Dinuclear Complexes of Transition Metals Containing Carbonate Ligands. IV.* Synthesis and Characterization of some Novel Dinuclear Complexes Derived from the Complex, μ-Amido-μ-Hydroxotetraamminebis(Carbonato)cobalt(III)†

GARFIELD G. SADLER and TARA P. DASGUPTA**

Department of Chemistry, University of the West Indies, Kingston 7, Jamaica

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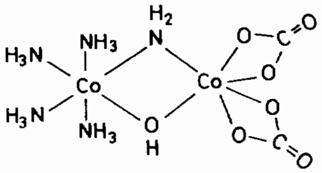
Abstract

Five novel dinuclear cobalt(III) complexes of the type $[(NH_3)_4Co(\mu\text{-}NH_2)(\mu\text{-}OH)CoL_4]$, where L = H_2O, CN, NO_2, 1/2 NTA and N_3, were prepared from the recently isolated complex $[(NH_3)_4Co(\mu\text{-}NH_2)(\mu\text{-}OH)Co(CO_3)_2]$. The complexes were characterized by UV-visible and infra-red spectroscopy. The acid dissociation constants of the terminal water molecules in the complex $[(NH_3)_4Co(\mu\text{-}NH_2)(\mu\text{-}OH)Co(H_2O)_4]^{4+}$ were determined by pH-metric titration.

Introduction

The reaction of a solution of μ-amido-μ-hydroxobis(tetraamminecobalt(III) chloride and sodium carbonate at 40 °C resulted in the isolation of black, needle-like crystals of μ-amido-μ-hydroxotetraamminebis(carbonato) dicobalt(III). The structure of this neutral complex has been characterized earlier [2] by means of a three dimensional X-ray diffraction study and can be represented as follows:



Both cobalt(III) ions are in an approximate octahedral environment in this compound. However, the molecule possesses significant zwitterionic character, since four neutral NH_3 ligands are attached to one cobalt(III) ion whereas two di-negatively charged $CO_3{}^{2-}$ ligands are chelated to other cobalt(III) ions. These terminal carbonate ligands are found to be comparatively labile. As a result the dinuclear complex dissolves in dilute mineral acids to form a light-brown red solution liberating carbon dioxide. This observation led us to investigate further the reactivity of this compound in acid solution, as well as in solutions of several different nucleophiles. We now report the detailed preparations and properties of several new dinuclear cobalt(III) complexes derived from the complex $[(NH_3)_4Co(\mu\text{-}NH_2)(\mu\text{-}OH)Co(CO_3)_2]$.

Experimental

Preparation of Complexes

Preparation of μ-amido-μ-hydroxo-tetraaminebis-(carbonato)dicobalt(III) pentahydrate, (bis-carbonato salt), $[(NH_3)_4Co(\mu\text{-}NH_2)(\mu\text{-}OH)Co(CO_3)_2]\cdot 5H_2O$

The compound was prepared as described by Churchill *et al.* [2]. *Anal.* Calc. for $Co_2N_5H_{25}O_{12}C_2$; Co, 27.50; N, 16.31; H, 5.83; C, 5.59; Found: Co, 27.20; N, 16.63; H, 5.72; C, 5.53. The purity of the complex was further checked by comparing the infrared spectrum with that reported in the literature.††

Preparation of μ-amido-μ-hydroxo-tetraamminetetracyano Dicobalt(III) Tetrahydrate, $[(NH_3)_4Co(\mu\text{-}NH_2)(\mu\text{-}OH)Co(CN)_4]\cdot 4H_2O$

0.43 g (1×10^{-3} mol) of finely powdered bis-carbonato salt was added to 10 ml of 0.4 M (4×10^{-3} mol) aqueous KCN solution. The mixture was stirred until all the black bis-carbonato complex dissolved to give a clear orange-red solution. The solution was then cooled in ice for 24 h. The red crystals which formed were filtered, washed with water and ethanol, and were air dried. Yield: 0.2 g. *Anal.* Calcd. for $Co_2N_9C_4H_{21}O_4$; Co, 31.26; N, 33.44; H, 5.57; C, 12.74. Found: Co, 31.30; N, 31.36; H, 5.44; C, 12.55.

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*For Part III see ref. 1.

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**Author to whom correspondence should be addressed.

††The infrared spectra shows two strong peaks at 1585 cm^{-1} and at 1265 cm^{-1} which are comparable to the strong peaks at 1593 cm^{-1} [ν(C=O)] and 1265 cm^{-1} [ν(C–O) + δ(O–C–O)] obtained [4] for $[Co(NH_3)_4CO_3]Cl$.

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Preparation of μ-amido-μ-hydroxo-tetraamminetetranitro Dicobalt(III), $[(NH_3)_4Co\text{-}(\mu\text{-}NH_2)(\mu\text{-}OH)\text{-}Co(NO_2)_4]$

0.43 g (1 × 10^{-3} mol) of bis-carbonato salt was dissolved in 10 ml of ice-cold 0.4 M $HClO_4$ solution. The resultant solution was filtered and the filtrate, which is essentially a solution of μ-amido-μ-hydroxo-tetraaquodicobalt(III) perchlorate, was stored at 0 °C. The filtrate was diluted to 25 ml with distilled water and 0.28 g (4 × 10^{-3} mol) of $NaNO_2$ was dissolved in the solution. The clear orange solution thus produced was cooled in ice for 6 h. The crystals produced were filtered, washed with water and ethanol, and were air dried. Yield: 0.24 g. *Anal.* Calcd. for $Co_2N_9H_{15}O_9$; Co, 29.25; N, 31.28; H, 3.72. Found: Co, 28.80; N, 30.80; H, 3.73.

Preparation of μ-amido-μ-hydroxo-tetraamminediazido Diaquodicobalt(III) Azide, $[(NH_3)_4Co(\mu\text{-}NH_2)(\mu\text{-}OH)Co(N_3)_2(H_2O)_2](N_3)_2$

0.26 g (4 × 10^{-3} mol) of NaN_3 was dissolved in 10 ml of 10^{-2} M solution of μ-amido-μ-hydroxo-tetraamminetetraaquodicobalt(III) perchlorate, as prepared earlier. The reaction mixture was ice-cooled, when an olive-green product was formed. The latter was filtered, washed thoroughly with ethanol, and dried in a desiccator. Yield: 0.3 g. *Anal.* Calcd. for $Co_2N_{17}H_{19}O_3$; Co, 27.9; N, 56.3; H, 4.49; Found: Co, 28.1; N, 57.0; H, 4.39.

Preparation of μ-amido-μ-hydroxo-tetraammine-nitrilotriacetatodicobalt(III) Perchlorate Dihydrate, $[(NH_3)_4Co(\mu\text{-}NH_2)(\mu\text{-}OH)Co(NTA)]ClO_4 \cdot 2H_2O$ *(where NTA = Nitrilotriacetate Ion)*

0.19 g (1 × 10^{-3} mol) of nitrilotriacetic acid was dissolved in 10 ml of 10^{-2} M solution of μ-amido-μ-hydroxo-tetraamminetetraaquodicobalt(III) perchlorate complex, as prepared earlier. The mixture was stirred and the pH was adjusted to approximately 6 with solid $NaHCO_3$. The solution was then cooled in ice for three h. The fine purple crystals produced were filtered, washed with ethanol, and dried. Yield: 0.2 g. *Anal.* Calcd. for $Co_2N_6H_{28}O_{13}$; Co, 21.72; N, 15.49; H, 5.16; C, 13.28. Found: Co, 21.2; N, 15.23; H, 4.79; C, 13.30.

Materials

All chemicals used were reagent grade. Distilled water was made from an all-glass distillation unit. Deionized water, obtained by passing the distilled water through the Milli-Q-Reagent grade water system (Millipore Co., Bedford, Mass., U.S.A.) 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 a Varian Cary 219 spectrophotometer. The extinction coefficients (ϵ) are reported in units of M^{-1} cm^{-1}. The infrared spectra of all the complexes were developed with a Pye Unicam SP3-300 spectrophotometer by employing a KBr disc technique.

pH and Conductance Measurements

An Orion model 701 digital pH meter fitted with a Markson combination electrode, and a Beckman 3500 digital pH meter fitted with a Beckman combination electrode, were used to measure pH. The meter was calibrated by standard buffer solutions and pH measurements were made in a water-jacketed cell which was thermostatted at the desired temperature. The conductance measurements were carried out on a Cambridge conductance bridge. The cell constant was determined with 0.01 M KCl solution.

Acid Dissociation Constant Measurements

Acid dissociation constants were measured with a Radiometer automatic titrator assembly consisting of an ABU12 autoburette, a PHM62 digital precision pH meter fitted with Radiometer glass and calomel electrodes, and a REC61 Servograph. The titration was carried out in a water-jacketed pH cell and the ionic strength was maintained to 0.5 M with standard $LiClO_4$ solution. Appropriate volume correction was made during the calculation of pK.

Measurements of Equilibrium Constants

The equilibrium constants were determined spectrophotometrically using the Cary 219 recording spectrophotometer. The required hydrogen ion concentration was achieved either by standard $HClO_4$ solution or by McIlvaine buffer [4]. The ionic strength was adjusted to 0.5 M by $LiClO_4$.

Results and Discussion

The bis-carbonato complex is insoluble in all protic and aprotic solvents at room temperature. In water at 80 °C it decomposes to yield a dark brown solution. However, in acidic solution the complex dissolves rapidly with the evolution of CO_2. The spectrum of this solution is very similar to that of the final product of the acid hydrolysis of the μ-amido-μ-hydroxobis(tetraamminecobalt(III)) [5] (Fig. 1). The final product was analysed to be approximately 75% cobalt(II) and 25% mononuclear cobalt(III)[‡] complex (Table I). However on careful addition of four times its molar quantity of acid the bis-carbonato complex dissolves to form the relatively stable μ-amido-μ-hydroxotetraamminetetraaquodicobalt(III) ion. The visible spectrum of this complex ion

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[‡] 25% cobalt(III) complex was estimated on the assumption that for a typical Co(III) ammine complex (ϵ 50 M^{-1} cm^{-1} at 495 nm).

TABLE I. Identification of Reaction Product for the Acid Hydrolysis of $(NH_3)_4Co(\mu\text{-}NH_2)(\mu\text{-}OH)(Co(CO_3)_2$.

Complex	λ_{max}(nm)	$\epsilon(M^{-1}\ cm^{-1})$	λ_{max}(nm)	$\epsilon(M^{-1}\ cm^{-1})$
$(NH_3)_4Co(\mu\text{-}NH_2)(\mu\text{-}OH)Co(CO_3)_2$ in 1 M $HClO_4$	502	67.6	345	53.6
Equimolar Quantities of $[Co(NH_3)_5(OH_2)]^{3+}$ and $Co(ClO_4)_2\cdot 6H_2O$ in 1 M $HClO_4$	501	66.6	344	56.1

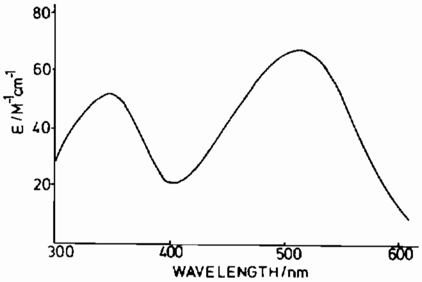

Fig. 1. The absorption spectrum of $[(NH_3)_4Co(\mu\text{-}OH)Co(CO_3)_2]$ in 1 M $HClO_4$.

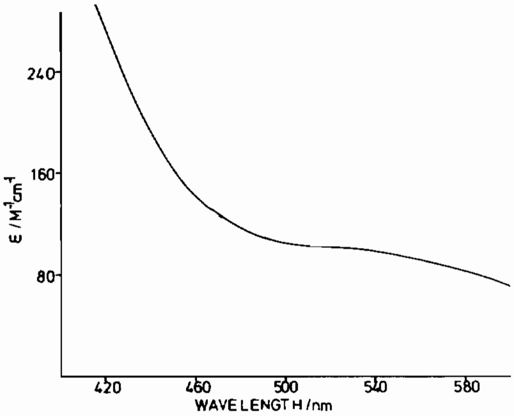

Fig. 2. The absorption spectrum of $[(NH_3)_4Co(\mu\text{-}NH_2)(\mu\text{-}OH)Co(H_2O)_4]^{4+}$ in water.

is shown in Fig. 2. When the tetraaquo complex is titrated with NaOH solution, the dissociation constants of only two aquo ligands (pK_1, 7.02 and pK_2, 8.51) could be determined, since the complex decomposes rapidly at higher pH. The relatively high pK values can be explained, at least partially, by the fact that other ligands coordinated to that cobalt(III) center (NH_2^- and OH^-) are negatively charged.

The complex μ-hydroxo-tetraamminetetracyanodicobalt(III) is insoluble in water and ethanol. This might be a direct result of the overall net zero charge of the complex. The infra-red spectrum shows a strong band at 2122 cm^{-1} which can be identified as a CN^- stretching frequency. The stretching frequency of free cyanide is 2080 cm^{-1}, while for the complex $K_3[Co(CN)_6]$ it occurs [3] at 2129 cm^{-1}. This confirms that the cyanide ions in the binuclear complex are in fact coordinated.

The orange-red crystals of μ-amido-μ-hydroxo-tetraamminetetranitrodicobalt(III) are also insoluble in water. The infrared spectra of the complex shows that the stretching frequencies for the nitro group occur at 1350 cm^{-1} and 1402 cm^{-1}. This indicates definitely that the nitro groups are coordinated via the nitrogen atoms.†

The purple complex, μ-amido-μ-hydroxo-tetraamminenitrititriacetatediocobalt(III) perchlorate, is soluble in water. The UV-visible spectra shows d–d transition bands at 545 nm (ϵ, 202) and 375 nm (ϵ, 537), and a charge transfer band at 302 nm (ϵ, 3560). The infrared spectra of the complex shows a stretching frequency at 1635 cm^{-1} (ν(C=O)), characteristic of a coordinated carboxylate group [6, 7] of NTA. The complex ion reacts rapidly in acidic solution to form the μ-amido-tetraamminenitrilotriacetatodiaquodicobalt(III) ion. The reaction is reversible and the extent of equilibrium depends on the H^+ concentration.

$$(NH_3)_4Co(\mu\text{-}NH_2)(\mu\text{-}OH)Co(NTA)^+ + H_3O^+ \longrightarrow$$
$$(NH_3)_4(H_2O)Co(\mu\text{-}NH_2)Co(H_2O)(NTA)^{2+}$$

The equilibrium constant, K, was determined at 25 °C. The series of UV spectra obtained when the complex is dissolved in different concentrations of acid are shown in Fig. 3. The equilibrium constant was calculated from the extinction coefficients at 287 nm by the following equation [8, 9]

$$(\epsilon_{obs} - \epsilon_{OH})^{-1} = (\epsilon_{H_2O} - \epsilon_{OH})^{-1}$$
$$+ (\epsilon_{H_2O} - \epsilon_{OH})^{-1}(K[H^+])^{-1}$$

where ϵ_{OH} and ϵ_{H_2O} are the molar absorption coefficients for the μ-amido-μ-hydroxo and bis-aquo complexes respectively. The plot of $(\epsilon_{obs} - \epsilon_{OH})^{-1}$ *vs.* $[H^+]^{-1}$ is shown in Fig. 4. The value obtained for K by the least-squares method is 8.84, ± 0.24. This value

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† Free NO_2^- exhibits stretching modes at 1250 cm^{-1} and 1335 cm^{-1}. In nitro complexes the stretching modes ($\nu(NO_2)$) shift markedly [4] to the higher frequencies in the range of 1340–1320 cm^{-1} and 1470–1370 cm^{-1}.

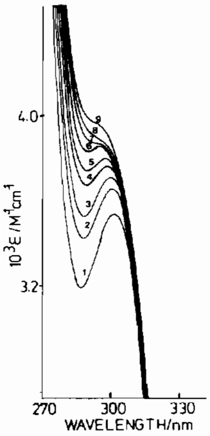

Fig. 3. Absorption spectra of $[(NH_3)_4Co(\mu\text{-}NH_2)(\mu\text{-}OH)Co(NTA)]^+$ in varying concentrations of perchloric acid. (1) 0.0 M; (2) 0.06 M; (3) 0.12 M; (4) 0.18 M; (5) 0.24 M; (6) 0.48 M; (7) 0.96 M; (8) 1.14 M; (9) 1.92 M.

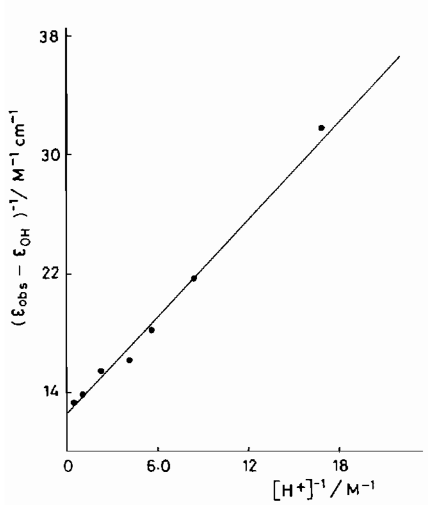

Fig. 4. A plot of $(\epsilon_{obs} - \epsilon_{OH})^{-1}$ *vs.* $[H^+]^{-1}$ for the reaction of $[(NH_3)_4Co(\mu\text{-}NH_2)(\mu\text{-}OH)Co(NTA)]^+$ in perchloric acid.

is somewhat higher than the values of 0.05 ± 0.02 and 0.6 ± 0.2 obtained for the dibridged complexes:

$(NH_3)_4Co(\mu\text{-}NH_2)(\mu\text{-}OH)Co(NH_3)_4{}^{4+}$

and

$(en)_2Co(\mu\text{-}NH_2)(\mu\text{-}OH)Co(en)_2{}^{4+}$

respectively. The higher value for NTA complex is understandable upon consideration of the electron donating ability of the nitrilotriacetate ion towards the cobalt(III) ion.

Cleavage of the hydroxo bridge of the NTA complex in acidic solution provides the opportunity for the preparation of some novel complexes of the type $(NH_3)_4Co(\mu\text{-}NH_2)(\mu\text{-}X)Co(NTA)^{2-n}$, where X represents different nucleophiles. In fact, the spectral changes observed when the NTA complex reacts with 7 M $HClO_4$ and 3.5 M H_2SO_4 is consistent with the formation of $[(NH_3)Co(\mu\text{-}NH_2)(\mu\text{-}ClO_4)Co(NTA)]^+$ and $[(NH_3)_4Co(\mu\text{-}NH_2)(\mu\text{-}SO_4)Co(NTA)]$ respectively, via a mechanism similar to that proposed [10] for the reaction of $[(NH_3)_4Co(\mu\text{-}NH_2)(\mu\text{-}OH)Co(NH_3)_4]^{4+}$ in these acids.

The complex, μ-amido-μ-hydroxo-tetraamminediazidodiaquoacobalt(III) azide, is also soluble in water. The UV-visible absorption spectra shows bands at 681 nm (ϵ = 413 ± 5) and at 314 nm (ϵ = 12350 ± 200). Only a small change in the absorption spectrum of a neutral solution occurs over a period of 24 h at 25 °C. The infrared spectrum shows two strong bands, 2090 cm^{-1} and 2060 cm^{-1}, due to asymmetrical NNN stretch [11, 12]. Support for the formulation of the azide complex as $[(NH_3)_4Co(\mu\text{-}NH_2)(\mu\text{-}OH)Co(N_3)_2(H_2O)_2](N_3)_2$ rather than the neutral complex $[(NH_3)_4Co(\mu\text{-}NH_2)(\mu\text{-}OH)Co(N_3)_4]\cdot 2H_2O$ comes from a molar conductance measurement study and a number of binuclear cobalt(III) complexes with cationic charge ranging from one to four. A summary of the results is shown in Table II. The results show the expected trend, that is, the molar conductance increases as the charge on the binuclear cation increases and the actual values compare favourably with the results obtained by Yang *et al.* [13] for the molar conductances of some peroxo and superoxo dinuclear cobalt(III) complexes. It is evident from Table II that the molar conductance value of 136 ohm^{-1} cm^2 mol^{-1} obtained for azido complex falls in the range expected for a cationic charge +2. This result led us to formulate the complex as diazido rather than tetraazido. Also, similar dinuclear complexes with an overall charge of zero are insoluble in water. It is interesting to note that while all four aquo ligands are substituted in

TABLE II. Molar Conductance Measurements for some Dinuclear Cobalt(III) Complexes at 30 °C.[a]

Complexes	Molar Conductance (ohm^{-1} mol^{-1} cm^{-2})
$[R(\mu\text{-}NH_2)(\mu\text{-}OH)R]Cl_4$	320
$[R(\mu\text{-}OH)_2R](ClO_4)_4$	332
$[R'(\mu\text{-}NH_2)(\mu\text{-}OH)R']Cl_4$	341
$[R''(\mu\text{-}OH)_3R''](ClO_4)_3$	263
$[R''(\mu\text{-}NO_2)(\mu\text{-}OH)_2R''](ClO_4)_3$	293
$[R'(\mu\text{-}NH_2)(\mu\text{-}CO_3)R'](ClO_4)_3$	281
$[R''(\mu\text{-}CO_3)(\mu\text{-}OH)_2R''](ClO_4)_2$	177
$[R''(\mu\text{-}CO_3)(\mu\text{-}NO_2)(\mu\text{-}OH)R''](ClO_4)_2$	158
$[R''(\mu\text{-}CO_3)(\mu\text{-}NH_2)(\mu\text{-}OH)R'']I_2$	175
$[NTACo(\mu\text{-}NH_2)(\mu\text{-}OH)R]ClO_4$	59
$[R(\mu\text{-}NH_2)(\mu\text{-}OH)Co(N_3)_2(H_2O)_2](N_3)_2$	136

[a] R = $Co(NH_3)_4$; R' = $Co(en)_2$; R'' = $Co(NH_3)_3$.

tetraaquodicobalt(III) complex by CN^-, NO_2^- and the chelating ligand NTA, only two of the aquo ligands are substituted by N_3^-. This is not surprising however considering that SCN, which shows no reactivity[§] towards the tetraaquo complex, lies below the azido group in the pseudohalogen nucleophilic reactivity series. The diazido complex also reacts in buffered carbonate to give the original bis-carbonato complex. In acidic solution the diazido complex decomposes rapidly to give a mixture of cobalt(II) and cobalt(III) products. A detailed kinetic investigation of this decomposition process will be published later.

Thus it can be concluded that the terminal carbonate ligands in the bis-carbonato salt can be substituted only by limited number of nucleophiles like H_2O, CN^-, NO_2^-, N_3^-, or by stereochemically rigid molecules such as NTA. The substitution is obviously dominated by the stereochemistry and the nucleophilic character of the incoming ligands.

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[§] We found that the complex ion, μ-amido-μ-hydroxotetraamminetetraaquodicobalt(III), has no tendency to react with SCN^-.