(Figure 3b) and Mg_2FeH_6[24] (Figure 3a) shows that the deuterium atom configuration around the transition metal changes from tetrahedral (Ni (d^{10})) to square-pyramidal (Co (d^8)) and octahedral (Fe (d^6)), in agreement with predictions from the 18-electron rule[26] and configurations found in other related ternary hydrides.[27] Thus the previously reported square-planar[11] or disordered[12] deuterium atom configurations around the Ni atoms in β-Mg_2NiH_4 can probably be ruled out. The latter studies presumably suffered from the low resolution of the diffraction data and the deficiencies of the structural models, which underlines the importance of using powder diffraction data of high resolution for the refinement of complex structures.

Magnetic measurements on a sample of composition $Mg_2NiH_{3.8}$ suggested that the susceptibility of the Mg_2NiH_4 phase was nearly zero.[28] This result is consistent with the above structure containing d^{10} nickel atoms in tetrahedral configuration, for which diamagnetism is expected. Furthermore the dark red color of fully hydrided samples as well as X-ray photoelectron spectroscopy analysis and theoretical band structure calculations[29] suggested that Mg_2NiH_4 is nonmetallic. These results are in agreement with a limiting ionic bond description based on Mg^{2+} cations and $[NiH_4]^{4-}$ anions (the actual charges are of course different). However, since the above band structure calculations were performed on the (cubic) β' modification by assuming octahedral deuterium configurations, they may not apply to the (monoclinic) β modification on which the X-ray emission spectroscopy measurements were performed.[29] As to the NMR results published in ref 30,31, they probably need to be reinterpreted in view of the structure model proposed above.

Finally, an analysis of the maximum hydrogen content of Mg_2NiH_4 in terms of the so-called geometrical model[32] shows that its structure could accommodate two more H atoms per formula unit than found experimentally, similar to the structure of Mg_2CoH_5,[25] which could accommodate one more H atom per formula unit. This demonstrates that the hydrogen content in these compounds is controlled by electronic rather than geometrical factors.

In conclusion we note that the knowledge of the hydrogen atom distribution in Mg_2NiH_4 is essential for theoretical energy band calculations, which in turn may give better insight into the chemistry and properties of this technologically important hydrogen storage material.

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Registry No. Mg_2Ni, 12057-65-7; Mg_2NiD_4, 77340-45-5.

Supplementary Material Available: Tables of raw neutron diffraction data and the results of the structure refinement, including structural data, interatomic distances, selected bond angles, *R* factors, and background values (11 pages); a table of structure factors (4 pages). Ordering information is given on any current masthead page.

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(26) Mingos, D. M. P. *Struct. Bonding (Berlin)* **1986**, *63*.

(27) Bau, R.; Chiang, M.Y.; Ho, D. M.; Gibbins, S. G.; Emge, T. J.; Koetzle, T. F. *Inorg. Chem.* **1984**, *23*, 2823.

(28) Stucki, F.; Schlapbach, L. *J. Less-Common Met.* **1980**, *74*, 143.

(29) Gupta, M.; Belin, E.; Schlapbach, L. *J. Less-Common. Met.* **1984**, *103*, 389.

(30) Genossar, J.; Rudman, P. S. *J. Phys. Chem. Solids* **1981**, *42*, 611.

(31) Senegas, J.; Pezat, M.; Darnaudery, J. P.; Darriet, B. *J. Phys. Chem. Solids* **1981**, *42*, 29.

(32) Westlake, D. G. *J. Less-Common Met.* **1980**, *75*, 177.

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Dinuclear Complexes of Transition Metals Containing Carbonate Ligands. 6.[1] Synthesis, Characterization, and Thermodynamic Studies of Dinuclear Complexes of Cobalt(III) Containing Bridging Hydroxide and Carbonate in Acidic Aqueous Solution

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Three new dinuclear cobalt(III) complexes containing carbonate as bridging group were prepared. The complexes are of the type $[(N)_3Co(\mu\text{-}CO_3)(\mu\text{-}OH)(\mu\text{-}X)Co(N)_3]^{2+}$ where $(N)_3$ stands for either dien (1,5-diamino-3-azapentane) or $(NH_3)_3$ and X is OH, NH_2, or NO_2. The complexes were characterized by UV–visible and infrared spectroscopy. These complexes equilibrate rapidly in acidic aqueous solution with $[(N)_3(H_2O)Co(\mu\text{-}CO_3)(\mu\text{-}X)Co(N)_3(OH_2)]^{3+}$. The thermodynamic parameters K, $\Delta H°$, and $\Delta S°$ were determined for these equilibrium reactions, and the results are compared with the thermodynamic parameters for some related dinuclear complexes.

Introduction

During the last 5 years we have been interested[2-4] in preparing some novel dinuclear complexes of cobalt(III) containing carbonate as a bridging ligand. In 1981 we made first report of the carbonate-bridged dinuclear cobalt(III) complex $[(NH_3)_3Co(\mu\text{-}CO_3)(\mu\text{-}OH)_2Co(NH_3)_3]^{3+}$. The compound was characterized[2] by a three-dimensional X-ray diffraction study. Recently we were able to modify our synthetic approach due to our greater understanding of the characteristics of tribridged cobalt(III) complexes and, hence, were able to synthesize a series of novel dinuclear complexes with carbonate as bridging ligand. We report here the synthesis and characterization of these complexes and their thermodynamic properties in aqueous solution.

Experimental Section

Preparation of Complexes. Preparation of Tris(μ-hydroxo)bis(triamminecobalt(III)) Perchlorate Dihydrate ("Triol"), $[(NH_3)_3Co(\mu\text{-}OH)_3Co(NH_3)_3](ClO_4)_3\cdot 2H_2O$. The compound was prepared by following the method of Linhard and Siebert.[5] The purity of the compound was

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(1) Part 5: Koshy, K.; Dasgupta, T. P. *Inorg. Chim. Acta* **1986**, *117*, 111.

(2) Churchill, M. R.; Lashewycz, R.; Koshy, K.; Dasgupta, T. P. *Inorg. Chem.* **1981**, *20*, 376.

(3) Koshy, K.; Dasgupta, T. P. *Inorg. Chim. Acta* **1982**, *61*, 207.

(4) Koshy, K.; Dasgupta, T. P. *J. Chem. Soc., Dalton Trans.* **1984**, 2781.

0020-1669/86/1325-3593$01.50/0

checked by its UV–visible spectra.[6]

Preparation of Bis(μ-hydroxo)bis(aquatriamminecobalt(III)) Perchlorate Pentahydrate, $[(NH_3)_3(H_2O)Co(\mu\text{-}OH)_2Co(H_2O)(NH_3)_3](ClO_4)_4 \cdot 5H_2O$. This compound was prepared by the method of Linhard and Siebert.[5] The purity of the compound was checked by its UV–visible spectrum[7] measured in 1 M $HClO_4$ at 20 °C.

Preparation of (μ-Carbonato)bis(μ-hydroxo)bis(triamminecobalt(III)) Perchlorate, $[(NH_3)_3Co(\mu\text{-}CO_3)(\mu\text{-}OH)_2Co(NH_3)_3](ClO_4)_2$. Two methods for preparing this compound were developed in our laboratory.

Method 1. The sulfate salt was prepared by following the method previously described.[1] Conversion of the sulfate salt to the perchlorate salt was achieved as follows: A 1.0-g sample of the sulfate salt was dissolved in 50 mL of water, and the solution was filtered to remove any solid particles. Twenty milliliters of saturated $NaClO_4$ solution was then added to the filtrate, and the solution was cooled in an ice bath for 1 h. The red crystals that separated were filtered, washed with ethanol, and air-dried. Yield: 0.8 g.

Caution! Perchlorate salts of complexes can be explosive and should be handled with care in a fume hood and behind a protective shield. They should not be heated as solids or as concentrated solutions.

Method 2. A 2.0-g sample of "triol" perchlorate was dissolved in 60 mL of 0.2 M $NaHCO_3$ solution. The solution was filtered and allowed to stand at room temperature for 24 h. Five milliliters of saturated $NaClO_4$ solution was then added, and the solution was cooled in ice. The fine needle-shaped crystals that separated were filtered, washed with dilute ethanol and ether, and air-dried. Yield: 1.4 g.

Both methods gave pure crystalline products. The purity was checked by microanalysis.[8] Anal. Calcd for $Co_2N_6H_{20}CO_{13}Cl_2$: C, 2.34; H, 3.90; N, 16.38. Found for the product from method 1: C, 2.21; H, 3.95; N, 16.40. Found for the product from method 2: C, 2.25; H, 3.90; N, 16.25.

Preparation of (μ-Carbonato)(μ-hydroxo)bis(aquatriamminecobalt(III)) Perchlorate, $[(NH_3)_3(H_2O)Co(\mu\text{-}CO_3)(\mu\text{-}OH)Co(H_2O)(NH_3)_3](ClO_4)_3$. A 1.0-g sample of ($\mu$-carbonato)bis($\mu$-hydroxo)bis(triamminecobalt(III)) perchlorate was dissolved in 10 mL of 1 M $HClO_4$ at 30 °C. The solution was filtered, and the filtrate was added dropwise with stirring to 20 mL of 40% $HClO_4$ at 5 °C. The reaction mixture was then cooled in ice for 1 h. The pink solid formed was filtered, washed free of acid with cold ethanol and ether, and air-dried. Yield: 0.9 g. Anal. Calcd for $Co_2N_6H_{23}O_{18}CCl_3$: Co, 18.66; N, 13.31; H, 3.64; Cl, 16.87; O, 45.62; C, 1.90. found: Co, 18.80; N, 13.31; H, 3.71; Cl, 16.51; O, 45.88; C, 1.70.

Preparation of Bis(μ-hydroxo)aqua(nitrato)bis((1,5-diamino-3-azapentane)cobalt(III)) Perchlorate, $[(C_4H_{13}N_3)(H_2O)Co(\mu\text{-}OH)_2Co(NO_3)(C_4H_{13}N_3)](ClO_4)_3$. The compound was prepared by the method described by Bestrow and Wieghardt.[9] The purity was checked by microanalysis. Anal. Calcd for $Co_2C_8H_{30}N_7O_{18}Cl_3$: C, 13.03; H, 4.07; N, 13.30. Found: C, 13.88; H, 4.02; N, 14.10.

Preparation of (μ-Carbonato)bis(μ-hydroxo)bis((1,5-diamino-3-azapentane)cobalt(III)) Perchlorate Hydrate, $[(C_4H_{13}N_3)Co(\mu\text{-}CO_3)(\mu\text{-}OH)_2Co(C_4H_{13}N_3)](ClO_4)_2 \cdot H_2O$. A 1.0-g sample of bis($\mu$-hydroxo)aqua(nitrato)bis((1,5-diamino-3-azapentane)cobalt(III)) perchlorate was dissolved in 50 mL of water containing 2.0 g of sodium bicarbonate. The reaction mixture was stirred for 24 h at room temperature and then cooled in ice. The pink solid produced was filtered, washed with ethanol, and air-dried. Yield: 0.60 g. Anal. Calcd for $Co_2C_9H_{30}N_6O_{14}Cl_2$: C, 17.01; H, 4.73; N, 13.23; Cl, 11.18, Co, 18.60. Found: C, 17.13; H, 4.69; N, 13.24; Cl, 10.83; Co, 18.7.

Preparation of (μ-Carbonato)(μ-hydroxo)bis(aqua(I,5-diamino-3-azapentane)cobalt(III)) Perchlorate, $[(C_4H_{13}N_3)(H_2O)Co(\mu\text{-}CO_3)(\mu\text{-}OH)Co(C_4H_{13}N_3)(H_2O)](ClO_4)_3$. A 1.0-g sample of ($\mu$-carbonato)bis($\mu$-hydroxo)bis((1,5-diamino-3-azapentane)cobalt(III)) perchlorate was dissolved in 10 mL of 0.1 M perchloric acid solution containing 1.0 g of NaCl. The solution was filtered and then the filtrate gradually added to 20 mL of 60% perchloric acid solution over a period of 15 min. The reaction was then cooled in ice for 1 h. The pink solid was filtered and washed free of acid with ethanol–water (1:2) mixture and then ether. The product was dried in a desiccator. Yield: 0.9 g. Anal. Calcd for $Co_2C_9H_{31}N_6O_{18}Cl_3$: C, 14.69; N, 11.42; H, 4.22; Co, 16.0; Cl, 14.1. Found: C, 14.73; N, 11.46; H, 4.63; Co, 15.7; Cl, 14.4.

Preparation of (μ-Carbonato)(μ-nitrito)(μ-hydroxo)bis(triamminecobalt(III)) Perchlorate Dihydrate, $[(NH_3)Co(\mu\text{-}CO_3)(\mu\text{-}NO_2)(\mu\text{-}OH)Co(NH_3)_3](ClO_4)_2 \cdot 2H_2O$. A 1.0-g sample of ($\mu$-carbonato)bis($\mu$-hydroxo)bis(triamminecobalt(III)) perchlorate was dissolved in 25 mL of 5 M aqueous sodium nitrite solution. Ten milliliters of 6 M $HClO_4$ was then added dropwise with stirring, and the resulting solution was thermostated at 35 °C for 1 h. Solid $NaHCO_3$ was then added slowly to adjust the pH of the reaction mixture to be approximately 6. The resultant solution when cooled in ice gave an orange red product. The red solid was filtered, washed with ethanol, and dried in a vacuum desiccator. Yield: 0.6 g. The product was recrystallized by dissolving in the minimum volume of water at 30 °C and by cooling in ice for several hours. Anal. Calcd for $Co_2N_7CH_{19}O_{14}Cl_2$: Co, 21.74; N, 18.09; C, 2.21; H, 3.51; Cl, 13.10; O, 41.34. Found: Co, 21.80; N, 18.33; C, 2.29; H, 3.61; Cl, 12.65; O, 41.32.

Preparation of (μ-Carbonato)(μ-nitrito)bis(aquatriamminecobalt(III)) Chloride Hydrate, $[(NH_3)_3(H_2O)Co(\mu\text{-}CO_3)(\mu\text{-}NO_2)Co(H_2O)(NH_3)_3]Cl_3 \cdot H_2O$. A 1.0-g sample of the (μ-nitrito)(μ-carbonato)(μ-hydroxo)bis(triamminecobalt(III)) perchlorate was dissolved in a mixture of 15 mL of concentrated HCl and 10 mL of concentrated HNO_3. The solution was then cooled in a refrigerator overnight. The orange-red crystals were filtered, washed free of acid with cold ethanol, and air-dried. Yield: 0.6 g. Anal. Calcd for $Co_2N_7H_{24}O_8Cl_3$: C, 2.47; H, 4.94; N, 20.15. Found: C, 2.26; H, 4.93; N, 20.90.

Preparation of (μ-Amido)(μ-hydroxo)bis(aquatriamminecobalt(III)) Nitrate Dihydrate, $[(NH_3)_3(H_2O)Co(\mu\text{-}NH_2)(\mu\text{-}OH)Co(H_2O)(NH_3)_3](NO_3)_4 \cdot 2H_2O$. The compound was prepared by following the method described by Werner.[10] The purity of the compound was checked by its visible spectrum[11] measured in 1 M $HClO_4$ and by microanalysis. Anal. Calcd for $Co_2N_{11}H_{29}O_{17}$: H, 5.06; N, 26.89. Found: H, 5.01; N, 26.77.

Preparation of (μ-Amido)(μ-carbonato)(μ-hydroxo)bis(triamminecobalt(III)) Iodide Dihydrate, $[(NH_3)_3Co(\mu\text{-}NH_2)(\mu\text{-}CO_3)(\mu\text{-}OH)Co(NH_3)_3]I_2 \cdot 2H_2O$. A 2.0-g sample of ($\mu$-amido)($\mu$-hydroxo)bis(aquatriamminecobalt(III)) nitrate dihydrate was dissolved in 40 mL of 0.2 M $NaHCO_3$ solution. The solution was filtered, and the filtrate was allowed to stand at room temperature for 24 h. Solid potassium iodide was then added gradually to the reaction mixture until the reddish brown solid precipitated out. The reaction mixture was then cooled in ice for 2 h, and the product was filtered, washed with dilute ethanol and ether, and dried in a vacuum desiccator. Yield: 1.1 g. The complex was recrystallized by dissolving in 25 mL of water and adding 5 mL of saturated potassium iodide solution. Anal. Calcd for $Co_2N_7H_{25}CO_6I_2$: Co, 19.6; N, 16.26; C, 1.99; H, 4.15; I, 42.12. Found: Co, 19.3; N, 16.13; C, 1.82; H, 3.84; I, 42.39.

Preparation of (μ-Amido)(μ-carbonato)bis(aquatriamminecobalt(III)) Perchlorate, $[(NH_3)_3(H_2O)Co(\mu\text{-}NH_2)(\mu\text{-}CO_3)Co(H_2O)(NH_3)_3](ClO_4)_3$. A 2.0-g sample of ($\mu$-amido)($\mu$-carbonato)($\mu$-hydroxo)bis(triamminecobalt(III)) iodide dihydrate was dissolved in 50 mL of water. A 1.3-g sample of $AgClO_4$ in 5 mL of water was then added slowly to the complex solution with stirring. The precipitated AgI was filtered off, and 35 mL of concentrated $HClO_4$ was added dropwise with stirring to the filtrate. The mixture was cooled in ice for 2 h. The red crystals were filtered, washed free of acid with ethanol–ether (1:2) mixture, and air-dried. Yield: 1.1 g. Anal. Calcd for $Co_2N_7H_{24}CO_{17}Cl_3$: Co, 18.7; C, 1.90; H, 3.81; N, 15.54. Found: Co, 18.7; C, 1.91; H, 3.82; N, 15.56.

Materials. All the chemicals used were of reagent grade. Distilled water made from a Corning distillation unit was used for preparative work. Deionized water, obtained by passing the distilled water through the Milli-Q reagent grade water system (Millipore Co., Bedford, MA) was used to make up solutions for physical measurements.

Spectrophotometric Measurements. The visible and ultraviolet spectra were recorded with either a Pye Unicam Model SP8-100 or Cary 219 spectrophotometer. The extinction coefficients (ϵ) are reported in units of M^{-1} cm^{-1}. The infrared spectra of the complexes were recorded on a Pye Unicam SP3-300 spectrophotometer, employing a KBr disk technique.

pH Measurements. A digital pH meter (either ORION Model 701 of Beckman Model 3500) fitted with a combination electrode was used to measure pH. The meter was calibrated with standard buffer solutions. A water-jacketed cell that was thermostated at the desired temperature was used during pH measurements.

Measurements of Equilibrium Constants. The equilibrium constants were determined spectrophotometrically with a Cary 219 spectrophotometer at a suitable wavelength where there is a large difference in

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(5) Linhard, M.; Siebert, H. *Z. Anorg. Allg. Chem.* **1969**, *24*, 364.

(6) The absorption coefficients of the complex are 137, 265, and 1798 M^{-1} cm^{-1} at 526, 364, and 296 nm, respectively (lit.[5] 135, 263, and 1778 M^{-1} cm^{-1} at 526, 364, and 296 nm, respectively).

(7) The absorption coefficients are 170, 170, and 2697 M^{-1} cm^{-1} at 543, 370, and 295 nm, respectively (lit.[5] 170, 170, and 2630 M^{-1} cm^{-1} at 543, 370, and 295 nm, respectively).

(8) Microanalyses were done by Dr. Ellent Pascher, Mikroanalytisches Laboratory, Buschstrasse 54, Bonn, W. Germany.

(9) Bestrow, H.; Wieghardt, K. *Chem. Ber.* **1978**, *122*, 832.

(10) Werner, A. *Justus Liebigs Ann. Chem.* **1910**, *1*, 375.

(11) The absorption coefficient of the complex in 1 M $HClO_4$ is 147 M^{-1} cm^{-1} at 520 nm (lit.[12] 148 M^{-1} cm^{-1} at 520 nm).

(12) Taylor, R. S.; Sykes, A. G. *J. Chem. Soc. A* **1970**, 1424.

Table I. Electronic Spectral Characteristic of μ-Carbonato Complexes[a]

	complex	spectral characteristics vis/UV λ_{max}, nm (ε)	IR ν, cm^{-1} 1*	 2*
1	$[R(\mu\text{-}CO_3)(\mu\text{-}OH)_2R]^{2+}$	525 (124)	1352	1495
2	$[(H_2O)R(\mu\text{-}CO_3)(\mu\text{-}OH)R(H_2O)]^{3+}$	526 (108); 295 (3320)	1330	1450
3	$[R'(\mu\text{-}CO_3)(\mu\text{-}OH)_2R']^{2+}$	525 (186)	1375	1502
4	$[(H_2O)R'(\mu\text{-}CO_3)(\mu\text{-}OH)R'(H_2O)]^{3+}$	525 (184); 298 (4830)	1380	1440
5	$[R(\mu\text{-}CO_3)(\mu\text{-}NO_2)(\mu\text{-}OH)R]^{2+}$	504 (181)	1385	1455
6	$[(H_2O)R(\mu\text{-}CO_3)(\mu\text{-}NO_2)R(H_2O)]^{3+}$	500 (171)	1380	1430
7	$[R(\mu\text{-}CO_3)(\mu\text{-}NH_2)(\mu\text{-}OH)R]^{2+}$	502 (166); 300 (2160)	1332	1480
8	$[(H_2O)R(\mu\text{-}CO_3)(\mu\text{-}NH_2)R(H_2O)]^{3+}$	498 (167); 300 (2900)	1388	1448

[a] ε in M^{-1} cm^{-1}. R = $(NH_3)_3Co$; R′ = (dien)Co (dien = 1,5-diamino-3-azapentane); 1* = $\delta(O_ICO_{II}) + \nu(C\text{–}O_I)$; 2* = $\nu(C\text{–}O_I) + \nu(C\text{–}O_{II}) + \delta(O_ICO_I)$.

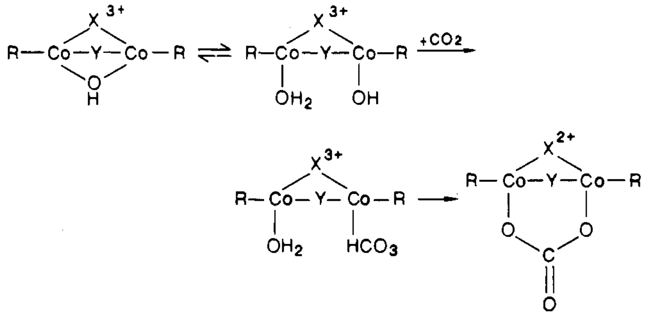
absorbance between protonated and an unprotonated species, and those wavelengths are listed in Table III. The required hydrogen ion concentration was obtained by adding an appropriate quantity of standard $HClO_4$ solution or by McIlvaine buffer.[13] The ionic strength was adjusted to 0.5 M by $LiClO_4$ solution. The equilibrium constants are then calculated from

$$\frac{\epsilon_A - \epsilon_{obsd}}{\epsilon_{obsd} - \epsilon_{AH}} = K[H^+]$$

where ϵ_A and ϵ_{AH} are the molar absorption coefficients for the unprotonated and protonated complexes and ϵ_{obsd} is the molar absorption coefficient of the equilibrium mixture at different concentration of hydrogen ions. A plot of $(\epsilon_A - \epsilon_{obsd})/(\epsilon_{obsd} - \epsilon_{AH})$ vs. $[H^+]$ should therefore be linear with a slope of K.

Results and Discussion

The preparation and the X-ray diffraction study of the complex (μ-carbonato)bis(μ-hydroxo)bis(triamminecobalt(III)) perchlorate has been reported previously.[1] We have now developed another method for making this complex starting from "triol". The principle behind the preparation of this complex is the same as for the preparation of mononuclear carbonato complexes of cobalt(III).[14] The mononuclear cobalt(III) complexes containing hydroxo groups effectively hydrate carbon dioxide in an irreversible manner[15] to form stable carbonato complexes. In the case of a dinuclear complex, such as "triol", the bridging hydroxo group undergoes cleavage generating an intermediate[3] containing a terminal hydroxo group, which then reacts with CO_2 in much the same way as it does in mononuclear systems, resulting in a complex with a bridging carbonato group. A generalized mechanistic scheme for the formation of dinuclear complexes containing a bridging carbonato group can be written as



where R = $(NH_3)_3$, dien, or any tridentate amine group and X and Y are either OH, NH_2, or NO_2 groups.

This reaction scheme has been successfully applied to the preparation of three new dinuclear complexes of cobalt(III) with a bridging carbonate group. These compounds are listed in Table I with their UV–visible and infrared spectral characteristics. It should be noted that in all of these μ-carbonato complexes one of the bridging groups is hydroxide and the other bridging group is either NH_2, NO_2, or OH. We have failed to introduce any other group besides NH_2, NO_2, or OH in the bridging position of these μ-carbonato complexes. Hence, it is obvious that the carbonate in the bridging position imposes structural restriction in the molecule as a result of which only a few small anions (like NH_2, NO_2, and OH) can act as a bridging partner. The μ-carbonato μ-hydroxo complexes readily form bis(diaqua) complexes in acidic solution. These diaqua complexes are also isolable, and their spectral characteristics are included in Table I.

Table II. Effect of Temperature on the Equilibrium Constants for the Reactions of Dinuclear Cobalt(III) Complexes in Acidic Aqueous Solution (I = 0.5 M ($LiClO_4$))

complex[a]	temp/°C	$10^{-2}K/M^{-1}$
$[R(\mu\text{-}CO_3)(\mu\text{-}OH)_2R]^{2+}$	21.1	86 ± 0.6
	25.1	76 ± 0.3
	34.3	46 ± 0.8
	39.0	41 ± 0.1
$[R'(\mu\text{-}CO_3)(\mu\text{-}OH)_2R']^{2+}$	20.0	107 ± 0.6
	25.0	86 ± 0.1
	30.0	72 ± 0.4
	34.8	55 ± 0.3
$[R(\mu\text{-}CO_3)(\mu\text{-}NH_2)(\mu\text{-}OH)R]^{2+}$	18.5	111 ± 0.8
	22.5	97 ± 0.5
	29.5	63 ± 1.0
	32.5	60 ± 0.6
$[R(\mu\text{-}CO_3)(\mu\text{-}NO_2)(\mu\text{-}OH)R]^{2+}$	19.2	34 ± 1.1
	23.0	32 ± 0.7
	30.8	27 ± 1.0
	35.0	26 ± 0.7
$[R(\mu\text{-}OH)_3R]^{3+}$	13.0	1.1 ± 0.02
	18.8	0.64 ± 0.01
	21.1	0.57 ± 0.01
	29.5	0.31 ± 0.01
$[R(\mu\text{-}NH_2)(\mu\text{-}OH)_2R]^{3+}$	11.5	0.93 ± 0.03
	18.2	0.59 ± 0.03
	22.2	0.48 ± 0.02
	26.8	0.42 ± 0.02
$[R'(\mu\text{-}OH)_3R']^{3+}$	18.1	1.1 ± 0.05
	22.7	0.90 ± 0.03
	26.4	0.77 ± 0.03
	30.3	0.55 ± 0.01

[a] R = $Co(NH_3)_3$; R′ = Co(dien).

The μ-carbonato bis(μ-hydroxo) complex has been well characterized by an X-ray diffraction study,[1] and hence its spectral characteristics, especially the infrared frequencies, ($\delta(O_IC\text{–}O_{II}) + \nu(C\text{–}O_I)$ and $\nu(C\text{–}O_I) + \nu(C\text{–}O_{II}) + \delta(O_IC\text{–}O_{II})$) are established[16] to be due to the bridging carbonate group. The similarity of the UV–visible and infrared spectral characteristics of all the μ-carbonato complexes listed in Table I further confirms the presence of bridging carbonate in the complexes. The bridging NO_2 group in complexes **5** and **6** of Table I has also been con-

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(13) Elving, P. J.; Markowitz, J. M.; Rosenthal, I. *Anal. Chem.* **1956**, *28*, 1179.

(14) Ficner, S.; Palmer, D. A.; Dasgupta, T. P.; Harris, G. M. *Inorg. Synth.* **1979**, *17*, 152.

(15) Dasgupta, T. P.; Harris, G. M. *J. Am. Chem. Soc.* **1977**, *99*, 2490.

(16) Greenaway, A.; Koshy, K.; Sadler, G.; Dasgupta, T. P. *Spectrochim. Acta*, in press.

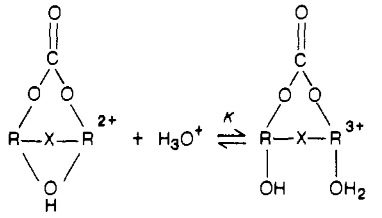
(17) The stretching frequencies due to the bridging NO_2 groups of compounds **5** and **6** are 1510 and 1210 cm^{-1} and 1508 and 1180 cm^{-1}, respectively.

Table III. Summary of Thermodynamic Data for the Equilibration in Acidic Aqueous Solution of Several Dinuclear Cobalt(III) Complexes (I = 0.5 M ($LiClO_4$))

complex[a] (λ, nm)[b]	K/M^{-1} (25 °C)	$\Delta H°$/(kcal mol^{-1})	$\Delta S°$/(cal mol^{-1} deg^{-1})
$[R(\mu\text{-}OH)_3R]^{3+}$ (285)	42 ± 1[c]	−13 ± 1	−35 ± 2
$[R'(\mu\text{-}OH)_3R']^{3+}$ (295)	70 ± 1	−7 ± 1	−15 ± 1
$[R(\mu\text{-}NH_2)(\mu\text{-}OH)_2R]^{3+}$ (270)	41 ± 1	−10 [illegible] 1	−25 ± 1
$[R(\mu\text{-}CO_3)(\mu\text{-}OH)_2R]^{2+}$ (270)	7500 ± 50	−8 ± 1	−10 ± 2
$[R'(\mu\text{-}CO_3)(\mu\text{-}OH)_2R']^{2+}$ (270)	8500 ± 20	−8 ± 1	−8 ± 2
$[R(\mu\text{-}CO_3)(\mu\text{-}NH_2)(\mu\text{-}OH)R]^{2+}$ (270)	8200 ± 30	−8 ± 1	−11 ± 3
$[R(\mu\text{-}CO_3)(\mu\text{-}NO_2)(\mu\text{-}OH)R]^{2+}$ (270)	3100 ± 15	−3 ± 1	5 ± 1

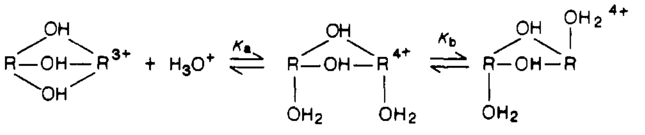
[a] R = $Co(NH_3)_3$; R′ = Co(dien). [b] Wavelengths at which the equilibrium constants were determined. [c] Value of K from ref 18 (I = 0.1 M) is 45 ± 4 M^{-1} at 25 °C.

firmed by its infrared spectra. All the μ-carbonato complexes undergo rapid protonation followed by hydroxo bridge cleavage. The carbonate bridge remains intact during this protonation equilibrium:



R = $Co(NH_3)_3$; X = NH_2, NO_2, OH

The products of the equilibrium reactions have been isolated and characterized (see Experimental Section). The equilibrium process has been illustrated in Figure 1, where the spectra of the μ-carbonato bis(μ-hydroxo) complex ion have been displayed at different concentrations of acid. The equilibrium constants were obtained by the plotting procedure explained in the Experimental Section. A linear least-squares analysis of all the data was done, and the values of the equilibrium constants, K, thus obtained at different temperatures are presented in Table II. The thermodynamic parameters are presented in Table II. The thermodynamic parameters $\Delta H°$ and $\Delta S°$ were also evaluated from the data in Table II and are presented in Table III along with the values of K at 25 °C. The equilibrium constant for the reaction of "triol" in acidic aqueous solution has been reported[18] at an ionic strength of 1 M. We have now studied this reaction more extensively under the conditions of our experiment to compare the thermodynamic parameters of this complex ion with that of other complexes we made; the results are included in Table III. The complexes listed in Table III on which equilibrium studies were carried out can be separated into two categories, depending on whether or not they contain a carbonate bridge. It is obvious from Table III that the equilibrium constants for the bridged carbonato complexes are all approximately 8000 M^{-1} (except for the μ-nitrito complex) while the values for the other complexes are in the range of 40–70 M^{-1}. It is known[18] that the "triol" equilibrates in acidic aqueous solution, with the *trans*-diaquabis(μ-hydroxo)bis(triamminecobalt(III)) ion, which has been characterized by an X-ray diffraction study.[19] Jentsch et al. reported[20] detailed kinetic studies of the reaction and proposed that it proceeds via the rapid formation of the *cis*-diaqua complex followed by a slower isomerization process:



R = $Co(NH_3)_3$

The values of K_a and K_b are reported to be 2.34 and 27.9 M^{-1}, respectively. The *trans*-diaqua complex decomposes slowly in acid solution to give the mononuclear complex ion triaquatriamminecobalt(III). A single-crystal X-ray diffraction study[1] has shown that the structure of the μ-carbonato bis(μ-hydroxo) complex[21] is appreciably different from the structure of the "triol", and as a result there are several differences between the reactions of the two complexes in acidic solutions. In the complex ion "triol" the two cobalt atoms are mutually bridged by three hydroxide ligands, resulting in a confacial bis(octahedron) stereochemical arrangement while in the μ-carbonato complex the ligand arrangement about the two cobalt(III) centers is an edge-shared bis(octahedron) with an axial–axial connection via the bridging carbonate ligand. This difference in structure exerts a tremendous influence on the lability of the bridging carbonate ligand as it was observed that the μ-carbonato complex has no tendency to decarboxylate even in moderately strong acidic solution at room temperature. This is in contrast[22] to the behavior of mononuclear carbonato complexes of cobalt(III).

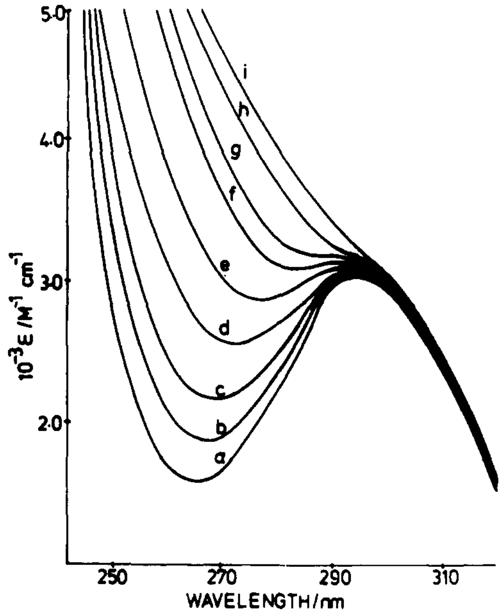


Figure 1. Spectra of $[(NH_3)_3Co(\mu\text{-}CO_3)(\mu\text{-}OH)_2Co(NH_3)_3]^{2+}$ in varying acid concentration (I = 0.5 M ($LiClO_4$)) with pH of (a) 0.0, (b) 2.79, (c) 3.20, (d) 3.51, (e) 3.76, (f) 4.12, (g) 4.30, (h) 4.54, and (i) 5.89.

As mentioned before, the products of equilibrium reactions, μ-carbonato complexes, were isolated, and the aquo ligands are assigned a cis configuration as a result of the following observations. The first pK_a of the diaqua(μ-carbonato)(μ-hydroxo)bis(triamminecobalt(III)) ion is 3.5 at 21 °C whereas the pK_a of the *trans*-diaqua bis(μ-hydroxo) complex ion is 5.6. The equilibrium position is pH-dependent, and the conversion of diaqua(μ-carbonato)(μ-hydroxo)bis(triamminecobalt(III)) is very fast over the entire pH range. This suggests that there are no rear-

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(18) Edwards, J.; Wieghardt, K.; Sykes, A. G. *J. Chem. Soc., Dalton Trans.* **1974**, 2108.

(19) Baur, W. H.; Wieghardt, K. *J. Chem. Soc., Dalton Trans.* **1973**, 2669.

(20) Jentsch, W.; Schmidt, W.; Sykes, A. G.; Wieghardt, K. *Inorg. Chem.* **1977**, *16*, 1935.

(21) Anderson, P. *Acta Chem. Scand.* **1967**, *21*, 243.

(22) Dasgupta, T. P. *International Review of Science: Inorganic Chemistry, Series Two*; Emelius, H. J., Ed.; Butterworth: London, 1974; Vol. 9, p 73.

rangements of the Co–N bonds that would be necessary for cis-trans isomerization to take place. It is also evident from the results in Table III that the formation of the diaqua complex from the μ-carbonato μ-hydroxo complexes is much more favorable than the formation of the diaqua complex from "triol".

It was also observed that while the *trans*-diaquabis(μ-hydroxo)bis(triamminecobalt(III)) complex ion could be constructed from a space-filling atomic model, the *trans*-diaqua(μ-carbonato)(μ-hydroxo)bis(triamminecobalt(III)) ion could not, which suggests that such a complex, if formed in aqueous solution, would be highly unstable.

It is also interesting to note that while the *trans*-diaquabis(μ-hydroxo)bis(triamminecobalt(III)) ion reacts with a number of ligands X (where X = NO_2^-, SO_3^{2-}, CH_3COO^-, and a wide variety of carboxylate ions) to form complexes of the type $[(NH_3)_3Co(\mu\text{-}OH)_2(\mu\text{-}X)Co(NH_3)_3]^{3+}$; NO_2^- is the only one of these ligands that reacts with the corresponding diaqua μ-carbonato complex to form a μ-carbonato μ-nitrito complex. The observed selectivity is believed to be the result of stereochemical constraints on the molecule due to the bridging carbonate ligand. The carbonate ligand bridges both Co(III) centers via an axial–axial connection, thus holding the aqua ligands in a rigid cis conformation. Therefore, only ligands of the correct size to span the cis position occupied by the aqua ligands will react with the diaqua complex.

These observations are true for all the bridged carbonato complexes whose equilibrium constants have been measured, and all the diaqua complexes prepared from them are hence characterized as *cis*-diaqua complexes. The equilibrium constants of the first three complexes in Table III, therefore, represent a combination of two equilibrium processes as shown for "triol" (see above). Since we have established that the isomerization of the *cis*-diaqua μ-carbonato complex does not take place, the equilibrium constant for the formation of the cis complex should therefore be compared with the value of K_a, 2.34 M^{-1}, for "triol". The large difference in the equilibrium constants for the two sets of complexes can probably be explained in terms of the difference in charge and the difference in their structure. The less positively charged unhydrolyzed μ-carbonato complexes will be more easily protonated, thereby indirectly increasing the basicity of the hydroxide group. The difference in the cofacial and edge-shared bis(octahedron) structures possessed by these complexes could also be partially responsible for the large difference in reactivity between the two sets of complexes.

Finally, it should be noted that the bridging NO_2^- group has quite a substantial influence on the basicity of the hydroxo group. As indicated in Table III, the value of the equilibrium constant of the μ-carbonato μ-hydroxo μ-nitrito complex has decreased from ~8000 to ~3000 M^{-1}. This is probably to be expected, as the NO_2^- group is known to be a powerful electron-withdrawing group and hence it will affect the basicity of the bridging hydroxide group.

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Registry No. triol, 22445-08-5; $[R(\mu\text{-}CO_3)(\mu\text{-}OH)_2R](ClO_4)_2$, 103621-42-7; $[(H_2O)R(\mu\text{-}CO_3)(\mu\text{-}OH)R(H_2O)](ClO_4)_3$, 103621-37-0; $[(H_2O)R'(\mu\text{-}OH)_2R'(NO_3)](ClO_4)_3$, 103621-39-2; $[R'(\mu\text{-}CO_3)(\mu\text{-}OH)_2R'](ClO_4)_2$, 103621-41-6; $[(H_2O)R'(\mu\text{-}CO_3)(\mu\text{-}OH)R'(H_2O)](ClO_4)_3$, 103621-44-9; $[R(\mu\text{-}CO_3)(\mu\text{-}NO_2)(\mu\text{-}OH)R](ClO_4)_2$, 103621-46-1; $[(H_2O)R(\mu\text{-}CO_3)(\mu\text{-}NO_2)R(H_2O)]Cl_3$, 103621-47-2; $[(H_2O)R(\mu\text{-}NH_2)(\mu\text{-}OH)R(H_2O)](NO_3)_4$, 49725-53-3; $[R(\mu\text{-}NH_2)(\mu\text{-}CO_3)(\mu\text{-}OH)R]I_2$, 103621-48-3; $[(H_2O)R(\mu\text{-}NH_2)(\mu\text{-}CO_3)R(H_2O)](ClO_4)_3$, 103621-50-7.

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Structure and Reactions of $Fe_2(CO)_8$: An IR Spectroscopic Study Using ^{13}CO, Photolysis with Plane-Polarized Light, and Matrix Isolation

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The UV/vis photolysis of $Fe_2(CO)_9$ isolated in Ar or Ar + 10% CO matrices at 15 K yields the CO-bridged isomer of $Fe_2(CO)_8$, B, as the primary photoproduct. Computer subtraction of the IR spectra in the ν(C–O) region is used to obtain the spectrum of "pure" B. The structure of B is determined by ^{13}CO enrichment. It is shown that the ν(C–O) IR bands of ^{13}CO-enriched $Fe_2(CO)_9$ can be analyzed *without* including coupling between the vibrations of bridging and terminal CO groups. Such a vibrational analysis is used to prove that isomer B of $Fe_2(CO)_8$ has two bridging CO groups with structure **2**, similar to that of $Co_2(CO)_8$ but with the $M(\mu\text{-}CO)_2M$ unit closer to planarity than in $Co_2(CO)_8$. The observed ν(C–O) IR spectra of the unbridged isomer, U, of $Fe_2(CO)_8$ are consistent with the D_{2h} structure **5**. Photolysis with plane-polarized light provides mechanistic evidence, both about the formation of B and also about the isomerization of B to U. Mechanisms are proposed for the isomerization and thermal reactions of B, involving the common singly bridged intermediate $(CO)_4Fe(\mu\text{-}CO)Fe(CO)_3$.

Introduction

There has long been interest in the photochemistry of transition-metal carbonyls.[1] Over the past few years, this interest has focussed increasingly on di- and polynuclear species,[2] from the viewpoint both of overall reactions and of detailed mechanisms. The understanding of these mechanisms frequently requires the identification of the appropriate intermediates, and it is in this area that matrix isolation techniques have played a key role.[3] Intermediates have been isolated at low temperature and their structures established by spectroscopic methods.

Some years ago, in the first application of matrix isolation to a dinuclear carbonyl,[4] we showed that UV/visible photolysis of $Fe_2(CO)_9$ produced both CO-bridged and unbridged isomers of $Fe_2(CO)_8$:

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(1) Geoffroy, G. L.; Wrighton, M. S. *Organometallic Photochemistry*; Academic: New York, 1979.

(2) Meyer, J. J.; Caspar, J. V. *Chem. Rev.* **1985**, *85*, 187.

(3) Burdett, J. K. *Coord. Chem. Rev.* **1978**, *27*, 1. Hitam, R. B.; Mahmoud, K. A.; Rest, A. J. *Coord. Chem. Rev.* **1984**, *55*, 1. Poliakoff, M.; Turner, J. J. In *Inorganic Chemistry-Toward the 21st Century*; Chisholm, M. H., Ed., ACS Symposium Series 211; American Chemical Society: Washington, DC, 1983; p 35.

(4) Poliakoff, M.; Turner, J. J. *J. Chem. Soc. A* **1971**, 2403.

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