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# Synthesis and Characterization of Protonated Alkylcobaloximes and Related Compounds

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Five alkylaquocobaloximes[1] have been protonated in aqueous solution to yield a series of crystalline compounds of the general formula $[Co(dmgH)(dmgH_2)(R)(Cl)]H_2O$ where $R^- = CH_3^-$, $C_2H_5^-$, $n\text{-}C_3H_7^-$, $i\text{-}C_3H_7^-$, or $C_6H_{11}^-$. Protonation can also be achieved under strictly anhydrous conditions to give the compound $Co(dmgH)(dmgH_2)(CH_3)(Cl)$. These new compounds are compared with the previously known cobaloximes of the general formula $Co(dmgH)(dmgH_2)(X)(Y)$ where $X^- = Y^- = Cl^-$, $X^- = Y^- = SCN^-$, $X^- = Y^- = CN^-$, or $X^- = SCN^-$ and $Y^- = CN^-$. Based primarily on infrared spectroscopy, it is concluded that protonation occurs at a hydrogen-bridged oxime oxygen of the dimethylglyoxime ligand system for all the cobaloximes studied.

## Introduction

Recent kinetic studies on alkylaquocobaloximes[1] of the type $Co(dmgH)_2(R)(H_2O)$ have demonstrated an acid dependence which was taken as evidence for the existence of an oxime oxygen protonated complex in solution.[2-4] Other reports have been made on pH-dependent shifts in the electronic spectra of these complexes, and on this basis protonation constants in aqueous solution were calculated.[3,5] Except for a brief comment on the isolation of a compound with approximate composition $MeHCo(dmgH)_2SCN$,[3] protonated alkylcobaloximes have not been isolated and characterized. We report here on the isolation and characterization of six protonated alkylcobaloximes of the type I. A preliminary report of the

$[Co(dmgH)(dmgH_2)(R)(Cl)]\cdot nH_2O$

Ia, $R = CH_3$, $n = 1$
b, $R = CH_3$, $n = 0$
c, $R = C_2H_5$, $n = 1$
d, $R = n\text{-}C_3H_7$, $n = 1$
e, $R = i\text{-}C_3H_7$, $n = 1$
f, $R = C_6H_{11}$, $n = 1$

isolation and X-ray crystal structure of Ic has been made.[6]

For purposes of comparison we have investigated the protonation of a related series of four diacidocobaloximes to yield the crystalline compounds II. These compounds have

$Co(dmgH)(dmgH_2)(X)(Y)$

IIa, $X^- = Y^- = Cl^-$
b, $X^- = Y^- = SCN^-$
c, $X^- = Y^- = CN^-$
d, $X^- = SCN^-$, $Y^- = CN^-$

been reported previously, usually in hydrated form, and formulated as the acid salt "$H[Co(dmgH)_2X_2]$."[7-9] The first such compound was synthesized by Feigl and Rubinstein[7] and later formulated as the acid salt $H[Co(dmgH)_2Cl_2]$. Ablov and coworkers[10] preferred this acid salt formulation on the basis of X-ray analysis, while Gillard and Wilkinson[11] supported formulation as $Co(dmgH)(dmgH_2)Cl_2$, denoting protonation at a dimethylglyoxime oxygen.[1] The anions $[Co(dmgH)_2(CN)_2]^-$,[9] $[Co(dmgH)_2(SCN)_2]^-$,[8] and $[Co(dmgH)_2(SCN)(CN)]^-$[9] have been protonated in solution by Ablov and coworkers, and the crystalline products isolated were formulated as acid salts; "$H[Co(dmgH)_2(CN)_2]$" and "$H[Co(dmgH)_2(CN)(SCN)]$" were isolated as hydrates.[9] We have isolated all of these protonated complexes in nonhydrated form.

We observe that both the alkylaquo- and diacidocobaloxime complexes exhibit similar infrared spectroscopic shifts on protonation to yield the series of complexes I and II, respectively. These data are interpreted to mean that the acid salt formulation is incorrect and that in all cases studied protonation occurs at an oxime oxygen in the solid state as shown in Figure 1. (We use the symbol $(dmgH_2)$ to represent protonation at a dimethylglyoxime oxygen.) This protonation results in the cleavage or weakening of a dimethylglyoximato intramolecular O–H···O hydrogen bond and the formation of two free or weakly hydrogen-bonded hydroxyl groups.

**Table I.** Analytical Data for Protonated Alkylcobaloximes

| Compd | % calcd | | | % found | | |
|---|---|---|---|---|---|---|
| | C | H | N | C | H | N |
| $[Co(dmgH)(dmgH_2)(CH_3)(Cl)]H_2O$ | 30.13 | 5.63 | 15.62 | 30.41 | 5.74 | 15.70 |
| $Co(dmgH)(dmgH_2)(CH_3)(Cl)$ | 31.73 | 5.34 | 16.45 | 31.43 | 5.22 | 16.46 |
| $[Co(dmgH)(dmgH_2)(C_2H_5)(Cl)]H_2O$ | 32.22 | 5.96 | 15.03 | 32.29 | 5.99 | 14.95 |
| $[Co(dmgH)(dmgH_2)(n\text{-}C_3H_7)(Cl)]H_2O$ | 34.16 | 6.27 | 14.49 | 33.85 | 6.47 | 14.45 |
| $[Co(dmgH)(dmgH_2)(i\text{-}C_3H_7)(Cl)]H_2O$ | 34.16 | 6.27 | 14.49 | 34.39 | 6.64 | 14.38 |
| $[Co(dmgH)(dmgH_2)(C_6H_{11})(Cl)]H_2O$ | 39.39 | 6.63 | 13.13 | 39.07 | 6.85 | 12.93 |

## Experimental Section

**Preparation of Alkylaquo- and Protonated Alkylcobaloximes.** All neutral alkylaquocobaloximes of the general formula $Co(dmgH)_2(R)(H_2O)$ were synthesized by the $NaBH_4$ reduction of $Co(OAc)_2\cdot 4H_2O$ in the presence of dimethylglyoxime and the appropriate alkyl halide.[12] *Anal.* Calcd for $Co(dmgH)_2(CH_3)(H_2O)$: C, 33.54; H, 5.96; N, 17.39. Found: C, 33.11; H, 5.79; N, 17.30. Calcd for $Co(dmgH)_2(C_2H_5)(H_2O)$: C, 35.71; H, 6.31; N, 16.65. Found: C, 35.26; H, 6.42; N, 16.29. Calcd for $Co(dmgH)_2(i\text{-}C_3H_7)(H_2O)$: C, 37.71; H, 6.63; N, 16.00. Found: C, 37.33; H, 6.41; N, 15.87. Calcd for $Co(dmgH)_2(n\text{-}C_3H_7)(H_2O)$: C, 37.71; H, 6.63; N, 16.00. Found: C, 37.34; H, 6.79; N, 16.14. Calcd for $Co(dmgH)_2(C_6H_{11})(H_2O)$: C, 43.07; H, 6.98; N, 14.36. Found: C, 42.82; H, 6.95; N, 14.41.

A typical synthesis of a protonated alkylcobaloxime is as follows. A saturated solution of $Co(dmgH)_2(R)(H_2O)$ was prepared by dissolving an excess (*ca.* 5 g) of $Co(dmgH)_2(R)(H_2O)$ in 6 *N* HCl (*ca.* 100 ml) with the addition of up to an equal volume of methanol, at 50°. This dark red solution was filtered to remove undissolved material and cooled to 0° for 24 hr. This resulted in the crystallization of compounds of the general formula $[Co(dmgH)(dmgH_2)(R)(Cl)]H_2O$ as thin, red, hexagonal plates; yields 40–50%. Analytical data are listed in Table I. Synthesis of the anhydrous protonated complex $Co(dmgH)(dmgH_2)(CH_3)(Cl)$ was performed by dissolving 1.0 g ($3.29 \times 10^{-3}$ mol) of $CH_3Co(dmgH)_2$[12] in 300 ml of $CHCl_3$ to give a red solution. Dry HCl gas was bubbled through the $CHCl_3$ solution for 24 hr. The volume of the resulting orange solution was reduced to 50 ml, and 50 ml of hexane was added before cooling to 0° for 2 hr to induce crystallization. Clear red crystals were filtered and became a yellow powder upon washing with ether and drying *in vacuo*. All solvents were rigorously dried, and all manipulations were carried out under a dry $N_2$ atmosphere; yield 80%. Analytical data are listed in Table I. The deuterated analog was synthesized in a completely analogous manner. Dry DCl gas was generated by the addition of 30–40 ml of $D_2O$ to 125 ml of hot $C_6H_5COCl$ and passing the gas evolved through a −78° trap and a $CaSO_4$ drying tower.

**Preparation of Anionic and Protonated Diacidocobaloximes. $Co(dmgH)(dmgH_2)Cl_2$ and $[AsPh_4][Co(dmgH)_2Cl_2]$.** The method of Nakahara[13] was used to synthesize $Co(dmgH)(dmgH_2)Cl_2$ in ethanol; yield 60%. *Anal.* Calcd for $Co(dmgH)(dmgH_2)Cl_2$: C, 26.61; H, 4.20; N, 15.52. Found: C, 26.39; H, 4.32; N, 15.31. $[AsPh_4]$-

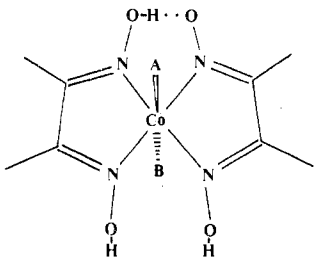



Figure 1. Proposed site of protonation in complexes of types I and II.

$[Co(dmgH)_2Cl_2]$ was prepared by dissolving 0.125 g ($3.46 \times 10^{-4}$ mol) of $Co(dmgH)(dmgH_2)Cl_2$ in 30 ml of NaCl-saturated anhydrous ethanol. To this solution was added 0.145 g ($3.46 \times 10^{-4}$ mol) of $[AsPh_4]Cl$ in 50 ml of anhydrous ethanol at room temperature. The volume of the resulting dark green solution (a brown color at this point signifies that appreciable aquation has occurred) was reduced by rotoevaporation. Cooling to 0° for 1 hr yielded olive-colored needles which were filtered, washed with water, ethanol, and ether, and dried *in vacuo*; yield 50%. *Anal.* Calcd for $[AsPh_4][Co(dmgH)_2Cl_2]$: C, 51.69; H, 4.62; N, 7.54. Found: C, 51.38; H, 4.57; N, 7.33.

**$Co(dmgH)(dmgH_2)(SCN)_2$ and $[AsPh_4][Co(dmgH)_2(SCN_2)]$.** The method of Ablov[8] was used to synthesize $Co(dmgH)(dmgH_2)(SCN)_2$; yield 85%. *Anal.* Calcd for $Co(dmgH)(dmgH_2)(SCN)_2$: C, 29.56; H, 3.74; N, 20.69. Found: C, 29.74; H, 3.43; N, 20.71. $[AsPh_4][Co(dmgH)_2(SCN)_2]$ was synthesized by adding 1 equiv of $[AsPh_4]Cl$ to an aqueous solution containing the $[Co(dmgH)_2(SCN)_2]^-$ anion. This resulted in the nearly quantitative precipitation of a light brown powder which was washed with water, ethanol, and ether and dried *in vacuo*. *Anal.* Calcd for $[AsPh_4][Co(dmgH)_2(SCN)_2]$: C, 51.77; H, 4.35; N, 10.67. Found: C, 51.60; H, 4.19; N, 10.58.

**$Co(dmgH)(dmgH_2)(CN_2)$ and $[AsPh_4][Co(dmgH)_2(CN)_2]$.** $Co(dmgH)_2(Cl)(py)$, 1.00 g ($2.48 \times 10^{-3}$ mol), was suspended in 50 ml of absolute ethanol at 40°. KCN, 0.323 g ($4.96 \times 10^{-3}$ mol), was dissolved in 20 ml of water and added to the above suspension to give a red solution after stirring for 20 min. HCl (3 *N*) was then added until the solution was acidic (pH ~1). (Care should be taken to avoid evolution of poisonous HCN gas.) The solution was concentrated, cooled to −20° for 1 hr, and filtered to isolate a yellow powder which was recrystallized from either 3 *N* HCl or $CHCl_3$–$C_6H_{12}$, washed with ethanol and ether, and dried *in vacuo*; yield 80%. *Anal.* Calcd for $Co(dmgH)(dmgH_2)(CN)_2$: C, 35.09; H, 4.43; N, 24.56. Found: C, 35.15; H, 4.62; N, 24.85. $[AsPh_4][Co(dmgH)_2(CN)_2]$ was synthesized in a similar manner, adding dropwise a solution of 1.04 g ($2.48 \times 10^{-3}$ mol) of $[AsPh_4]Cl$ in 20 ml of $H_2O$, instead of 3 *N* HCl. This resulted in the precipitation of a yellow powder which was recrystallized from methanol, washed with water, ethanol, and ether, and dried *in vacuo*; yield 90%. *Anal.* Calcd for $[AsPh_4][Co(dmgH)_2(CN)_2]$: C, 56.35; H, 4.74; N, 11.60. Found: C, 56.79; H, 4.80; N, 11.16.

**$Co(dmgH)(dmgH_2)(SCN)(CN)$ and $[AsPh_4][Co(dmgH)_2(SCN)(CN)]$.** $Co(dmgH)_2(SCN)(py)$,[12] 2.50 g ($5.86 \times 10^{-3}$ mol), was suspended in 100 ml of methanol and treated with 0.382 g ($5.86 \times 10^{-3}$ mol) of KCN dissolved in a minimum of water. The resulting solution was heated at 40° for 30 min during which time the brown suspension gradually changed to a red solution. The solution was concentrated and cooled to give red crystals of $K[Co(dmgH)_2(CN)(SCN)]$, which were filtered, washed with methanol and ether, and dried *in vacuo*. $Co(dmgH)(dmgH_2)(CN)(SCN)$ was synthesized by treating 2.00 g ($4.85 \times 10^{-3}$ mol) of $K[Co(dmgH)_2(CN)(SCN)]$ dissolved in 20 ml of water with 10 ml of 6 *N* HCl, at 50°. The desired product precipitated as a yellow powder and was washed with water, ethanol, and ether and dried *in vacuo*; yield 90%. *Anal.* Calcd for $Co(dmgH)(dmgH_2)(CN)(SCN)$: C, 32.09; H, 4.05; N, 22.46. Found: C, 31.84; H, 3.87; N, 22.28. $[AsPh_4][Co(dmgH)_2(CN)(SCN)]$ was synthesized by treating 0.10 g ($2.42 \times 10^{-4}$ mol) of $K[Co(dmgH)_2(CN)(SCN)]$ dissolved in 10 ml of $H_2O$ with a saturated aqueous solution containing 1 equiv of $[AsPh_4]Cl$, at 50°. The desired product precipitated immediately as a yellow powder; yield 90%. *Anal.* Calcd for $[AsPh_4][Co(dmgH)_2(CN)(SCN)]$: C, 53.97; H, 4.54; N, 11.11. Found: C, 53.94; H, 4.72; N, 10.93.

**Preparation of Monoacidocobaloximes.** $Co(dmgH)_2(Cl)(py)$ and $Co(dmgH)_2(SCN)(py)$ were synthesized according to the method of Schrauzer[12] and recrystallized from ethanol–water; yield 60–80%. *Anal.* Calcd for $Co(dmgH)_2(Cl)(py)$: C, 38.67; H, 4.75; N, 17.35. Found: C, 38.35; H, 4.41; N, 17.39. Calcd for $Co(dmgH)_2(SCN)(py)$: C, 39.43; H, 4.50; N, 19.71. Found: C, 39.81; H, 4.34; N, 19.47. $Co(dmgH)_2(CN)(py)$ was synthesized by treating 1.00 g ($2.34 \times 10^{-3}$ mol) of $Co(dmgH)_2(SCN)(py)$ dissolved in 100 ml of methanol with 0.152 g ($2.34 \times 10^{-3}$ mol) of KCN in 50 ml of $H_2O$. Pyridine, 5 ml, was added and the resulting red solution was stirred at 50° for 24 hr. The methanol was removed under reduced pressure, and water was added to induce the crystallization of the desired product as a yellow powder, which was recrystallized from methanol–water, washed with water, ethanol, and ether, and dried *in vacuo*; yield 60%. *Anal.* Calcd for $Co(dmgH)_2(CN)(py)$: C, 42.64; H, 4.87; N, 21.32. Found: C, 42.54; H, 5.06; N, 21.57.

**Physical Measurements.** All infrared spectra were obtained from KBr disks or $CHCl_3$ solutions in 0.5-mm path length KBr cells, on a Perkin-Elmer 621 spectrophotometer to a resolution of 2 $cm^{-1}$. Electronic spectra were recorded on a Beckman Acta III recording spectrophotometer. Elemental analyses were performed by MHW Laboratories, Garden City, Mich.

## Results and Discussion

Five alkylaquocobaloximes have been protonated in aqueous solution with HCl to yield a series of crystalline monoprotonated complexes, Ia, c–f. Protonation also occurs under anhydrous conditions, as is evidenced by the reaction of dry HCl gas with five-coordinate $Co(dmgH)_2(CH_3)$ in anhydrous $CHCl_3$ to yield Ib. The composition of the protonated complexes shown in I is supported by elemental analysis (Table I). The presence of chloride ion in the inner coordination shell is demonstrated by the appearance of a new infrared absorption at 480–495 $cm^{-1}$ which is not present in the corresponding unprotonated alkylaquo complex. This absorption is assigned to a Co–Cl vibration.[14] The protonated complexes, I, readily dissolve in water to give an acidic solution.

The protonation and isolation of the diacidocobaloximes to yield II can be performed with HCl in water or aqueous alcohol solvents. Synthetic routes which differ from those found in the literature are noted in the Experimental Section. Elemental analyses are consistent with formulating these compounds as protonated compounds, as is the observation that aqueous solutions of these compounds are acidic.

The two most reasonable possibilities for the structure of the protonated complexes are the acid salt formulation H-$[Co(dmgH)_2XY]$ and the oxime oxygen protonated form shown in Figure 1. Electronic spectra are of little help in deciding between these two possibilities. The protonated alkylcobaloximes exhibit the same electronic spectra when dissolved in aqueous solution as their unprotonated counterparts. This is consistent with the measured protonation constants in aqueous solution,[3,5] which indicate that complete dissociation should occur in an aqueous medium. Only small differences in electronic spectra obtained in $CHCl_3$ solution and Nujol mulls are observed between the protonated and unprotonated alkylcobaloximes.

Infrared spectroscopic data provide the primary evidence supporting our formulation of these compounds as cobaloximes which have been protonated at a hydrogen-bridged oxime oxygen as shown in Figure 1. These infrared data are presented in Table II and are discussed below in terms of the pertinent regions of the spectrum. For the purpose of relevant comparisons, the protonated alkylcobaloximes are listed with the corresponding unprotonated complex, and the protonated diacidocobaloximes are listed with the corresponding tetraphenylarsonium salt and monopyridine complex. Figure 2 provides sample spectra showing the spectral shifts observed upon protonation or deuteration of $Co(dmgH)_2(CH_3)(H_2O)$ and $Co(dmgH)_2(CH_3)$. Protonation of the other cobaloximes reported here provides similar spectroscopic results, as can be seen from Table II.

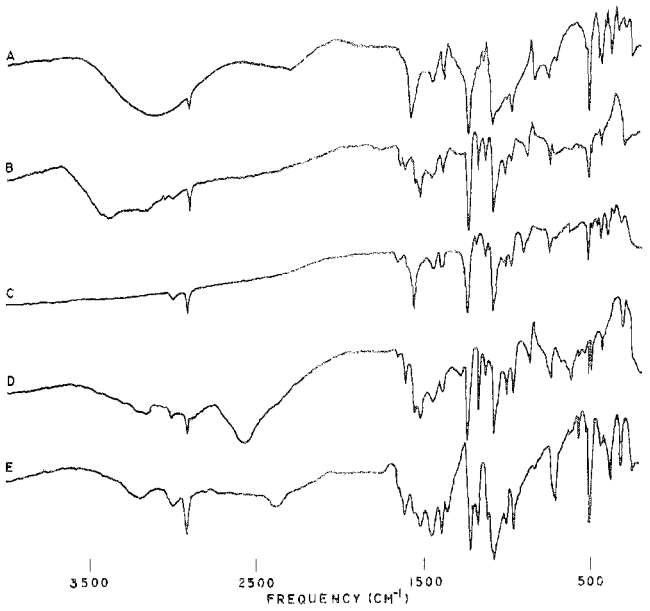



**Figure 2.** Infrared spectra obtained from KBr pellets: (A) $Co(dmgH)_2(CH_3)(H_2O)$; (B) $[Co(dmgH)(dmgH_2)(CH_3)(Cl)]H_2O$; (C) $Co(dmgH)_2(CH_3)$; (D) $Co(dmgH)(dmgH_2)(CH_3)(Cl)$; (E) $Co(dmgH)(dmgHD)(CH_3)(Cl)$.

**O–H Stretching Vibrations.** The alkylaquocobaloximes, $Co(dmgH)_2(R)(H_2O)$, all exhibit a broad smooth absorption centered at *ca.* 3120 $cm^{-1}$ which is assigned to the O–H vibration of a free or very weakly hydrogen-bonded coordinated water. Hydrogen-bonded hydroxyl groups are found to absorb at much lower energy depending on the extent of hydrogen bonding. For example, the O–H stretch for the hydroxyl groups of the bis(dimethylglyoxime) ligand system occurs as a broad, weak absorption at *ca.* 1700 $cm^{-1}$, the shift to lower energy being due to strong intramolecular hydrogen bonding.[15] An additional broad $\nu_{OH}$ absorption centered at *ca.* 2300 $cm^{-1}$ is also found for the alkylaquocobaloximes. The intensity of this absorption varies with each compound; it is of maximum intensity in the methyl compound (see Figure 2) and is barely discernible in the isopropyl compound. A crystal structure determination of $Co(dmgH)_2(CH_3)(H_2O)$[16] shows intermolecular association in the solid state by way of hydrogen bonding involving the aquo ligand. This interaction would then account for the presence of the broad absorption at 2300 $cm^{-1}$ in $Co(dmgH)_2(CH_3)(H_2O)$, and presumably a similar association occurs in the other alkylaquocobaloximes. Further support for the assignment of these absorptions in the 2300–3500-$cm^{-1}$ range to free or weakly hydrogen-bonded hydroxyl vibrations comes from the absence of broad absorptions in this region for the complexes $Co(dmgH)_2(CH_3)$ (see Figure 2), $[AsPh_4][Co(dmgH)_2XY]$, and $Co(dmgH)_2(X)(py)$, none of which contain coordinated or hydrated water molecules.

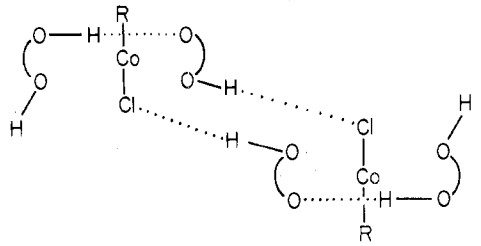
Comparison of the solid-state infrared spectrum of the alkylaquocobaloximes after protonation shows that the broad absorption centered at *ca.* 3120 $cm^{-1}$ is split into two broad absorptions centered around 3400 and 3300 $cm^{-1}$ (a third, weaker intensity shoulder at *ca.* 3200 $cm^{-1}$ is also present in Ic–f). This indicates formation of a new, free or weakly hydrogen-bonded hydroxyl group, suggesting that protonation has occurred at an oxime oxygen to give the structure shown in Figure 1. However, the assignment of these absorptions and their structural interpretation are somewhat complicated by the presence of a water of crystallization. For example, the X-ray crystal structure of $[Co(dmgH)(dmgH_2)(C_2H_5)(Cl)]H_2O$ shows that the lattice water molecules are involved in hydrogen bonding.[6] An unambiguous interpretation of the spectroscopic shifts in this region is afforded by considering data for the protonation of anhydrous $Co(dmgH)_2(CH_3)$ to yield $Co(dmgH)(dmgH_2)(CH_3)(Cl)$ and the deuterated analog. $Co(dmgH)(dmgH_2)(CH_3)(Cl)$ shows two broad absorptions centered at *ca.* 3200 and 2575 $cm^{-1}$; the lower energy absorption is shifted to 2375 $cm^{-1}$ in the deuterated complex (see Figure 2). Given the strong tendency for cobaloximes to crystallize in such a fashion so as to allow for dimer association by way of intermolecular hydrogen bonding,[10,16] it seems reasonable to assign the higher of these two absorptions to a non-hydrogen-bonded hydroxyl group (which

**Table II.** Infrared Data ($cm^{-1}$)[a]

| Compd | $\nu_{OH}$ | $\nu_{CN}$ | $\nu_{NO}$ |
|---|---|---|---|
| $Co(dmgH)_2(CH_3)$ | | 1547 | 1230, 1078 |
| $Co(dmgH)(dmgH_2)(CH_3)(Cl)$ | 3200 | 1600 | 1230, 1070 |
| | 2575 | 1550 | |
| | | 1510 | |
| $Co(dmgH)(dmgHD)(CH_3)(Cl)$ | 3200 | 1605 | 1215, 1068 |
| | 2375 | 1550 | |
| | | 1505 | |
| $Co(dmgH)_2(CH_3)(H_2O)$ | 3120 | 1570 | 1230, 1085 |
| $[Co(dmgH)(dmgH_2)(CH_3)(Cl)]H_2O$ | 3400 | 1605 | 1225, 1070 |
| | 3200 | 1550 | |
| | | 1515 | |
| $Co(dmgH)_2(C_5H_5)(H_2O)$ | 3140 | 1575 | 1233, 1088 |
| $[Co(dmgH)(dmgH_2)(C_2H_5)(Cl)]H_2O$ | 3390 | 1593 | 1230, 1070 |
| | 3310 | 1533 | |
| | 3220 | 1505 | |
| $Co(dmgH)_2(n\text{-}C_3H_7)(H_2O)$ | 3150 | 1565 | 1230, 1085 |
| $[Co(dmgH)(dmgH_2)(n\text{-}C_3H_7)(Cl)]H_2O$ | 3420 | 1600 | 1230, 1070 |
| | 3300 | 1550 | |
| | 3200 | 1540 | |
| | | 1510 | |
| $Co(dmgH)_2(i\text{-}C_3H_7)(H_2O)$ | 3110 | 1565 | 1230, 1085 |
| $[Co(dmgH)(dmgH_2)(i\text{-}C_3H_7)(Cl)]H_2O$ | 3400 | 1595 | 1230, 1072 |
| | 3300 | 1550 | |
| | 3200 | 1540 | |
| | | 1510 | |
| | | 1465 | |
| $Co(dmgH)_2(C_6H_{11})(H_2O)$ | 3210 | 1565 | 1230, 1090 |
| $[Co(dmgH)(dmgH_2)(C_6H_{11})(Cl)]H_2O$ | 3390 | 1600 | 1230, 1072 |
| | 3300 | 1550 | |
| | 3230 | 1510 | |
| $Co(dmgH)_2(Cl)(py)$ | | 1564 | 1243, 1092 |
| $[AsPh_4][Co(dmgH)_2(Cl)_2]$ | | 1570 | 1247, 1085 |
| $Co(dmgH)(dmgH_2)(Cl)_2$ | 3175 | 1610 | 1225, 1070 |
| | | 1500 | |
| | | 1480 | |
| $Co(dmgH)_2(CN)(py)$ | | 1560 | 1245, 1095 |
| $[AsPh_4][Co(dmgH)_2(CN)_2]$ | | 1560 | 1245, 1080 |
| $Co(dmgH)(dmgH_2)(CN)_2$ | 3175 | 1600 | 1240, 1075 |
| | | 1570 | |
| | | 1510 | |
| $Co(dmgH)_2(SCN)(py)$ | | 1565 | 1247, 1097 |
| $[AsPh_4][Co(dmgH)_2(SCN)_2]$ | | 1565 | 1245, 1097 |
| $Co(dmgH)(dmgH_2)(SCN)_2$ | 3100 | 1600 | 1220, 1075 |
| | | 1550 | |
| | | 1530 | |
| | | 1465 | |
| $[AsPh_4][Co(dmgH)_2(CN)(SCN)]$ | | 1562 | 1245, 1098 |
| $Co(dmgH)(dmgH_2)(CN)(SCN)$ | 3175 | 1600 | 1215, 1075 |
| | | 1550 | |
| | | 1520 | |
| | | 1500 | |

[a] All data were obtained from samples in the solid state as pressed KBr disks.

arises due to protonation of an oxime oxygen) and the second, lower absorption to a hydroxyl group which is intermolecularly hydrogen bonded in the solid state. This is represented schematically in III. A decrease in hydroxyl group stretching



III

frequency upon deuteration is expected. Support for the assignment of the lower energy absorption to an intermolecularly hydrogen-bonded hydroxyl group in the solid state comes from a comparison with solution infrared spectra. $Co(dmgH)(dmgH_2)(CH_3)(Cl)$ in $CHCl_3$ solution exhibits only one broad hydroxyl absorption at 3250 $cm^{-1}$. The deuterated analog exhibits an additional absorption at *ca.* 2500 $cm^{-1}$ in $CHCl_3$. These results are consistent with the interpretation that protonation of $Co(dmgH)_2(CH_3)$ and therefore $Co(dmgH)_2(R)(H_2O)$ occurs at a dimethylglyoxime oxygen resulting in the formation of two hydroxyl groups, one of which may be involved in intermolecular hydrogen bonding in the solid state.

The same spectroscopic changes are observed upon protonation to give complexes of the type II. Whereas the neutral monoacido complexes $Co(dmgH)_2(X)(py)$ ($X^-$ = $Cl^-$, $SCN^-$, $CN^-$) and anionic diacido complexes $[AsPh_4][Co(dmgH)_2(X)(Y)]$ ($X^-$ = $Y^-$ = $Cl^-$; $X^-$ = $Y^-$ = $SCN^-$; $X^-$ = $Y^-$ = $CN^-$; $X^-$ = $CN^-$, $Y^-$ = $SCN^-$) show no free hydroxyl group stretching absorptions, protonated complexes of type II do display weak but nevertheless discernible absorptions centered around 3200 $cm^{-1}$. This observation has led previous workers to postulate the structure shown in Figure 1 for the compound $Co(dmgH)(dmgH_2)(Cl)_2$.[11] Here we confirm this behavior for other diacidocobaloximes as well and propose the protonated oxime oxygen structure shown in Figure 1 as the best representation of their structure.

**C–N Stretching Vibrations.** The strong absorption envelope at *ca.* 1560 $cm^{-1}$ has been assigned to a C–N stretching vibration in coordinated dimethylglyoxime by previous workers.[17,18] For complexes of the types $Co(dmgH)_2(R)(H_2O)$, $Co(dmgH)_2(R)$, $Co(dmgH)_2(X)(py)$, and $[AsPh_4][Co(dmgH)_2(X)(Y)]$, this absorption occurs as one intense band listed in Table II. Upon protonation to give complexes of types I and II, this absorption band is broadened and consists of a multiplet of peaks and shoulders. These are listed in Table II, the most intense absorption being the lowest energy band listed.

Previous workers have noted that changes in electron density on the cobalt result in a shift in the C–N stretching frequency of coordinated dimethylglyoxime.[18] Our results confirm this observation, as $\nu_{CN}$ varies with changes in ligands R, X, and Y in the unprotonated compounds. The observed shift in $\nu_{CN}$ upon protonation is consistent with protonation occurring at the hydrogen-bridged oxime oxygens, thus causing a change in electron density in the C–N linkage and a reduction in dimethylglyoxime ligand symmetry.

**N–O Stretching Vibrations.** Two intense, sharp absorption bands occurring at *ca.* 1220–1250 and 1070–1100 $cm^{-1}$ have been assigned to vibrations arising from the N–O linkage of coordinated dimethylglyoxime.[17,18] As can be seen from Table II, the alkylcobaloximes exhibit up to a 5-$cm^{-1}$ decrease in the higher energy absorption and a 10–20-$cm^{-1}$ decrease in the lower energy absorption upon protonation to give the complexes I. Protonation of the diacidocobaloximes to give II results in a 5–30- and 10–25-$cm^{-1}$ decrease in the higher and lower energy absorptions, respectively. This decrease is consistent with protonation of the complexes at a hydrogen-bridged oxime oxygen, in that such a protonation would be expected to result in a removal of electron density from the N–O bond and a corresponding decrease in the N–O stretching frequency.

It has been noted that N–O distances in dimethylglyoxime complexes are sensitive to whether a proton is covalently or hydrogen bonded to the oxygen.[19] An X-ray crystal structure of $[Co(dmgH)(dmgH_2)(C_2H_5)(Cl)]H_2O$ shows that the N–O bond lengths exhibit some variation, from 1.32 to 1.39 Å (esd 0.014 Å).[6] The longer N–O bond lengths include those oxygens at the proposed site of protonation, as determined by the elongation to nonbonded O–O distances (2.71 *vs.* 2.43 Å).[6] Similar bond length variations are observed for the protonated isopropylcobaloxime Id.[20]

**Other Infrared Absorption Bands.** As noted above, upon protonation the alkylcobaloximes exhibit a new absorption in the region 480–495 $cm^{-1}$, which is assigned to a Co–Cl vibration.[14] All complexes reported here display a strong, sharp absorption in the region 510–515 $cm^{-1}$, which has been assigned to a cobalt–dimethylglyoxime nitrogen vibration.[18] In the case of the alkylcobaloximes this absorption is reduced in intensity upon protonation. C–H vibrations for the methyl groups of the dimethylglyoxime ligands and for the coordinated alkyl groups are found in the 2800–3100-$cm^{-1}$ region as expected. Protonation does not affect these absorptions.

## Summary and Conclusions

We conclude that the protonated complexes of types I and II should not be viewed as acid salts or as containing lattice hydronium ions but rather that protonation occurs at a hydrogen-bridged oxime oxygen of the dimethylglyoxime ligand as shown in Figure 1. This conclusion is based primarily on the following observations taken from solid-state and solution infrared spectra. (1) Changes in the $\nu_{OH}$ region of the spectrum indicate that protonation of alkyl- and diacidocobaloximes in aqueous or nonaqueous medium results in the formation of free or weakly hydrogen-bonded O–H groups. Thus formulation of the anhydrous protonated cobaloxime Ib as containing a lattice proton, *i.e.*, "$H[Co(dmgH)_2(CH_3)(Cl)]$," can be discounted by the observation of absorptions in the $\nu_{OH}$ region of the spectrum taken in $CHCl_2$ solution. A lattice proton cannot account for this behavior. These absorptions also appear in the solid-state infrared spectrum obtained in KBr. Formulation of the hydrated protonated alkylcobaloximes Ia, c–f as containing lattice hydronium ions, *i.e.*, "$[H_3O][Co(dmgH)_2(R)(Cl)]$," can be discounted by noting that the anhydrous protonated complex $Co(dmgH)(dmgH_2)(CH_3)(Cl)$ exhibits absorptions in KBr similar to those of the corresponding hydrated complex $[Co(dmgH)(dmgH_2)(CH_3)(Cl)]H_2O$ in the $\nu_{OH}$ region of the spectrum. Furthermore, the hydrated compound Ia can be dehydrated *in vacuo* at room temperature without loss of HCl, as determined by mass spectrometry, to produce a compound whose infrared spectrum in KBr is identical with that of the anhydrous compound Ib in KBr. Finally, formulation of the compounds of type II as containing lattice protons, *i.e.*, "$H[Co(dmgH)_2(X)_2]$," can be discounted by the observation of these same types of absorptions in the $\nu_{OH}$ region of the spectrum as well as by the observation that the infrared spectra of all compounds of types I and II behave according to the following observations. (2) Upon protonation, the absorption band due to $\nu_{CN}$ of the dimethylglyoxime imine linkage is broadened into a multiplet. (3) The two $\nu_{NO}$ absorptions of the dimethylglyoxime ligand are shifted to lower energy upon protonation.

Our interpretation that these infrared spectroscopic shifts

are due to protonation at an oxime oxygen is further supported by the results of an X-ray crystallographic study of [Co(dmgH)(dmgH$_2$)(C$_2$H$_5$)(Cl)]H$_2$O[6] and [Co(dmgH)(dmgH$_2$)(*i*-C$_3$H$_7$)(Cl)]H$_2$O.[20] Both protonated compounds are observed to have one intramolecular dimethylglyoxime O–O distance greater than the other. This is consistent with protonation at an oxime oxygen resulting in cleavage of the intramolecular O–H···O bond with concomitant elongation to the nonbonded O–O distance. The N–O bond distances at this proposed site of protonation are longer than that observed in the same molecule where protonation has not occurred and the intramolecular O–H···O hydrogen bond is still intact.[6,20]

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**Registry No.** [Co(dmgH)(dmgH$_2$)(CH$_3$)(Cl)]H$_2$O, 53516-27-1; Co(dmgH)(dmgH$_2$)(CH$_3$)(Cl), 53495-31-1; Co(dmgH)(dmgH$_2$)(C$_2$H$_5$)(Cl), 53432-72-7; Co(dmgH)(dmgH$_2$)(*n*-C$_3$H$_7$)(Cl), 53432-73-8; Co(dmgH)(dmgH$_2$)(*i*-C$_3$H$_7$)(Cl), 53432-74-9; Co(dmgH)(dmgH$_2$)(C$_6$H$_{11}$)(Cl), 53432-75-0; Co(dmgH)(dmgH$_2$)(CN)$_2$, 53537-51-2; [AsPh$_4$][Co(dmgH)$_2$(CN)$_2$], 43065-09-4; Co(dmgH)$_2$(CH$_3$)(H$_2$O), 25360-55-8; Co(dmgH)$_2$(C$_2$H$_5$)(H$_2$O), 26025-30-9; Co(dmgH)$_2$(*i*-C$_3$H$_7$)(H$_2$O), 30974-89-1; Co(dmgH)$_2$(*n*-C$_3$H$_7$)(H$_2$O), 28182-23-2; Co(dmgH)$_2$(C$_6$H$_{11}$)(H$_2$O), 52970-74-8; [AsPh$_4$][Co(dmgH)$_2$(SCN)$_2$], 39494-95-6; Co(dmgH)(dmgH$_2$)(SCN)(CN), 53495-32-2; [AsPh$_4$][Co(dmgH)$_2$(SCN)(CN)], 53432-71-6; Co(dmgH)$_2$(CN)(py), 23318-65-2; Co(dmgH)$_2$(CH$_3$), 36609-02-6; Co(dmgH)(dmgHD)(CH$_3$)(Cl), 53432-66-9.

## References and Notes

(1) The term cobaloxime is used to describe any bis(dimethylglyoximato) complex of cobalt(III). The symbol dmgH represents the dimethylglyoxime monoanion (CH$_3$C(=NO)C(=NOH)CH$_3$)$^-$ and dmgH$_2$ neutral dimethylglyoxime (CH$_3$C(=NOH)C(=NOH)CH$_3$). This symbolism differs from that used in ref 6.
(2) P. Abley, E. R. Dockal, and J. Halpern, *J. Amer. Chem. Soc.*, **95**, 3166 (1973).
(3) A. Adin, and J. H. Espenson, *Chem. Commun.*, 653 (1971).
(4) J. H. Espenson and J. S. Shveima, *J. Amer. Chem. Soc.*, **95**, 4468 (1973).
(5) D. Dodd and M. D. Johnson, *J. Organometal. Chem.*, **52**, 1 (1973).
(6) A. L. Crumbliss, J. T. Bowman, P. L. Gaus, and A. T. McPhail, *J. Chem. Soc., Chem. Commun.*, 415 (1973).
(7) F. Feigl and H. Rubinstein, *Justus Liebigs Ann. Chem.*, **433**, 183 (1923).
(8) A. V. Ablov and G. P. Syrtsova, *J. Gen. Chem. USSR*, **25**, 1247 (1955).
(9) A. V. Ablov and G. P. Syrtsova, *Russ. J. Inorg. Chem.*, **10**, 1079 (1965).
(10) Y. A. Simonov, A. A. Dvorkin, O. A. Bologa, A. V. Ablov, and T. L. Minovskii, *Dokl. Akad. Nauk SSSR*, **210**, No. 3, 615 (1973).
(11) R. D. Gillard and G. Wilkinson, *J. Chem. Soc.*, 6041 (1963).
(12) G. N. Schrauzer, *Inorg. Syn.*, **11**, 61 (1968).
(13) A. Nakahara, *Bull. Chem. Soc. Jap.*, **28**, 207 (1955).
(14) D. M. Adams, "Metal Ligand and Related Vibrations," 1st ed, St. Martin's Press, New York, N. Y., 1968, p 26.
(15) A. Nakahara, J. Fujita, and R. Tsuchida, *Bull. Chem. Soc. Jap.*, **29**, 296 (1956).
(16) D. L. McFadden and A. T. McPhail, *J. Chem. Soc.*, 363 (1974).
(17) R. Blinc and D. Hadzi, *J. Chem. Soc.*, 4536 (1958).
(18) N. Yamazaki and Y. Hohokabe, *Bull. Chem. Soc. Jap.*, **44**, 63 (1971).
(19) K. Bowman, A. P. Gaughan, and Z. Dori, *J. Amer. Chem. Soc.*, **94**, 727 (1972).
(20) A. T. McPhail and D. L. McFadden, personal communication.

Contribution from the Evans Chemical Laboratory, The Ohio State Unversity, Columbus, Ohio 43210, and the Savannah River Laboratory, E. I. du Pont de Nemours and Company, Aiken, South Carolina 29801

# Five- and Six-Coordinate Complexes of Iron(II) and -(III) with a Macrocyclic Tetradentate Ligand

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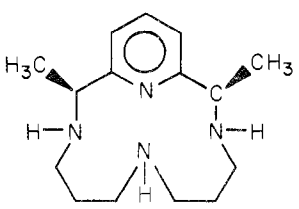
Iron(II) and iron(III) complexes have been prepared with the 14-membered macrocyclic tetradentate ligand *meso*-2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene (abbreviated *ms*-CRH). The iron(II) derivatives include both high-spin and low-spin six-coordinate complexes and a series of high-spin five-coordinate complexes related in structure to deoxyhemoglobin. The iron(III) derivatives are all high-spin and six-coordinate. All complexes were characterized by infrared and visible spectra, magnetic susceptibilities, molar conductivity, elemental analyses, and Mössbauer spectra. Assignments of the probable structures of a number of these complexes are based on the results of the Mössbauer spectral studies.

## Introduction

During the last several years, many synthetic macrocyclic ligands have been prepared and their metal complexes characterized.[2,3] The similarities between these synthetic ligand systems and such naturally occurring macrocyclic ligands as the porphyrins lend special significance to the study of those of iron. We report here the synthesis and characterization of the complexes of iron with the synthetic macrocyclic ligand *meso*-2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene (*ms*-CRH, I). Previous studies with nickel and cobalt have revealed the rich chemistry of this ligand.[4-7]




I

The six-coordinate complexes of both iron(II) and iron(III) were found to be predominantly high spin in electronic configuration, the only exception being a low-spin dithiocyanatoiron(II) derivative. A series of five-coordinate high-spin iron(II) complexes has also been isolated and their configurations assigned on the basis of their distinctive Mössbauer spectra.[8] These compounds and certain other synthetic iron(II) porphyrin derivatives[9,10] are of special interest because they are among the first synthetic complexes which have the high-spin, five-coordinate structure that has been assigned to deoxyhemoglobin and deoxymyoglobin. Prior to the discovery of the synthetic high-spin pentacoordinate complexes, there was some tendency to treat the natural products as being unique in coordination structure. Indeed, it now appears that such configurations are not rare.

## Experimental Section

**Materials.** 2,6-Diacetylpyridine (Aldrich Chemical Co.) was recrystallized before use from ethanol, and 3,3'-diaminodipropylamine (Aldrich Chemical Co.) was used as supplied. The iron(II) salts were obtained from Alfa Inorganics Inc. and used as supplied. Solvents termed dry and degassed were dried over molecular sieves for several days before being refluxed under nitrogen for 1 hr. The syntheses