ... ^b | 1260 | ... | 856 | 756 | 97 |
| | | | 1021 | | | |
| $[\text{Co}(\text{NH}_3)_2\text{enCO}_3]\text{Cl} \cdot 0.5\text{H}_2\text{O}$ (<i>cis</i>) | 1630 | 1260 | 1054 | 830 | 762 | 162 |
| $[\text{Co}(\text{NH}_3)_2\text{enCO}_3]\text{Cl} \cdot \text{H}_2\text{O}$ (<i>trans</i>) | 1640 | 1260 | 1055 | 830 | 759 | 162 |

^a Values in cm^{-1} . The frequency notation used for ν_1 , ν_6 , 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 ($10^{-2} M \text{Na}_2\text{CO}_3$) shows a steep shoulder in the region 230–210 $m\mu$ with no maximum. Under similar conditions

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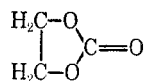
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both aqueous bicarbonate ion ($10^{-2} M$ NaHCO_3) and CO_3^{2-} (aq), however, exhibit extremely weak absorption, also with no maximum. This difference in the ultraviolet absorption spectra has been utilized in developing a spectrophotometric titration method¹⁶⁰ for the analytical determination of carbonate-bicarbonate and carbonate-hydroxide mixtures.

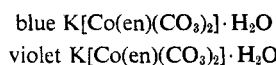
The ultraviolet absorption spectra of a great majority of the carbonato complexes, mostly cobalt(III) mixed ligand types, show intense absorption ($\alpha_M \approx 10^4$) in the region 220–270 $m\mu$. The pentaammine-carbonato complex, $[\text{Co}(\text{NH}_3)_5\text{CO}_3]^+$, has a broad band between 250 and 280 $m\mu$ in the solid state whereas in aqueous solution only a shoulder at 233 $m\mu$. The tetraammine-carbonato complex, $[\text{Co}(\text{NH}_3)_4\text{CO}_3]^+$, exhibits a *blue shift* of nearly 20 $m\mu$ in solution compared to the ultraviolet maximum in the solid state. The organic carbonates (ethylene carbonate¹⁶⁸)



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 $>\text{C}=\text{O}$ group.^{159, 169}

The visible as well as the ultraviolet absorption spectra of $[\text{Co}(\text{en})_2\text{L}]\text{Br}$, 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 $m\mu$, confirming the well-characterized spin-allowed transitions.^{171–173}

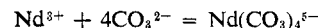
By successive replacement of the carbonate in $\text{Co}(\text{CO}_3)_3^{3-}$ with other ligands three series of cobalt(III) complexes have been synthesized and their absorption spectra reveal interesting details concerning stereochemistry. One such series is⁸⁸



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, $\text{K}[\text{Co}(\text{NH}_3)_2(\text{C}_2\text{O}_4)_2] \cdot \text{H}_2\text{O}$ and $\text{K}[\text{Co}(\text{en})(\text{C}_2\text{O}_4)_2] \cdot \text{H}_2\text{O}$. The authors⁸⁸ 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



The formation constant $K \approx 12$ has been reported for $\text{Nd}(\text{CO}_3)_4^{5-}$ at a constant ionic strength 5.35 and $\text{Nd}(\text{III}) = 0.0298 M$.

The infrared absorption spectra of numerous simple ionic carbonates both of laboratory and mineral origin (Li_2CO_3 , Na_2CO_3 , K_2CO_3 , $(\text{NH}_4)_2\text{CO}_3$, MgCO_3 , $3\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$, 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 compounds⁹⁷ 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 $>\text{C}=\text{O}$ 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: $\text{Co}(\text{NH}_3)_4\text{CO}_3^+$, $\text{Co}(\text{en})_2\text{CO}_3^+$, $\text{Co}(\text{pn})_2\text{CO}_3^+$, $\text{Co}(\text{tn})_2\text{CO}_3^+$, $\text{Co}(\text{trien})\text{CO}_3^+$, $[\text{Co}(\text{NH}_3)_2(\text{CO}_3)_2]^-$, $\text{Co}(\text{CO}_3)_3^{3-}$. Similar estimates 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 $\text{Cr}(\text{CO}_3)_3^{3-}$ as opposed to the extraordinarily stable $\text{Cr}(\text{C}_2\text{O}_4)_3^{3-}$ ion.

The proton magnetic resonance spectra of *cis*- and *trans*- $[\text{Co}(\text{NH}_3)_2\text{enCO}_3]^+$ 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'' | ν_{C-O}, cm^{-1} | $\nu_{C=O}, cm^{-1}$ | 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 |
| $n-C_6H_{13}$ | $n-C_6H_{13}$ | 1738 | | E | 166 |
| CH_3 | $t-C_4H_9O$ | 1795 | | C | 167 |
| | | 1764 | | | |
| | | 1795 | | | |
| | | 1776 | | M | 167 |
| CCl_3 | CCl_3 | 1832 | 1178 | C | 165 |
| CCl_2 | 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 | $C_6H_5OCO_2C_2H_5$ | 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- <i>p</i> -tolyl | | 1770 | | N | 166 |
| Di- <i>m</i> -tolyl | | 1775 | | N | 166 |
| | | 1783 | | N | 167 |
| | | 1783 | | | |
| | | 1761 | | M | 166 |
| Di- <i>o</i> -tolyl | | 1765 | | N | 166 |
| | | 1779 | | C | 167 |
| | | 1779 | | | |
| | | 1757 | | M | 167 |
| Bis(<i>o</i> -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 |

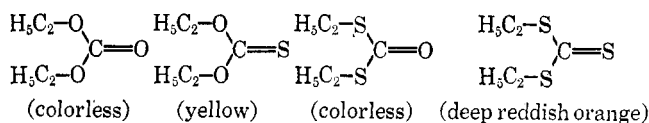
Table IX (Continued)

| R | $\nu_{C-O}, \text{cm}^{-1}$ | $\nu_{C-O}, \text{cm}^{-1}$ | Medium ^a | Ref |
|--|-----------------------------|-----------------------------|---------------------|-----|
| Cyclic Carbonates | | | | |
| -CH ₂ CH ₂ - | 1805 | | M | 167 |
| | 1779 | | | |
| | 1817 | 1138 | C, S | 165 |
| | 1763 | sh,w | | |
| | 1795 | | L | 165 |
| | 1770 | sh,w | | |
| | 1788 | sh,w | F | 165 |
| 1762 | 1160 | | | |
| -CH=CH- | 1833 | | C | 165 |
| | ~1770 | w | | |
| | 1830 | | L | 165 |
| | 1801 | sh, w | | |
| | 1822 | | F | 165 |
| 1796 | s | | | |
| [-CH-CH-] _n -CH(CH ₂)CH ₂ - | 1833 | 1162 | N | 165 |
| | 1809 | 1171 | C | 165 |
| -CHClCHCl- | 1792 | | L | 165 |
| | 1852 | 1115 | L | 165 |
| 1794 | sh, m | | | |
| -CHClCH ₂ - | 1828 | 1151 | L | 165 |
| | 1797 | sh, m | | |
| -CH(CH ₂ Cl)CH ₂ - | 1803 | 1165 | L | 165 |
| | 1816 | | C | 165 |
| -CH(C ₆ H ₅)CH ₂ - | 1770 | 1164 | KCl disk | 165 |
| | 1832 | | S | 165 |
| | ~1770 | w | | |
| (CH ₃) ₂ SbCO ₂ | 1730 | s | 1280 s | 89 |

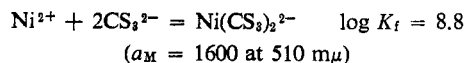
^a C = carbon tetrachloride, L = liquid, N = Nujol, E = neat, M = methanol, S = carbon disulfide, F = thin film, s = strong, m = medium, w = weak. ^b Two values are for stereoisomers.

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 N¹⁴ nucleus and the rapid exchange of protons on these groups with solvent D₂O.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



The only metal thiocarbonato complex¹⁸⁷ is that of Ni(II) with CS₃²⁻.

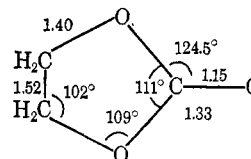


4. Crystal Structure

Since carbonic acid has never been isolated, no crystal-structure information is available for H₂CO₃. However, several simple ionic carbonates, basic carbonates of mineral origin (*cf.* azurite^{188, 189} and malachite¹⁹⁰), and two mixed

ligand type carbonato complexes of cobalt(III) have been investigated, one of which, [Co(NH₃)₃CO₃]Br·H₂O, 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 CaCO₃ (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 CO₃ being in one plane and the ethylenic carbons in a different plane making a 20° angle. In a subsequent study¹⁸⁸ 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_{2v} 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-C _{2h} ⁵ | 3.51 | 9.71 | 8.05 | 111° 51' | 196, 197 |
| KHCO ₃ | Monoclinic | P(2 ₁)/c-C _{2h} ⁵ | 15.11 | 5.67 | 3.71 | 103° 45' | 198 |
| NH ₄ HCO ₃ | Monoclinic | | | | | | 199 |
| Na ₂ CO ₃ ·NaHCO ₃ ·2H ₂ O | Monoclinic | C(2)/c | 20.41 | 3.49 | 10.31 | 106° 20' | 200 |
| KAgCO ₃ | Orthorhombic | IbcA-D _{2h} ²⁷ | 20.23 | 5.75 | 5.95 | | 201 |
| Ag ₂ CO ₃ | Monoclinic | P(2 ₁)-C ₂ ² | 4.83 | 9.52 | 3.23 | 92° 42' | 202 |
| [Co(NH ₃) ₄ CO ₃]Br | Orthorhombic | P(cmn) | 6.76 | 7.629 | 16.886 | | 194 |
| [Co(NH ₃) ₃ CO ₃]Br·H ₂ O | Orthorhombic | P(2 ₁)/na | 12.37 | 12.14 | 6.43 | | 191 |
| [Co(NH ₃) ₄ CO ₃]SO ₄ ·3H ₂ O | 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 carbonate complexes.

The crystal structure of [Co(NH₃)₄CO₃]⁺ has been studied by several workers¹⁹³⁻¹⁹⁵ 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(NH₃)₃CO₃]⁺ confirms carbonate acting as a monodentate ligand and internal hydrogen bonding between ammine nitrogen and the carbonate¹⁹¹ in the solid state.

5. Miscellaneous Structural Evidence

The molar electrical conductance of K₃[Co(NO₂)₂(CO₃)₂]·2H₂O corresponds to a four-ion electrolyte and is confirmed by cryoscopic measurements.¹⁴¹ Similar observation on a related binuclear compound, K₈[Co₂(NO₂)₈(CO₃)₃]·2H₂O, confirms its structure in the same study. Conductance measurements also offer supporting evidence for the following compounds: K[Co(NH₃)₂(CO₃)₂],²⁰³ Na₃[Co(NO₂)₄CO₃],⁸⁶ Cs₈[Co₂(NO₂)₈(CO₃)₃],⁸⁶ Na₃[Co(NO₂)₂(CO₃)₂],⁸⁶ Co(NH₃)₆[Co(NH₃)₂(NO₂)₂CO₃]₃,¹⁰¹ Co(en)₂[Co(NH₃)₂(NO₂)₂CO₃]₃,¹⁰¹ and K[Co(NH₃)₂(NO₂)₂CO₃].¹⁰¹

Hydrazine hydrate and CO₂ react with [Co(NH₃)₄CO₃]⁺ ion to form a new coordination compound having the formula, (N₂H₃COO)₂Co(N₂H₅)₂CO₃, 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 carbonate 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 1957²¹³ 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(NH₃)₆³⁺ and Co(en)₃³⁺ ions in carbonate solutions (0.01-1.0 M) and a comparison of the resulting spectra with that of [Co(NH₃)₅CO₃]⁺ 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(NH₃)₆³⁺·

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Table XI
Stability Constants on Carbonato Complexes^a

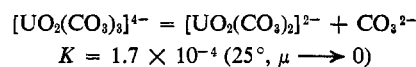
| Complex | Log K | Temp, °C | Conditions, μ | Method | Ref |
|---|-------|----------|--|-------------------------------|----------|
| [CaHCO ₃] ⁺ | 1.26 | 25 | →0 | Potentiometry | 27, 28 |
| [MgHCO ₃] ⁺ | 1.16 | 25 | →0 | Potentiometry | 27, 28 |
| [MnHCO ₃] ⁺ | 1.80 | 25 | →0 | Solubility | 223 |
| [NaHCO ₃] ⁰ | -0.25 | 25 | →0 | Potentiometry | 28 |
| [NPO ₂ HCO ₃] ⁰ | 2.43 | ... | →0 | | 244 |
| [Cu(HCO ₃) ₂] ²⁻ | 11.52 | 25 | 1 M KNO ₃ | Polarography | 233 |
| [Pu(CO ₃) ₂] ²⁺ | 46.96 | 20 | 7.0 | Solubility | 221 |
| [Co(NH ₃) ₆ ³⁺ ·CO ₃ ²⁻] | 1.73 | 18-20 | ... | Spectrophotometry | 215, 216 |
| [Co(en) ₃ ³⁺ ·CO ₃ ²⁻] | 1.95 | 18-20 | ... | Spectrophotometry | 215, 216 |
| [MgCO ₃] ⁰ | 3.4 | 25 | →0 | Potentiometry | 29 |
| [CaCO ₃] ⁰ | 3.2 | 25 | →0 | Potentiometry | 28 |
| [Cd(Moen) ₂ CO ₃] ⁰ | 6.92 | 25 | 0.1-1.0 M Na ₂ CO ₃ | Polarography | 234 |
| [Cd(Dien) ₂ CO ₃] ⁰ | 6.02 | 25 | 0.1-1.0 M Na ₂ CO ₃ | Polarography | 234 |
| [Zn(Moen) ₂ CO ₃] ⁰ | 9.78 | 25 | 0.1-1.0 M Na ₂ CO ₃ | Polarography | 235 |
| [NaCO ₃] ⁻ | 1.27 | 25 | →0 | Potentiometry | 29 |
| [PuO ₂ (CO ₃)(OH)] ⁻ | 23.85 | 20 | →0 | Solubility potentiometry | 48 |
| [PuO ₂ (CO ₃)(OH) ₂] ²⁻ | 23.0 | 20 | →0 | Solubility glass electrode | 48 |
| [Pu(CO ₃) ₃] ²⁻ | 2.09 | 20 | →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 | →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 | →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; →0 = approaching zero μ ; K refers to cumulative or gross stability constant, M + nL = ML_n.

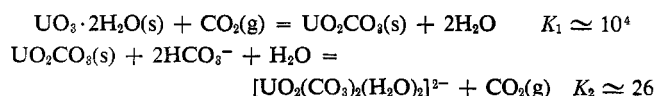
CO₃²⁻. Calculations on the degree of ion-pair formation show greater than 40% in a 0.01 M Na₂CO₃ and a tenfold increase in carbonate concentration results in nearly 70% ion pairs.^{215, 216} Such ion-pair formation is well known in coordination chemistry.²¹⁷

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 m μ 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 evaluation⁵⁶ of the Nd(III)-CO₃²⁻ spectral data gives the composition and the dissociation constant for Nd(CO₃)₄⁵⁻ ($K_{\text{diss}} = 0.0863$, $K_{\text{formation}} \approx 12.0$). An independent ion-exchange study followed by thermodynamic analysis¹³⁴ of the anion-exchange behavior of Nd(III) in K₂CO₃ solutions confirms the presence of Nd(CO₃)₄⁵⁻ among several other complexes.

Job's method of continuous variation²¹⁸ has been used in the study of uranium(VI)-carbonato complexes,²¹⁹ and the following complexes, [UO₂(CO₃)₃]⁴⁻, [UO₂(CO₃)₂]²⁻, and [U₂O₃(OH)(HCO₃)]⁰, are reported to occur at pH 11.2, 7.7, and 5.7, respectively. Conductometric studies¹³⁷ show discontinuities at U:CO₃ ratios 1:3 and 1:2 suggesting the existence of [UO₂(CO₃)₃]⁴⁻ and [UO₂(CO₃)₂]²⁻ ions in equilibrium.



Spectrophotometric and potentiometric methods have been used in conjunction to study the equilibria¹⁴⁸



In addition carbonato complexes of uranium(IV) of the composition Na₆U(CO₃)₅·11H₂O and the ion U(CO₃)₅⁶⁻ have been characterized.

(215) H. Yoneda, *Bull. Chem. Soc. Jap.*, **28**, 125 (1955).

(216) S. R. Cohen, Thesis, Cornell University, 1956; University Microfilms 20406.

(217) G. H. Nancollas, "Interaction in Electrolyte Solutions," Elsevier Publishing Co., New York, N. Y., 1966.

(218) P. Job, *C. R. Acad. Sci., Paris*, **180**, 928 (1925); *Ann. Chim.*, [10] **9**, 113 (1928); [11] **6**, 97 (1936).

(219) C. A. Blake, C. F. Coleman, K. B. Brown, D. G. Hill, R. S. Lowrie, and J. M. Schmitt, *J. Amer. Chem. Soc.*, **78**, 5978 (1956).

Table XII
Evidence for Carbonato Complex Ion Formation

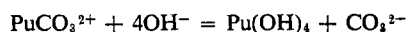
| Complex | Temp, °C | Conditions | Method | Ref |
|--|----------|---|--------------------------|---------|
| [Eu(HCO ₃) ₂] ⁺ | 25 | KHCO ₃ | Ion exchange | 55 |
| [Nd(HCO ₃) ₂] ⁺ | 25 | KHCO ₃ | Ion exchange | 55 |
| [Eu(HCO ₃) ₄] ⁻ | 25 | KHCO ₃ | Ion exchange | 55 |
| [Nd(HCO ₃) ₄] ⁻ | 25 | KHCO ₃ | 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) ₂ CO ₃] ⁺ | 25 | Na ₂ CO ₃ | Polarography | 238 |
| [Fe(Dien) ₂ CO ₃] ⁰ | 25 | Na ₂ CO ₃ | Polarography | 238 |
| [Fe(trien)CO ₃] ⁰ | 25 | Na ₂ CO ₃ | Polarography | 238 |
| [Co(Dien) ₂ CO ₃] ⁰ | 25 | Na ₂ CO ₃ | Polarography | 236 |
| [Co(Moen) ₂ CO ₃] ⁰ | 25 | Na ₂ CO ₃ | Polarography | 236 |
| [Ni(Moen) ₂ CO ₃] ⁰ | 25 | Na ₂ CO ₃ | Polarography | 237 |
| [Ni(Moen) ₃ CO ₃] ⁰ | 25 | Na ₂ CO ₃ | Polarography | 237 |
| [Ni(Moen) ₂ CO ₃] ⁰ | 25 | Na ₂ CO ₃ | Polarography | 237 |
| [Ni(Dien)CO ₃] ⁰ | 25 | Na ₂ CO 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 ₂ CO ₃ | Ion exchange | 55 |
| [Nd(CO ₃) ₂] ⁻ | 25 | K ₂ CO ₃ | Ion exchange | 55 |
| [Ce(CO ₃) ₂] ⁻ | ... | Excess CO ₃ | Polarography | 239 |
| [Be(CO ₃) ₂] ⁻ | ... | 0.1 M (NH ₄) ₂ CO 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) ₂ CO 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 ₂ CO ₃ | Polarography | 241 |
| | | NaHCO ₃ | | |
| [Pu(CO ₃) ₄] ⁴⁻ | ... | Excess CO ₃ ²⁻ | Preparative | 48 |
| | | | Conductance | |
| | | | Solubility | 52 |
| | | | Freezing point | |
| [PuO ₂ (CO ₃) ₂] ⁴⁻ | ... | 45% K ₂ CO ₃ | Solubility | 49 |
| [Pr(CO ₃) ₄] ⁵⁻ | 25 | Excess K ₂ CO ₃ | Ion exchange | 134 |
| [Sm(CO ₃) ₄] ⁵⁻ | 25 | Excess K ₂ CO ₃ | Ion exchange | 57, 134 |
| [Eu(CO ₃) ₄] ⁵⁻ | 25 | Excess K ₂ CO ₃ | Ion exchange | 134 |
| [Nd(CO ₃) ₄] ⁵⁻ | 25 | Excess K ₂ CO ₃ | Ion exchange | 134 |
| [Th(CO ₃) ₃ (OH) ₂] ⁵⁻ | ... | ... | Preparative | 60 |
| [U(CO ₃) ₃ (OH) ₂] ⁵⁻ | ... | Excess CO ₃ ²⁻ | Preparative | 60 |
| | | | Solubility | |
| [Be ₂ O(CO ₃) ₆] ⁶⁻ | ... | ... | Preparative | 95, 248 |
| [Eu(OH)(CO ₃) ₄] ⁶⁻ | 25 | K ₂ CO ₃ | Ion exchange | 55 |
| [Nd(OH)(CO ₃) ₄] ⁶⁻ | 25 | K ₂ CO ₃ | Ion exchange | 55 |
| [Ce(CO ₃) ₆] ⁶⁻ | ... | Excess K ₂ CO ₃ | Polarography | 239 |
| | | | Preparative | |
| [Th(CO ₃) ₅] ⁶⁻ | ... | Excess Na ₂ CO ₃ | Solubility | 245 |
| | | | Preparative | 246 |
| | | | Potentiometric | 61 |
| | | | Freezing point | 60 |
| <i>trans</i> -[Th(CO ₃) ₄ (OH) ₂] ⁶⁻ | ... | ... | Spectrophotometry | 242 |
| [Mo(CO ₃) ₆ (H ₂ O) ₂] ⁶⁻ | ... | Excess CO ₃ ²⁻ | Preparative | 59 |
| | | | Conductance | |
| [U(CO ₃) ₆] 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] ³⁻ | ... | Excess HCO ₃ ⁻ and CO ₃ ²⁻ | Polarography | 241 |
| [Pu(CO ₃) ₅] ⁴⁻ | ... | Excess CO ₃ ²⁻ | Preparative Solubility | 48 |
| [Fe ₄ O ₃ (CO ₃) ₅] ⁶⁻ | ... | Saturated (NH ₄) ₂ CO ₃ | Preparative Solubility | 124 |
| [Ce(CO ₃) ₆] ³⁻ | ... | Excess CO ₃ ²⁻ | Preparative | 50 |
| [Pu(CO ₃) ₅] ⁴⁻ | ... | ... | Preparative, solubility | 48 |
| Zr(IV) anionic complex | ... | Excess (NH ₄) ₂ CO ₃ | Ion exchange | 227 |
| V(IV) complex | ... | Excess Na ₂ CO ₃ | Ion exchange | 228 |
| Pu(III) complex | ... | Excess K ₂ CO ₃ | Spectrophotometry | 48, 49 |
| Pu(IV) complex | ... | Excess K ₂ CO ₃ | Spectrophotometry Polarography | 49 |
| Am(III) complex | ... | Excess K ₂ CO ₃ | Transference number Solubility, ion-exchange Spectrophotometry | 247 49 220 |
| Am(VI) complex | ... | Excess Na ₂ CO ₃ | Solubility Spectrophotometry | 49 49 |
| Cm(III) complex | ... | Excess CO ₃ ²⁻ | Solubility | 49 |
| Ga(III) anionic complex | ... | Excess (NH ₄) ₂ CO ₃ | Ion exchange | 229 |
| In(III) anionic complex | ... | Excess (NH ₄) ₂ CO ₃ | Ion exchange | 230 |

Based on the absorption spectrum of americium(VI) in 0.1 M Na₂CO₃ 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.

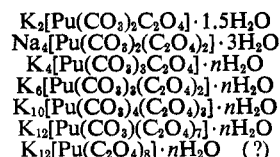
Spectral evidence also suggests the formation of anionic complexes in the plutonium(III)-carbonate system.⁴⁸ The absorption spectra of plutonium(IV) in carbonate solutions (35–45% K₂CO₃) in the range 400–1100 mμ show evidence for the complexes Pu(CO₃)₂⁰, Pu(CO₃)₃²⁻, Pu(CO₃)₄⁴⁻, and Pu(CO₃)₅⁶⁻. At lower carbonate concentration, however, there is evidence for PuCO₃²⁺ (*K*_{inst} = 1.5 × 10⁻⁴⁷) which undergoes partial decomposition at elevated pH's (>11.3) according to the reaction²²¹



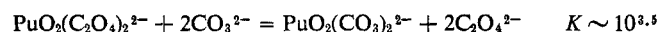
Plutonium(VI) forms several sparingly soluble carbonates and carbonato complexes of which [PuO₂(CO₃)₂]²⁻ (*K*_{inst} = 1 × 10⁻¹⁵) is well known⁴⁸ and is analogous to [UO₂(CO₃)₂]²⁻ (*K*_{inst} = 3 × 10⁻¹⁵). Interestingly plutonium in various oxidation states shows the following order, Pu⁴⁺ > Pu³⁺, PuO₂²⁺ > PuO₂⁺, toward complexing, and this order more or less parallels their ionic potential (*e/r*). In the absence of reliable data on the Pu-CO₃ systems, this might be illustrated with the well-known oxalato complexes.

| Oxidation state | +4 | +3 | +6 | +5 |
|-------------------|--|--|--|--------|
| Oxalate complex | Pu(C ₂ O ₄) ₂ ⁰ | Pu(C ₂ O ₄) ₂ ⁻ | PuO ₂ (C ₂ O ₄) ₂ ²⁻ | ... |
| <i>pK</i> | 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⁻ | ... |
| <i>pK</i> | 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



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.



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 UO₂(OH)₂ (*K*_{sp} = 1.8 × 10⁻²²) in aqueous carbonate solutions at pH 7.0–9.0 has been accounted in terms of the well-known complexes⁴² UO₂(CO₃)₂²⁻ and UO₂(CO₃)₃⁴⁻. The respective stability constants are shown in Table XI. A related investigation²²² on the solubility of uranyl 8-hydroxyquinolate in 1.3 M (NH₄)₂CO₃ and 2 M NH₄Cl gives a value for the dissociation constant of UO₂(CO₃)₃⁴⁻, *K*_{diss} = 1.7 × 10⁻²³ (25°, μ → 1.0). The solubility of Pu(OH)₄ in K₂CO₃ at a high ionic strength of 10.0 has been measured as a function of pH and CO₃²⁻ ion concentration.²²¹ The reported value for *K*_{inst} for PuCO₃²⁺ is 1.1 × 10⁻⁴⁷. Solubility studies also indicate several complexes

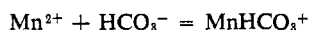
(220) J. S. Coleman, T. K. Keenan, L. H. Jones, W. T. Carnall, and R. A. Penneman, *Inorg. Chem.*, **2**, 58 (1963).

(221) A. I. Moskvina and A. D. Gel'man, *Russ. J. Inorg. Chem.*, **3**, 198 (1958).

(222) A. E. Klygin and I. D. Smirnova, *ibid.*, **4**, 16 (1959).

of the types $[\text{Pu}(\text{CO}_3)(\text{OH})_2(\text{H}_2\text{O})]_0$, $[\text{Pu}(\text{CO}_3)(\text{OH})_3(\text{H}_2\text{O})_3]^-$, and $[\text{PuCO}_3(\text{OH})_4(\text{H}_2\text{O})_2]^{2-}$.

The role of manganese(II)-carbonate complex in water-supply chemistry and in natural waters has been elucidated through solubility studies.²²³ Solubility of $\text{MnCO}_3(\text{s})$ in water at 25° in a solution saturated with CO_2 was studied by analyzing the equilibrium concentrations of $\text{Mn}(\text{II})$ and HCO_3^- ions by periodate and potentiometric titrations, respectively. The thermodynamic activities, $a_{\text{MnHCO}_3^+}$, $a_{\text{Mn}^{2+}}$, and $a_{\text{HCO}_3^-}$, were computed from concentration data using the Debye-Hückel relation. An average value of 63 has been reported for the equilibrium constant for



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

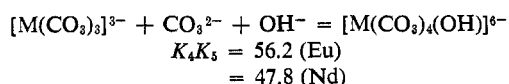
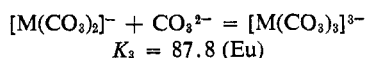
Studies on $\text{Sc}(\text{III})$,⁹⁶ $\text{Ce}(\text{III})$,¹³³ $\text{Fe}(\text{III})$,¹²⁴ $\text{Am}(\text{III})$,⁴⁹ $\text{Cm}(\text{III})$,⁴⁹ $\text{Th}(\text{IV})$,⁶⁰⁻⁶² $\text{U}(\text{IV})$,⁶⁰ $\text{Pu}(\text{IV})$,⁶³ $\text{Pu}(\text{VI})$,⁴⁹ and $\text{Am}(\text{VI})$ ⁴⁹ give qualitative evidence for various types of carbonate complexes (cf. Table XII).

c. Ion-Exchange Method

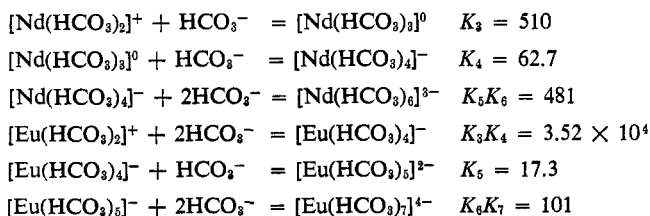
The method of studying metal complexes in solution by ion exchange is described in detail in the literature.²²⁴⁻²²⁶ Excellent studies have been made on the carbonate and bicarbonate complexes of the lanthanide elements^{55, 134} using radioisotopes, ¹⁴¹Ce, ¹⁴³Pr, ¹⁴⁷Nd, ¹⁴⁷Pm, ¹⁵³Sm, and ^{152, 154}Eu, 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 $\text{M}(\text{CO}_3)_4^{5-}$ type species in solution but also confirms solubility studies⁵⁰ on $\text{Ce}(\text{IV})$.

Detailed thermodynamic analysis of $\text{Eu}(\text{III})$ – $\text{Nd}(\text{III})$ –carbonate–bicarbonate systems suggests the presence of $[\text{M}(\text{OH})(\text{CO}_3)_4]^{6-}$ and $\text{M}(\text{CO}_3)_2^-$ complex ions at high and low concentrations of the ligand, respectively. The various equilibria are as follows.

Carbonate system



Bicarbonate system



Studies³⁸ on the absorption of $\text{Be}(\text{II})$, $\text{Ce}(\text{IV})$, $\text{Th}(\text{IV})$, and $\text{U}(\text{VI})$ in $(\text{NH}_4)_2\text{CO}_3$ solutions using batch equilibration technique as a function of ligand concentration in 0–1.2 *M* $(\text{NH}_4)_2\text{CO}_3$ proved the formation of $[\text{Be}(\text{CO}_3)_2]^-$ complex and

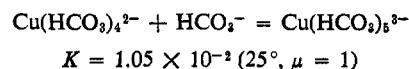
complexes of $\text{Ce}(\text{IV})$ and $\text{Th}(\text{IV})$ with charges of -6 and -8 . These might very well be hydroxy carbonate complexes. The differences in the distribution behavior of $\text{U}(\text{VI})$ and $\text{Th}(\text{IV})$ as carbonate complexes form the basis of a method of separation of one from the other by ion exchange.

Carbonato complexes have been detected by ion-exchange technique in the case of $\text{Y}(\text{III})$,³⁷ $\text{Zr}(\text{IV})$,²²⁷ $\text{V}(\text{IV})$,²²⁸ $\text{Am}(\text{III})$,²²⁰ $\text{Co}(\text{III})$,⁴⁵ $\text{Ga}(\text{III})$,²²⁹ and $\text{In}(\text{III})$.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 $\text{Cu}(\text{CO}_3)_2^{2-}$ and $\text{Cu}(\text{CO}_3)_3^{4-}$ ions.^{39, 233} The drastic change in the value of the stability constant in going from $\text{Cu}(\text{CO}_3)_2^{2-}$ to $\text{Cu}(\text{CO}_3)_3^{4-}$ 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 $\text{Cu}(\text{HCO}_3)_4^{2-}$ complex. At higher bicarbonate ion concentration there is evidence for the equilibrium



(Evidence for a hexacoordinated copper(II) of the formula $\text{Cu}(\text{HC}_2\text{O}_4)_6^{4-}$, stable on the resin phase, is available.²⁵)

Lead(II) resembles³⁹ copper(II) in forming a complex ion, $\text{Pb}(\text{CO}_3)_2^{2-}$. Investigation on the nature of cadmium(II) in carbonate medium⁴⁶ proves the existence of $\text{Cd}(\text{CO}_3)_3^{4-}$ 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 carbonate 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, $[\text{M}(\text{Moen})\text{CO}_3]_0$, $[\text{M}(\text{Dien})\text{CO}_3]_0$, $[\text{M}(\text{Trien})\text{CO}_3]_0$, and $[\text{M}(\text{Amine})\text{CO}_3]_x^{(2-2x)-}$, where M is a bivalent metal, Moen = monoethanolamine, Dien = diethanolamine, and Trien = triethanolamine.

(227) I. P. Alimarin, T. A. Belyavskaya, and B. V. Mu, *Radiokhimiya*, **1**, 645 (1959).

(228) R. I. Walter, *J. Inorg. Nucl. Chem.*, **6**, 58 (1958).

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(230) I. P. Alimarin, E. P. Tsintsevich, and V. P. Burlaka, *ibid.*, **25**, 1287 (1959).

(231) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, New York, N. Y., 1952.

(232) L. Meites, *J. Amer. Chem. Soc.*, **72**, 184 (1950).

(233) L. Meites, *ibid.*, **72**, 184 (1950).

(234) R. S. Subrahmanya, *Proc. Indian Acad. Sci., Sect. A*, **43**, 383 (1956).

(235) R. S. Subrahmanya, *ibid.*, **44**, 443 (1957).

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(237) R. S. Subrahmanya, *ibid.*, **44**, 184 (1957).

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

(223) J. D. Hem, *J. Chem. Eng. Data*, **8**, 99 (1963).

(224) F. Helfferich, "Ion-Exchange," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

(225) P. Krueger and J. Schubert, *J. Chem. Educ.*, **30**, 196 (1953).

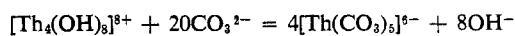
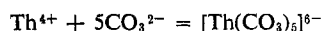
(226) J. E. Salmon, *Rev. Pure Appl. Chem.*, **6**, 24 (1956).

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.

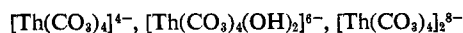
e. Potentiometric Method

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 equimolar in carbonate and bicarbonate ions with MgCl₂ and measuring the accompanying changes in pH at various stages of the titration. Deviation of the activity coefficients of CO₃²⁻ and HCO₃⁻ in MgCl₂, NaCl-MgCl₂, and NaCl solutions can be attributed to the formation of complexes of the types MgCO₃⁰, MgHCO₃⁺, and NaCO₃⁻ (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(NO₃)₄ and [Th₄(OH)₈](NO₃)₈ in KOH and KHCO₃ medium with HNO₃, evidence has been presented for the equilibria⁶¹



ruling out the following species reported earlier.^{242, 243}



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 re-determination of the stability constants by more than one procedure is possible.

D. REACTIONS AND REACTION KINETICS

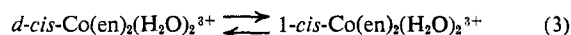
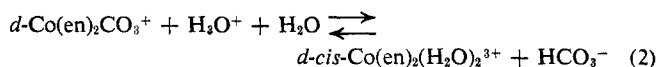
1. Racemization

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

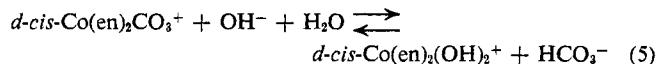
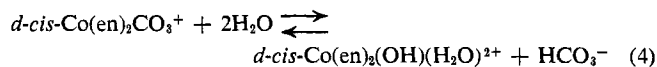
Harris,⁷² who examined the species Co(en)₂CO₃⁺ in the neighborhood of pH ~9. They concluded that the racemization reaction bore no kinetic relationship to the much more rapid carbonate exchange process, indicating that the diacido ligand replacement could occur with complete retention of configuration. 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

$$R = k[(\text{H}^+)(\text{Co}(\text{en})_2\text{CO}_3^+)]^{1/2} \quad (1)$$

The suggested mechanism for this consisted of the equilibria



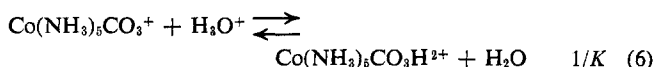
with reaction 3 being rate-determining. However, at pH ~9, hydroxo forms of the aquated species predominate, and several other paths for loss of optical activity exist. These include not only racemization but *cis-trans* isomerization of each of the species *d-cis*-Co(en)₂(H₂O)₂³⁺, *d-cis*-Co(en)₂(OH)(H₂O)₂²⁺, and *d-cis*-Co(en)₂(OH)₂²⁺. Much more information is also needed concerning various other equilibration of the type of reaction 2, including



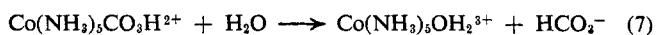
Clearly much more work needs to be done on this system before a thorough understanding of the nature of this type of racemization reaction becomes possible.

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(NH₃)₅CO₃⁺ (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



followed by substitution of water for the protonated carbonate



Later work utilizing oxygen-18 labeling^{250, 251} has shown that

(239) J. Dolezal and J. Novak, *Chem. Listy*, **52**, 582 (1958).

(240) W. E. Harris and I. M. Kolthoff, *J. Amer. Chem. Soc.*, **69**, 446 (1947).

(241) A. I. Stabrovskii, *Zh. Neorg. Khim.*, **5**, 811 (1960).

(242) Yu. M. Tolmachev, *Bull. Akad. Nauk SSSR*, **320**, 4 (1944).

(243) B. Franck, *Ann. Univ. Mariae Curie-Sklodowska, Lublin-Polonia*, **11**, 47 (1956); *Chem. Abstr.*, **53**, 13743b (1959).

(244) A. I. Moskvina, I. Geleceanu, and A. V. Lapitskii, *Dokl. Akad. Nauk SSSR*, **149**, 611 (1963); *Chem. Abstr.*, **59**, 2366a (1963).

(245) P. T. Cleve, *Bull. Soc. Chem. Fr.*, **21**, 115 (1874).

(246) A. Rosenheim, V. Samter, and I. Davidsohn, *Z. Anorg. Allg. Chem.*, **35**, 424 (1903).

(247) G. N. Yokalev and V. N. Kosyakov, *Proc. Intern. Conf. Peaceful Uses At. Energy, Geneva, 1955*, **7**, 363 (1955).

(248) R. G. Monk, *Talanta*, **14**, 1367 (1967).

(249) A. B. Lamb and R. G. Stevens, *J. Amer. Chem. Soc.*, **61**, 3229 (1939).

(250) J. B. Hunt, A. C. Rutenberg, and H. Taube, *ibid.*, **74**, 268 (1952).

(251) C. A. Bunton and D. R. Llewellyn, *J. Chem. Soc.*, 1692 (1953).

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



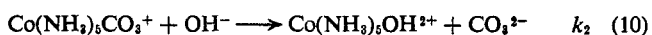
(It is of interest that carbonate removal by Pb^{2+} or Hg^{2+} in aqueous solution also occurs without Co-O bond fission, though the situation with respect to Ba^{2+} is not so clearly defined.)

Recent kinetic studies¹⁶⁴ covering the wide acidity range $1 < \text{pH} < 8$ have clarified existing disagreements^{109, 253, 254} concerning the magnitudes of K (the acid dissociation constant of $\text{Co}(\text{NH}_3)_5\text{CO}_3\text{H}^{2+}$) 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

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

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

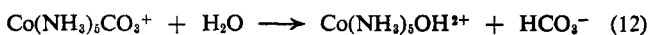
In strongly basic solution, a hydrolysis occurs²⁵⁴ but is very much slower than the acid-catalyzed reaction and yields the hydroxo product



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

$$R = k_2(\text{complex})(\text{OH}^-) \quad (11)$$

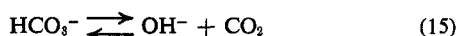
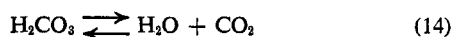
The value of k_2 is $3.3 \times 10^{-6} M^{-1} \text{ sec}^{-1}$ at 25° and $\mu = 1.0 M$, and its temperature dependence is described by the parameters $\Delta H^\ddagger = 30 \text{ kcal/mole}$ and $\Delta S^\ddagger = 18 \text{ eu}$. There is no evidence for any appreciable contribution to the hydrolysis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



Related studies^{168, 255} of the isotopic exchange reaction



have been made in the range $9 < \text{pH} < 10$. 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 appear¹⁶⁴ to be the ones by means of which carbon can exchange between CO_2 and carbonate, namely



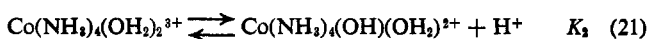
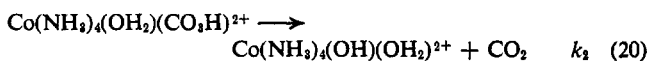
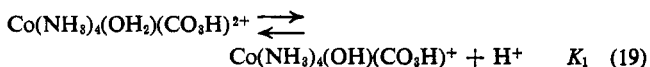
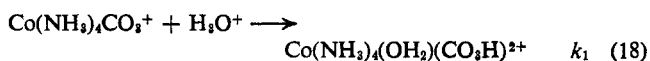
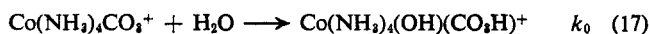
We turn now to consideration of the ligand replacement process with respect to chelated carbonate species of the general form $\text{CoN}_4\text{CO}_3^+$ (where N_4 represents $(\text{NH}_3)_4$, $(\text{NH}_3)_2$, en, en₂, pn₂, tn₂, tren, α -trien, β -trien, etc.). In these compounds, there is good evidence that the bidentate carbonate 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.²⁶⁶ The reactivity of the bidentate carbonate 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 $\text{Co}(\text{NH}_3)_4\text{CO}_3^+$ within the limited acidity range $3 < \text{pH} < 4$ established by glycolate and acetate buffers. The rate law was shown to be of the form

$$k_{\text{obs}} = k_0 + k_1(\text{H}^+) \quad (16)$$

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^{267b} over a much wider acidity range ($1 < \text{pH} < 5$), 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.



k_2 is known to be large by analogy to the decarboxylation of $\text{Co}(\text{NH}_3)_5\text{CO}_3\text{H}^+$ as discussed above and also based on an estimate²⁵⁸ of $k_1 \sim 2 \text{ sec}^{-1}$ for $[\text{Co}(\text{en})_2(\text{OH}_2)(\text{CO}_2\text{H})]^{2+}$ at 20° . K_1 and K_2 govern "instantaneous" proton-transfer equilibria, so Pedersen's rate law (eq 16) is applicable. At 25° and $\mu = 0.5 M$, $k_0 = 1.3 \times 10^{-4} \text{ sec}^{-1}$ and $k_1 = 1.5 M^{-1} \text{ sec}^{-1}$, and the corresponding temperature dependence parameters are, for ΔH^\ddagger , 12 ± 5 and $15.3 \pm 1.0 \text{ kcal/mole}$, and for ΔS^\ddagger , -37 ± 19 and $-6.3 \pm 3.8 \text{ eu}$. 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 carbonate oxygens must remain attached to cobalt during decarboxylation. It is of interest that a polarographic study^{258b}

(252) R. B. Jordan, A. M. Sargeson, and H. Taube, *Inorg. Chem.*, **5**, 486 (1966).

(253) H. A. Scheidegger, Doctoral Thesis, E. T. H., Zurich, 1966.

(254) D. J. Francis and R. B. Jordan, *J. Amer. Chem. Soc.*, **89**, 5591 (1967).

(255) D. R. Stranks, *Trans. Faraday Soc.*, **51**, 505 (1955).

(256) (a) S.-F. Ting, H. Kelm, and G. M. Harris, *Inorg. Chem.*, **5**, 696 (1966); (b) C. Andrade and H. Taube, *ibid.*, **5**, 1087 (1966).

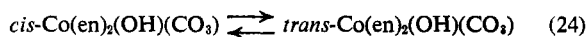
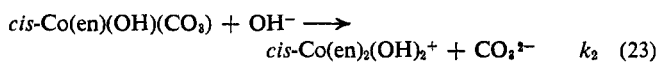
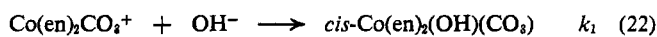
(257) (a) K. J. Pedersen, *J. Amer. Chem. Soc.*, **53**, 18 (1931); (b) T. P. Dasgupta and G. M. Harris, *ibid.*, **91**, 3207 (1969); Proceedings of the XIth International Conference on Coordination Chemistry, Haifa, Israel, 1968.

(258) (a) F. A. Posey and H. Taube, *J. Amer. Chem. Soc.*, **75**, 4099 (1953); (b) R. Ralea, G. Burlacu, and D. Giurgiu, *Rev. Chim. (Bucharest)*, **7**, 1187 (1962).

of the hydration of $\text{Co}(\text{NH}_3)_4\text{CO}_3^+$ 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.

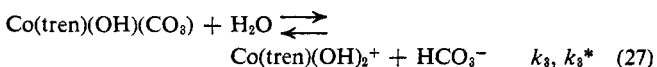
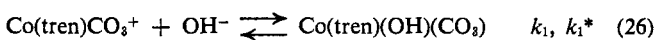
All other studies of the acid hydrolysis of the $\text{CoN}_4\text{CO}_3^+$ type of complex can be readily fitted into the outlined scheme. For $\text{Co}(\text{en})_2\text{CO}_3^+$, the published^{259,260} data are interpreted very satisfactorily by means of eq 16, with $k_0 = 1.3 \times 10^{-4} \text{ sec}^{-1}$ and $k_1 = 0.52 \text{ M}^{-1} \text{ sec}^{-1}$ at 25° and $\mu \sim 0.3 \text{ M}$, values quite close to those for the tetraammine under these conditions.^{267b} An additional term in the rate law previously proposed^{260,261} for $\text{Co}(\text{en})_2\text{CO}_3^+$ is probably in error, since it can contribute significantly only at $\text{pH} > 4$, where the process becomes complicated by the fact that hydrolysis is no longer essentially complete. Studies of the pn_2 and tn_2 analogs¹⁶¹ 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 $\text{Co}(\text{en})_2\text{CO}_3^+$ has been studied by several workers^{263,262-264} 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.



At 25° and $\mu \sim 1 \text{ M}$, $k_1 \sim 4 \times 10^{-8} \text{ M}^{-1} \text{ sec}^{-1}$ and $k_2 \sim 10^{-6} \text{ M}^{-1} \text{ sec}^{-1}$. In strongly basic solution both reactions 22 and 23 go essentially to completion, and the rate of isomerization of $\text{cis-Co}(\text{en})_2(\text{OH})(\text{CO}_3)$ is much too slow²⁶² 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 $\text{Co}(\text{NH}_3)_4\text{CO}_3^+$, and that these two rate constants differ by only a small factor, if at all, at 25° .

Substitution of tren for $(\text{en})_2$ 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.²⁶³ For the complex $\text{Co}(\text{tren})\text{CO}_3^+$ 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.

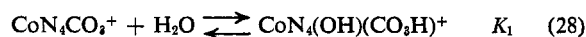


At 20° and $\mu \sim 0.1 \text{ M}$, $k_1 = 6.0 \times 10^{-8} \text{ M}^{-1} \text{ sec}^{-1}$, $k_1^* = 6.5 \times 10^{-5} \text{ sec}^{-1}$, $k_3 = 4.5 \times 10^{-6} \text{ sec}^{-1}$, and $k_3^* = 2.3 \times 10^{-3} \text{ sec}^{-1}$. It is noteworthy that the latter figure is the only directly observed rate constant so far reported for a carbonate anation reaction. Data²⁵⁴ on the acid hydrolysis of $\text{Co}(\text{NH}_3)_4\text{CO}_3^+$ (eq 8) do show that this reaction is also an equi-

libration in the range of $8.4 < \text{pH} < 9.4$. 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 carbonate ligand replacement reaction—one which can be investigated conveniently only in the range $7 < \text{pH} < 10$, where net decomposition of carbonate 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 carbonate cobaltic complex, it is now evident¹⁶⁴ that the residual acid-catalyzed hydrolysis rate, which of course could provide an exchange path, is still much more rapid even at $\text{pH} \sim 10$ 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, $\text{CoN}_4\text{CO}_3^+$, the situation is quite different since ring opening of the chelated carbonate 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 $\text{N}_4 = (\text{NH}_3)_4, (\text{en})_2, (\text{pn})_2$, and $(\text{tn})_2$ and an additional study has been reported⁸⁵ where $\text{N}_4 = \text{cis}-(\text{NH}_3)_2\text{en}$. 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 rationalized¹⁶⁸ in terms of a multistep mechanism involving (a) aquo-dechelation to form a ring-opened aquocarbonate 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,^{258,257b,262} and it is now possible to confirm and reinforce several aspects of the proposed general mechanism.

The aquo-dechelation step was given¹⁶⁸ as²⁶⁸



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 known²⁶² to be close to 10^{-8} , 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 aquo-dechelation, as previously assumed, and will involve various

(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).

(264) R. B. Jordan, private communication, 1967.

(265) G. M. Harris and D. R. Stranks, *Trans. Faraday Soc.*, **48**, 137 (1952).

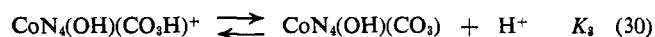
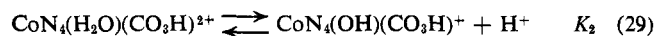
(266) D. R. Stranks, *ibid.*, **48**, 911 (1952).

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

(268) The product was previously assumed^{168,263,262} to be in the form $\text{CoN}_4(\text{OH}_2)(\text{CO}_2)^+$. However, recent data on the pK of the closely related complex $\text{CoN}_4(\text{OH}_2)(\text{C}_2\text{O}_4)^+$ (S. C. Chan, private communication) indicate that the water ligand must be much more acidic than the carbonate 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



The magnitudes of K_2 and K_3 are close to 5×10^{-6} and 2×10^{-9} , respectively, at room temperatures²⁶² 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 $\text{CoN}_4(\text{OH})(\text{CO}_3)$ either to hydrolysis or isomerization^{262, 263} suggests that it is probably inactive in the exchange process. However, $\text{CoN}_4(\text{H}_2\text{O})(\text{CO}_3\text{H})^{2+}$ is known to decarboxylate rapidly (see discussion above regarding reaction 20) and $\text{CoN}_4(\text{OH})(\text{CO}_3\text{H})^+$ 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



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

$$R_A = k[\text{CoN}_4(\text{H}_2\text{O})(\text{CO}_3\text{H})^{2+}] + k_2[\text{CoN}_4(\text{OH})(\text{CO}_3\text{H})^+] \quad (33)$$

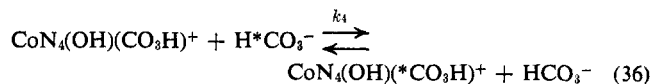
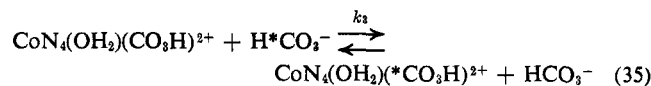
Symbolizing the total concentration of all forms of the carbonate complex, chelated or not, by a , and recalling that K_1 is very small, one may recast eq 33 in the form

$$R_A = k_1 K_1 (\text{H}^+) a / K_2 + k_2 K_1 a \quad (34)$$

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 data¹⁶³ with respect to the "free" carbonate-independent exchange rate of $(\text{pn})_2$ and to some new data¹⁴² on the ions *cis*- and *trans*- $\text{Co}(\text{NH}_3)_2\text{enCO}_3^+$, 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 $k_1 \sim 1 \text{ sec}^{-1}$ and $k_2 \sim 2 \times 10^{-8} \text{ sec}^{-1}$ 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 HCO_3^- , which is true within 5% in the range $7 < \text{pH} < 9$), $\text{CoN}_4(\text{OH}_2)(\text{CO}_3\text{H})^{2+} \cdot \text{HCO}_3^-$ or $\text{CoN}_4(\text{OH})(\text{CO}_3\text{H})^+ \cdot \text{HCO}_3^-$. Alternatively, one can visualize attack by "free" carbonate to displace H_2O or OH^- and form the unstable intermediate $\text{CoN}_4(\text{CO}_3\text{H})_2^+$ 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



The rate of direct carbonate exchange is thus given by

$$R_B = k_3[\text{CoN}_4(\text{OH}_2)(\text{CO}_3\text{H})^{2+}][\text{HCO}_3^-] + k_4[\text{CoN}_4(\text{OH})(\text{CO}_3\text{H})^+][\text{HCO}_3^-] \quad (37a)$$

which, using the symbolism of eq 34 with the definition $b = [\text{total free carbonate}]$, yields the expression

$$R_B = k_3 K_1 (\text{H}^+) ab / K_2 + k_4 K_1 ab \quad (37b)$$

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

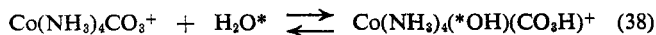
Mention should be made of the fact that, while the values of k_1 , k_2 , k_3 , and k_4 do not deviate by more than a factor of 2 or 3 for the various N_4 species when N_4 is $(\text{NH}_3)_4$, $(\text{en})_2$, $(\text{pn})_2$, or $(\text{NH}_3)_2\text{en}$, the complex $\text{Co}(\text{tn})_2\text{CO}_3^+$ undergoes carbonate exchange with rate constants smaller by a factor of about an order of magnitude.²⁶⁷ The ring-opened $(\text{tn})_2$ 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 carbonate 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 $\text{Co}(\text{NH}_3)_4\text{CO}_3^+$ ion and oxygen-18-labeled solvent water.²⁷¹ The rate constant observed at 25°, pH ~ 9 , and low ionic strength is $k_{\text{ex}} = 1.7 \times 10^{-5} \text{ sec}^{-1}$, and was equated to the rate of the previously suggested ring-opening process of reaction 17. However, for this, $k_0 = 1.3 \times 10^{-4} \text{ sec}^{-1}$, 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 $\text{Co}(\text{NH}_3)_4\text{CO}_3^+$, $R_A/a \sim 1.0 \times 10^{-5} \text{ sec}^{-1}$ 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

(270) R. G. Pearson and R. D. Lanier, *J. Amer. Chem. Soc.*, **86**, 765 (1964).

(271) D. McKenzie, C. O'Connor, and A. L. Odell, *J. Chem. Soc.*, **A**, 184 (1966).

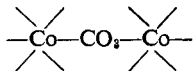
the fact that k_{ex} need not be as great as k_0 even if it results from the same process. The exchange mechanism is assumed to be



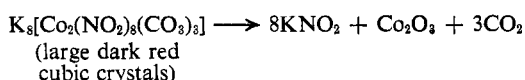
However, k_{ex} will be identical with k_0 of reaction 17 *only if every ring-opening-ring-closing event results in oxygen atom exchange between water and complex*. This clearly need not be so, since in the reverse of reaction 38 the labeled oxygen has at a maximum a one-third chance of remaining in 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 $\text{Co}(\text{CO}_3)_3^{3-}$ ion has been reported¹⁴¹ to result in the formation of a *sesquicarbonato ion* corresponding to $[\text{Co}_2(\text{NO}_2)_6(\text{CO}_3)_3]^{3-}$. The presence of binuclear cobalt is confirmed by preparation and identification of $\text{K}_8[\text{Co}_2(\text{NO}_2)_6(\text{CO}_3)_3] \cdot 2\text{H}_2\text{O}$. The change in molar conductance and cryoscopic measurements of the mean ionic weight confirm the presence of nine ions, and a bridged structure

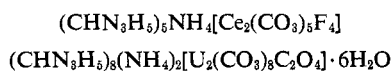


has been proposed to account for the presence of binuclear cobalt. On heating the compound loses water first and the anhydrous material decomposes to yield CO_2 .



A binuclear sesquicarbonato anion, $[\text{Co}_2(\text{NO}_2)_6(\text{CO}_3)_3]^{6-}$, 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



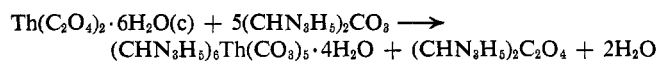
are known. Both complexes are unstable in aqueous solutions and the uranium(IV) carbonate oxidizes even in the dry state.⁶⁴

The Be(II) polynuclear complex anion, $\text{Be}_4\text{O}(\text{CO}_3)_6^{6-}$, has been well characterized^{65, 95} and a related binuclear species, $[\text{Be}_2(\text{H}_2\text{O})_2(\text{CO}_3)_2(\text{OH})_2]^{3-}$, 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).

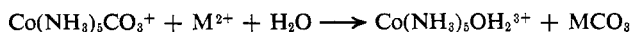
4. Heterogeneous Reactions

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 example⁶²



Lead(II) and Hg^{2+} are reported to cause instantaneous precipitation of the carbonate in $\text{Co}(\text{NH}_3)_5\text{CO}_3^+$ 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



5. Thermal Decomposition

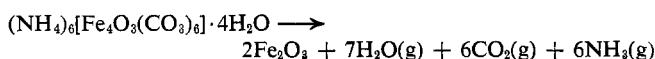
Extensive studies have been made on the thermal decomposition of simple carbonates and mixed carbonates both of natural and synthetic origin on account of their scientific interest and industrial value. An example of such studies²⁷² is the thermal decomposition of $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ (nesquehonite) and $\text{MgCO}_3 \cdot (\text{NH}_4)_2\text{CO}_3 \cdot 4\text{H}_2\text{O}$ 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, $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$; lansfordite, $\text{MgCO}_3 \cdot 5\text{H}_2\text{O}$; hydromagnesite, $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$; and artinite, $\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$.

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, $\text{NH}_4\text{Sc}(\text{CO}_3)_2 \cdot 1.5\text{H}_2\text{O}$, decomposes in three stages,⁹⁶ first losing water at 120° , carbon dioxide at $140-190^\circ$, forming crystalline $\text{ScO}(\text{OH})$ at $280-305^\circ$, and finally Sc_2O_3 at $435-480^\circ$. Thermal studies indicate that one water is somehow most firmly held in $\text{Na}_6\text{Th}(\text{CO}_3)_5 \cdot 12\text{H}_2\text{O}$ suggesting nonequivalence of water molecules in the hydrates.²⁷⁸ The corresponding guanidinium salt, $(\text{CH}_3\text{N}_3)_6\text{Th}(\text{CO}_3)_5 \cdot n\text{H}_2\text{O}$, begins to lose all water at $50-80^\circ$ and decomposes above 150° .⁶² The crystals of $(\text{NH}_4)_2[\text{ZrO}(\text{CO}_3)_2] \cdot 3\text{H}_2\text{O}$ dehydrate readily and on further heating decompose to yield CO_2 and NH_3 and ZrO_2 at 600° .⁴¹



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

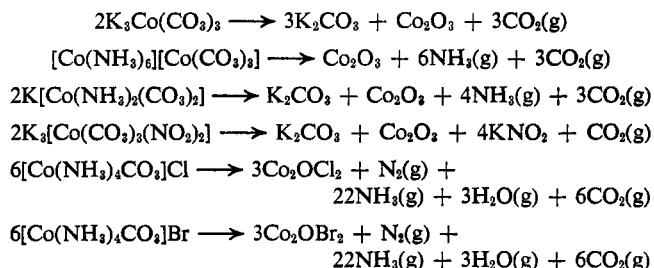


The thermal decomposition of several cobalt(III)-carbonato complexes ($\text{K}_3\text{Co}(\text{CO}_3)_3 \cdot 3\text{H}_2\text{O}$,¹⁰⁰ $[\text{Co}(\text{NH}_3)_4][\text{Co}(\text{CO}_3)_3]$,¹⁰⁰ $\text{K}[\text{Co}(\text{NH}_3)_2(\text{CO}_3)_2] \cdot \text{H}_2\text{O}$,¹⁰⁰ $\text{K}_3[\text{Co}(\text{CO}_3)_2(\text{NO}_2)_2]$,¹⁴¹ $[\text{Co}$ -

(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).

$(\text{NH}_3)_4\text{CO}_3[\text{NO}_3 \cdot 1.2\text{H}_2\text{O}]^{274}$ and $\text{Co}(\text{NH}_3)_4\text{CO}_3\text{X}$, where $\text{X} = \text{Cl}, \text{Br}, \text{I}^{274}$) may be represented by the following equations.



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 $[\text{Co}(\text{NH}_3)_4\text{CO}_3]\text{X}$ type complexes, the exact nature of $\text{Co}_2\text{OX}_2(\text{s})$ is not known. Also the iodide and nitrate complexes are reported to yield complex stoichiometric results with varying $\text{NH}_3(\text{g})/\text{complex}(\text{s})$, $\text{CO}_2(\text{g})/\text{complex}(\text{s})$ ratios as well as free iodine in the case of the iodide complex.²⁷⁴ In an earlier TGA study²⁷⁵ the anhydrous mixed ligand type carbonate complexes exhibited the following order of decreasing thermal stability: $[\text{Co}(\text{en})_2\text{CO}_3]\text{Cl} > [\text{Co}(\text{pn})_2\text{CO}_3]\text{Cl} > [\text{Co}(\text{tn})_2\text{CO}_3]\text{Cl} > [\text{Co}(\text{NH}_3)_4\text{CO}_3]\text{NO}_3$ (explosively unstable). The dehydration endothermic peak maxima temperatures obtained in DTA, however, indicate the following order of stability for the corresponding hydrates: $[\text{Co}(\text{pn})_2\text{CO}_3]\text{Cl} \cdot \text{H}_2\text{O} < [\text{Co}(\text{NH}_3)_4\text{CO}_3\text{NO}_3] \cdot \text{H}_2\text{O} < [\text{Co}(\text{tn})_2\text{CO}_3]\text{Cl} \cdot \text{H}_2\text{O} < [\text{Co}(\text{en})_2\text{CO}_3]\text{Cl} \cdot \text{H}_2\text{O}$.

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 as 350° .²⁷⁹

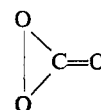
6. Mass Spectral Studies

Coordinated carbonate in complexes of the type $[\text{Co}(\text{NH}_3)_4\text{CO}_3]\text{X}$ 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, $\text{C}(\text{OH})_3^+$, 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.).²⁸⁸ Subsequently additional experimental evidence for the related $\text{C}(\text{OH})_3^+$ ion has been reported by an nmr study²⁸⁴ 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 studies²⁹⁵⁻²⁹⁷ have been reported for carbonic acid and simple carbonates but none on carbonate complexes. The effect of iron(II) on the photoreduction of CO_2 in aqueous solution to form oxalic

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(292) A. Cohen and B. Wolfgang May, *Z. Phys. Chem., B*, **26**, 117 (1934).

(293) W. Groth, *ibid.*, **37** (1937).

(294) B. H. Mahan, *J. Chem. Phys.*, **33**, 959 (1960).

(295) E. Baur, *Z. Phys. Chem.*, **131**, 143 (1928); *Helv. Chim. Acta*, **20**, 387 (1937); E. Baur, *et al.*, *ibid.*, **6**, 959 (1923); **8**, 828 (1922); **21**, 1038 (1938).

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Table XIII

Vibrational Frequencies of Various Related "CO₃" Species

| Carbon tri-oxide (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) ¹³ 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 ₂ | ν ₃ | ν ₄ | ν ₅ | ν ₆ | ν ₇ |
| 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 ₂ : C-O asymmetric stretching; ν ₃ : in-plane deformation; ν ₄ : 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) ₄ CO ₃]Cl | 1593 | 1030 | 760 | 395 | 1265 | 673 | 430 834 |

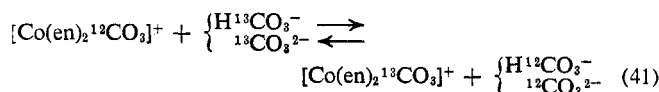
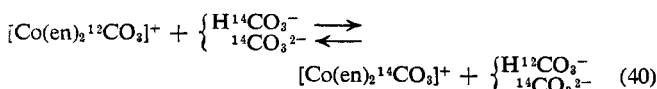
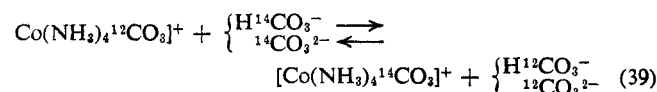
^a Frequency data taken from ref 286; ¹³C¹⁸O₃²⁻ from Urey.²⁸⁷

^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 CO₂, dimethyl ether, and occasionally methanol, depending on imposed experimental conditions.³⁰⁰

8. Isotope Effects

Although deuterium,¹⁸³ 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) carbonate 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.

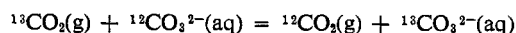


For reaction 39 the equilibrium isotope effect reported^{301, 302} is 0.875 at 0° and 0.900 at 30°, suggesting depletion of ¹⁴C in the complex ion relative to free carbonate, the latter being the strongly bonded state of carbon. For reaction 40 the equilibrium isotope effect³⁰³ is 0.990 ± 0.019 at 25° and for reaction 41³⁰³ more or less the same, 0.991 ± 0.014 at 25°. All the three reactions, however, in a subsequent study³⁰⁴ 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 explanation³⁰⁷ takes into account that the isotope effect is indeed only apparent and might be due to colloidal decomposition products (CoCO₃) holding the *CO₃²⁻ in a nonexchangeable form.

The exchange equilibrium constants: [Co(NH₃)₄¹²CO₃]⁺—H¹⁴CO₃⁻, K₁, [Co(NH₃)₄¹²CO₃]⁺—¹⁴CO₃²⁻, K₂, and [Co(NH₃)₄¹²CO₃]⁺—¹⁴CO₂, K₃, 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(NH₃)₄CO₃]⁺, a substitute molecular species, COCl₂ (phosgene), has been used for evaluating the ratio partition functions: $f = Q_{14\text{COCl}_2}/Q_{12\text{COCl}_2}$. (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 Mg²⁺ ion effect on the ¹⁸C fractionation in the equilibrium



derives mainly from the fact that magnesium is the third major constituent among the various ionic species in sea water. It has been suggested²⁹ sea water contains nearly 67% of its total CO₃²⁻ as MgCO₃⁰ neutral complex, the actual structure of which, however, is conjectural at the present time although magnesium(II) is known²⁸⁶ to exhibit hexacoordination in Mg-(H₂O)₆²⁺ and Mg(C₂O₄)₂(H₂O)₂²⁻. If one assumes a coordination complex of the type [Mg(H₂O)₄CO₃]⁰ in which carbonate acts as bidentate, then the symmetrical XY₃ form of free car-

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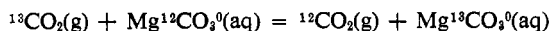
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bonate changes to what is in effect an XYZ₂ type of structure resulting in altered symmetry and perhaps changes in the characteristic vibrational frequencies. This would lead to preferential ¹³C enrichment in MgCO₃⁰ neutral complex according to the following equilibrium.



Experimentally it was found to be so as shown by the increased value of the equilibrium isotope effect in the presence of Mg²⁺ ions²⁸⁶ in CO₂-CO₃²⁻ exchange ($K_{\text{MgCO}_3^0} > 1.012$). Frequency data are not available for Mg¹²CO₃⁰ and Mg¹³CO₃⁰ to calculate the theoretical equilibrium constant. However, by using a substitute like COF₂ (carbonyl fluoride) in place of the actual MgCO₃⁰ complex, an inverse isotope effect (0.935) has been reported²⁸⁶ stressing on the inadequacy of the COF₂ model. It would therefore be of interest to make the normal coordinate calculations for the MgCO₃⁰ neutral complex and obtain frequency data that might permit evaluation of the partition function ratio, $Q_{\text{Mg}^{13}\text{CO}_3^0}/Q_{\text{Mg}^{12}\text{CO}_3^0}$, 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 unreactive³⁰⁸ with the hydrated electron (e_{aq}⁻) in a 10⁻⁸ M CH₃OH medium; the second-order rate constants were estimated as <10⁶ M⁻¹ sec⁻¹. No carbonate complex, however, has been studied.

Several kinetic studies³⁰⁹⁻³¹³ 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-carbonate 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 carbonate 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(CO₃)₃⁸⁻ ion as an intermediate³¹⁴ 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(NH₃)₆][Be(H₂O)₂(CO₃)₂(OH)₂]·3H₂O. Analytical separation of uranium(VI) from iron(III) and other elements has

been accomplished by way of the carbonate 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 exchangers²³⁰ (KU-2 in NH₄ form and EDE-10P in CO₃ 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 carbonate complexes play in uranium metallurgy. Carbonate leaching of pitchblende³¹⁵ and the precipitation of uraninite from a solution containing the uranyl carbonate complexes³¹⁶ and recovery of uranium from carbonate leach solutions by solvent extraction³¹⁷ have received considerable attention in view of the importance of uranium as a nuclear material. The occurrence of UO₂(CO₃)₂²⁻ at pH 4.5-6.5 and UO₂(CO₃)₃⁴⁻ 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)-carbonate complexes seem to participate in the extraction of manganese from its minerals by (NH₄)₂CO₃ leaching.³¹⁹ In the hydrometallurgical processing of manganese carbonate ore, CO₂ at high pressure brings manganese into solution, perhaps as a complex, and reprecipitates MnCO₃ (also FeCO₃) while keeping MgCO₃ and CaCO₃ in solution when the pressure of CO₂ is released.³²⁰ The ion-pair complex MnHCO₃⁺ 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 Mn²⁺ in aerated water increases with increasing pH and markedly decreases if HCO₃⁻ 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)₂CO₃]₂Cl up to a concentration of 0.2 g/l. Other uses for the cobalt ammine compounds like [Co(NH₃)₄CO₃]₂NO₃ and [Co(NH₃)₄CO₃]₂SO₄·3H₂O 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 carbonate complexes.

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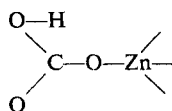
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C. BIOLOGICAL APPLICATIONS

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 $\text{Ca}(\text{HCO}_3)_2^0$ 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 $\text{O}=\text{C}=\text{O}$ in the dehydration reactions.

Protonated carbonic acid, $\text{C}(\text{OH})_3^+$, 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, $[\text{Co}(\text{en})_2\text{CO}_3]^+$ ion is reported to have no catalytic effect³²⁴ on the oxidative demethylation of $(\text{CH}_3)_3\text{N}-\text{O}$. While studying the fate of cobalt uptake, it has been found after subcutaneous injection of $[\text{Co}(\text{NH}_3)_4\text{CO}_3]\text{Cl}$; 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 $\text{UO}_2(\text{CO}_3)_3^{4-}$ in sea water³²⁶ and in hydrothermal solutions³²⁷ 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 , $\text{UO}_2(\text{CO}_3)_2 \cdot (\text{H}_2\text{O})_2^{2-}$, $\text{UO}_2(\text{CO}_3)_3^{4-}$ 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 correspond-

ing to $p_{\text{CO}_2} = 10^{-3.52}$ atm, it was concluded³²⁸ 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 $\text{Cu}(\text{CO}_3)_2^{2-}$ is well known.

Several carbonato complexes of the ion-pair type have been reported to occur in small abundance²⁸ 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 water²⁸ 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 $\text{Ca}(\text{CO}_3)_2^{2-}$ and $\text{Ca}(\text{OH})_2(\text{CO}_3)_2^{4-}$ 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 $\text{Pb}_3(\text{OH})_2(\text{CO}_3)_2$, hydrocerussite; $\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2$, azurite; and $\text{Cu}_2(\text{OH})_2\text{CO}_3$, malachite. Malachite is stable relative to azurite under normal earth conditions ($p_{\text{CO}_2} = 10^{-3.52}$ 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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