Intermolecular Hydrogen Bonding in Protonated Diacidocobaloximes

ALVIN L. CRUMBLISS* and PAUL L. GAUS

The protonated diacidocobaloximes Co(dmgH)(dmgH$_2$)(X)(Y), where X = Y = Cl$^-$, X = Y = SCN$^-$, X = Y = CN$^-$, or X = SCN$^-$ and Y = CN$^-$, have been shown from their infrared spectra to crystallize in such a way that intermolecular hydrogen bonding occurs. This intermolecular association involves the hydroxyl group formed by the protonation of the oxime oxygen of one molecule and (1) the Cl$^-$ ligand in Co(dmgH)(dmgH$_2$)(Cl)$_2$, (2) the S-bonded thiocyanato ligand in Co(dmgH)(dmgH$_2$)(SCN)(NCS), (3) the cyano ligand of Co(dmgH)dmgH$_2$)(SCN)(CN), and (4) one of the cyano ligands in Co(dmgH)(dmgH$_2$)(CN)$_2$. The linkage isomer for the thiocyanate containing compounds has been identified in the solid state and solution. The relative basicities of the free end of the coordinated cyanide, thiocyanate, and isothiocyanate are found to be in the order CN$^-$ > SCN$^-$ $\gg$ NCS$^-$.

Introduction

It has become increasingly apparent that the class of chelate compounds known as the cobaloximes[1] tends to crystallize in such a fashion so as to allow for intermolecular hydrogen bonding in the solid state. Most recently, the alkylaquo-cobaloximes, Co(dmgH)$_2$(R)(H$_2$O), have been shown both through crystallographic[2] and infrared spectroscopic[3] studies to dimerize in the solid state as a result of intermolecular hydrogen bonding involving the aquo ligands. The newly characterized protonated alkylcobaloximes of the general formula [Co(dmgH)(dmgH$_2$)(R)(Cl)]·nH$_2$O (R = CH$_3^-$, C$_2$H$_5^-$, n-C$_3$H$_7^-$, i-C$_3$H$_7^-$, or C$_6$H$_{11}^-$, n = 0 or 1) have also been seen to associate by way of solid state hydrogen bonding.[3,4] In these examples an extra impetus for intermolecular hydrogen bonding is provided by the protonation of these complexes at an oxime oxygen.[3] The hydroxyl groups of this protonated dimethylglyoxime ligand are hydrogen bonded in the solid state not only with the chloride ligand of a second complex, but with a water of crystallization as well.[4]

We now report infrared spectroscopic evidence to suggest a similar type of intermolecular hydrogen bonding in the crystalline protonated diacidocobaloximes of the general formula Co(dmgH)(dmgH$_2$)(X)(Y), where X = Y = Cl$^-$, X = Y = CN$^-$, X = Y = SCN$^-$ or X = SCN$^-$ and Y = CN$^-$. In particular, the evidence cited below indicates hydrogen bonding in the solid state between a protonated dimethyl-glyoxime ligand of one molecule and an acido ligand of another molecule.

Experimental Section

Preparation of Complexes. The dichloro-, dicyano-, and cyano-thiocyanatocobaloximes were prepared and isolated as anhydrous solids according to the methods described previously.[3] The N,N- and S,S-bonded dithiocyanatocobaloximes were prepared according to the methods of Marzilli and Epps.[5] Isomeric purity (>95%) was demonstrated on the basis of ^{1}H NMR data in C$_6$H$_5$NO$_2$ and DMF where the dimethylglyoxime methyl groups are known to be non-equivalent.[5] The protonated dithiocyanatocobaloxime, Co-(dmgH)(dmgH$_2$)(SCN)(NCS), was synthesized according to the methods of Ablov.[6] Satisfactory analyses were obtained on all compounds used in this study.

The compound [AsPh$_4$][Co(dmgH)$_2$(SCN)(CN)] is shown to be isomerically pure based on the observation that it gives only one dimethylglyoxime proton resonance in C$_6$H$_5$NO$_2$ (δ 2.37 ppm). C$_6$H$_5$NO$_2$ is the solvent which gives the greatest separation among the dimethylglyoxime resonances for the three isomers of the di-thiocyanatocobaloxime anions, and it was therefore chosen as the solvent which would be the least likely to give a coincidental overlap of chemical shifts should two isomers of [AsPh$_4$][Co(dmgH)$_2$-(CN)(CNS)] exist.

Methods. Infrared spectra were obtained using a Perkin-Elmer 621 spectrophotometer to a resolution of 2–4 cm^{-1}. ^{1}H NMR spectra were obtained using a JEOL JNM-MH-100 spectrometer. The CHCl$_3$ and C$_6$H$_5$NO$_2$ solvents used in these spectroscopic studies were freshly distilled from CaCl$_2$ under a purge of dry N$_2$ gas (CHCl$_3$) or under reduced pressure (C$_6$H$_5$NO$_2$). When necessary, the C$_6$H$_5$NO$_2$ was also repeatedly crystallized prior to distillation. All solutions were prepared under anhydrous conditions using a dry N$_2$ glove bag so as to preclude the possibility for deprotonation of the complexes in the presence of water.

The integrated absorption band intensities, A, for CN vibrations of coordinated thiocyanate were determined from solution ir spectra according to the method of Ramsay.[7] A modification of this method was used to obtain the solid state absorption band intensities, A_r, relative to the intensity of the absorption arising from the NO linkage of the dimethylglyoxime ligand. This relative SCN absorption band intensity, A_r, was determined from the equation

$$A_r = \frac{A_{SCN}}{A_{NO}} = \frac{\left[\ln (T_0/T)\Delta\nu_{1/2}\right]_{SCN}}{\left[\ln (T_0/T)\Delta\nu_{1/2}\right]_{NO}}$$

where A_{SCN} = the intensity of the SCN group ν_{CN} absorption from a KBr spectrum, per mole SCN responsible for the ν_{CN} absorption, A_{NO} = the intensity of the NO group absorption at ca. 1230 cm^{-1} from the same KBr spectrum, T_0 = zero point transmittance measured from a line drawn through the base of the SCN or NO group absorption band, T = transmittance at the SCN or NO group absorption band maximum, and $\Delta\nu_{1/2}$ = absorption band width at half peak height in cm^{-1}.

The NO absorption band was chosen for this type of comparison because of its high intensity, and because its band shape is similar to that of the SCN ligand ν_{CN} absorption. The NO absorption band shape is also unchanged upon protonation. This allows use of the method for a wide variety of cobaloxime complexes.

The compound [AsPh$_4$][Co(dmgH)$_2$(NCS)$_2$] was shown by integrated absorption intensity data in solution to be the di-N-bonded isomer[8] (Table II) and was therefore used as a standard to establish a value of $A_r \sim$ 3–4 as being typical of N-bonded thiocyanate ligands. Similarly, the compound [AsPh$_4$][Co(dmgH)$_2$(SCN)$_2$] serves as a standard for an S-bonded thiocyanate ligand (Table II), establishing a value of $A_r < 1$ as being typical of a solid state absorption due to an S-bonded SCN.

This method, although less sensitive than the solution method, has the advantage of determining directly the linkage isomerism in the solid state and thereby precluding the possibility of isomerization upon dissolution of the complex. That the compounds used as standards for this solid state method did not themselves isomerize in solution is supported by agreement between the solution values reported here for N- and S-bonded thiocyanate and those of other workers,[7–9] and by the fact that both in the solid state method and in solution the N-bonded thiocyanate ν_{CN} absorption is more intense than that assigned to the S-bonded thiocyanate ν_{CN} absorption. ^{1}H NMR evidence also suggests that although an isomerization of [AsPh$_4$]-[Co(dmgH)$_2$(CNS)$_2$] can occur in solution, its rate is slow.[5]

Results

O–H Group Absorptions. The infrared absorptions due to the hydroxyl groups of the protonated dimethylglyoxime ligand in the compounds Co(dmgH)(dmgH$_2$)(X)(Y) are listed in Table I. The spectra of crystalline samples exhibit broader

Table I. Hydroxyl Group Infrared Absorptions

Compd	ν_{OH}, cm^{-1}		
	KBr	Solution	
Co(dmgH)(dmgH$_2$)(Cl)$_2$	3175	3675^a	3590^a
Co(dmgH)(dmgH$_2$)(SCN)(NCS)	3100^c	3670^a	3585^a
Co(dmgH)(dmgH$_2$)(SCN)(CN)	3175	3680^b	3200^b
Co(dmgH)(dmgH$_2$)(CN)$_2$	3175	3560^b	3000^b

^{a} Dry nitrobenzene solution at ca. 10^{-4} M. ^{b} Dry chloroform solution at ca. 10^{-3} M. ^{c} Very weak and very broad.

absorptions at lower energy than those obtained from solution samples. One of these absorptions remains broad and at low energy for the compounds Co(dmgH)(dmgH$_2$)(CN)(SCN) and Co(dmgH)(dmgH$_2$)(CN)$_2$ in moderately concentrated solutions (10^{-3} M). Such hydroxyl group absorptions are absent in the solid state and solution infrared spectra of the corresponding nonprotonated compounds [AsPh$_4$][Co-(dmgH)$_2$(X)(Y)], as is expected.[3]

SCN Ligand Absorptions. C–N stretching frequencies for coordinated thiocyanate are listed in Table II along with the value of the integrated absorption band intensity for each thiocyanate absorption in solution. These integrated absorption band intensities in solution have been determined by the method of Ramsay,[7] and have been used according to established methods[8,9] in making the solution linkage isomer assignments also listed in Table II. Isomer purity was determined by ^{1}H NMR measurements (see Experimental Section). A technique utilizing relative solid state absorption band intensities (see Experimental Section) was used to make the solid state linkage isomer assignments found in Table II.

It is evident that, with the exception of Co(dmgH)-(dmgH$_2$)(SCN)(NCS), the SCN ligand ν_{CN} bands remain essentially unchanged upon going from the solid state to solution. While two SCN ligand ν_{CN} absorptions are apparent for Co(dmgH)(dmgH$_2$)(SCN)(NCS) in the solid state, only one absorption appears in solution.

CN Ligand Absorptions. C–N infrared absorptions for coordinated cyanide are listed in Table III. A high-energy absorption is observed in the solid state and in more concentrated solutions of the protonated dicyano and cyano–thiocyanato complexes at 2154 and 2160 cm^{-1}, respectively. This high-energy absorption is not present in dilute solution or in the corresponding nonprotonated tetraphenylarsonium salts.
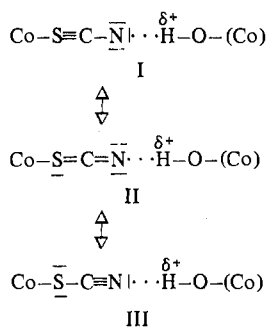
Discussion

Evidence for intermolecular hydrogen bonding is found in shifts in the hydroxyl region of the infrared spectrum and shifts in ν_{CN} for coordinated thiocyanate and cyanide.

A direct interpretation of these results is possible for the compound Co(dmgH)(dmgH$_2$)(Cl)$_2$. X-Ray structural data[10] suggest intermolecular hydrogen bonding in the solid state involving the hydroxyl groups which are formed through

protonation at an oxime oxygen.[3] It is this hydrogen bonding which is responsible for the broadness, low-energy position, and weak intensity of the hydroxyl group absorptions in the solid state. In solution, this intermolecular hydrogen bonding is disrupted, and the hydroxyl group absorptions appear at higher energy with an increased intensity and sharpness typical of free or unassociated hydroxyl groups. (See Table I.)

The cyanide-containing compounds Co(dmgH)(dmgH$_2$)-(CN)(SCN) and Co(dmgH)(dmgH$_2$)(CN)$_2$ also engage in solid state intermolecular hydrogen bonding involving a protonated oxime hydroxyl group and a cyano ligand. This conclusion is based on data shown in Table III, which lists a high energy ν_{CN} absorption for coordinated cyanide in the crystalline compounds. This is characteristic of a bridging cyanide bonded through both the C and N atoms.[11] This absorption is shifted to lower energy in dilute solution, or in the solid state and solution spectra of the corresponding unprotonated tetraphenylarsonium salts [AsPh$_4$][Co-(dmgH)$_2$(CN)(SCN)] and [AsPh$_4$][Co(dmgH)$_2$(CN)$_2$] where intermolecular associations are less likely to occur. The shift of the solid state ν_{OH} absorption to higher energy upon dissolving these complexes in chloroform also supports intermolecular hydrogen bonding involving the protonated oxime hydroxyl groups. The occurrence of one low energy ν_{OH} absorption for these compounds in solution suggests the persistence of these intermolecular associations in solution. (See Table I.)

Intermolecular hydrogen bonding in the solid state is also indicated for the protonated dithiocyanato complex Co-(dmgH)(dmgH$_2$)(SCN)(NCS). While the hydroxyl group absorptions for this compound are broad and at low energy in the solid state, they appear as two sharp absorptions, at high energy, in solution (Table I). Similarly, while two ν_{CN} absorptions due to coordinated thiocyanate are apparent in the solid state, only one such absorption is present in solution (Table II). We interpret these results in terms of intermolecular hydrogen bonding in the solid state between a protonated oxime oxygen and the S-bonded thiocyanate ligand. This type of hydrogen bonding can account for the anomalously low energy position (1984 cm^{-1}) of the S-bonded

$$Co-S{\equiv}C-\underline{N}|\cdots\overset{\delta+}{H}-O-(Co)$$
$$I$$
$$\updownarrow$$
$$Co-S{=}C{=}\underline{\bar{N}}\cdots\overset{\delta+}{H}-O-(Co)$$
$$II$$
$$\updownarrow$$
$$Co-\underline{S}-C{\equiv}N|\cdots\overset{\delta+}{H}-O-(Co)$$
$$III$$

Table II. Solid State and Solution ν_{CN} Absorptions for Coordinated Thiocyanate

Compd	Solid state^a			Solution		
	ν_{CN}, cm^{-1}	$A_r{}^b$	Isomer^c	ν_{CN}, cm^{-1}	A^d	Isomer^e
[AsPh$_4$][Co(dmgH)$_2$(SCN)$_2$]	2110	0.5	SCN, SCN	2109^f	2 × 10^4	SCN, SCN
[AsPh$_4$][Co(dmgH)$_2$(NCS)$_2$]	2120	3.4	NCS, NCS	2110^f	1 × 10^5	NCS, NCS
Co(dmgH)(dmgH$_2$)(SCN)(NCS)	2112	3.2	NCS	2107^f	h	
	1984	0.4	SCN			
[AsPh$_4$][Co(dmgH)$_2$(CN)(SCN)]	2111	0.6	SCN^i	2108^g	4 × 10^4	SCN^i
Co(dmgH)(dmgH$_2$)(CN)(SCN)	2111	0.7	SCN^i	2115^g	1 × 10^4	SCN^i

^{a} KBr disk. ^{b} A_r is defined to be the solid state intensity of the SCN ligand absorption (per mole of SCN) relative to the intensity of the NO absorption at ca. 1230 cm^{-1} arising from the dimethylglyoxime ligand. See the Experimental Section. ^{c} Based on a value of A_r of ca. 3–4 for N-bonded NCS (standard = [AsPh$_4$][Co(dmgH)$_2$(NCS)$_2$]) and a value of A_r < 1 for S-bonded SCN (stanndard = [AsPh$_4$][Co(dmgH)$_2$-(SCN)$_2$]). ^{d} The integrated absorption band intensity (per mole of SCN) as determined by the method of Ramsay.[7] ^{e} Isomer assignments are based on the value of the integrated absorption band intensity according to the work of Ramsay[7] and Norbury and Sinha.[9] ^{f} Dry C$_6$H$_5$NO$_2$ solution. ^{g} Dry CHCl$_3$ solution. ^{h} An accurate determination of absorption band intensity in solution was not possible due to the low solubility of the complex. ^{i} See ref 14.

Table III. Solid State and Solution ν_{CN} Absorptions for Coordinated Cyanide

	ν_{CN}, cm^{-1}	
Compd	KBr	Solution^a
[AsPh$_4$][Co(dmgH)$_2$(SCN)(CN)]	2130	2132
Co(dmgH)(dmgH$_2$)(SCN)(CN)	2160	2133
[AsPh$_4$][Co(dmgH)$_2$(CN)$_2$]	2135	2130
Co(dmgH)(dmgH$_2$)(CN)$_2$	2154, 2138	2140

^{a} Dry CHCl$_3$ solution at ca. 10^{-5} M.

thiocyanate ν_{CN} absorption.[12] Such an interaction would serve to increase the relative importance of the C–N single bond thiocyanate resonance form (I) by favoring the electrostatic force of attraction between the highest amount of negative formal charge (2–) on the N atom of the S-bonded thiocyanate and the partial positive charge (δ+) on the protonated oxime oxygen of the adjacent molecule.

Three linkage isomers are found for the unprotonated dithiocyanato complex, and Marzilli reports their relative stabilities as follows: N,N > N,S ~ S,S.[5] We have found only the mixed N,S bonded isomer listed in Table II for the protonated compound and attribute this to the enhanced stability of this isomer which is provided through the intermolecular hydrogen bonding discussed above. This is analogous to an earlier report of the influence of potentially hydrogen-bonding solvents on the relative stabilities of N and S bonded thiocyanate in Co(dmgH)$_2$(t-Bupy)(CNS) (t-Bupy ≡ tert-butylpyridine).[13] It is possible, however, that all three thiocyanate linkage isomers of [Co(dmgH)(CNS)$_2$]$^-$ may be protonated, the mixed isomer Co(dmgH)(dmgH$_2$)(SCN)-(NCS) being precipitated due to favorable crystal packing forces.

Our results, neglecting any steric effects, serve to point out the relative basicities of the free end of the coordinated cyanide, thiocyanate, and isothiocyanate to be of the order: CN > SCN ≫ NCS. Intermolecular associations are strongest in the dicyano complex Co(dmgH)(dmgH$_2$)(CN)$_2$, as evidenced by the persistence of the high-energy ν_{CN} and low-energy ν_{OH} absorptions in solution. For the mixed cyano–thiocyanato complex, Co(dmgH)(dmgH$_2$)(CN)(SCN), intermolecular association involves hydrogen bonding with the N atom of the coordinated cyanide rather than the thiocyanate. This is shown by an increase in the energy of the ν_{CN} absorption for the coordinated cyanide upon crystallization, while the SCN absorption remains unchanged. Evidently the lone electron pair on the S atom in N-bonded thiocyanate is not sufficiently basic for the type of intermolecular associations described here, as protonation of solutions containing a mixture of isomers of the dithiocyanato complex [Co(dmgH)$_2$(CNS)$_2$]$^-$ results in the isolation of the mixed N,S-bonded protonated complex Co(dmgH)(dmgH$_2$)(SCN)(NCS) exclusively. The N atom lone pair of the S-bonded thiocyanate is that which is involved in intermolecular hydrogen bonding, as was discussed above.

This does, however, provide a convenient synthetic route to the pure N,S mixed bonded complex.

It is concluded that, in keeping with a general tendency for other cobaloximes as well, the protonated diacidocobaloximes also crystallize in such a fashion so as to allow for intermolecular associations by way of hydrogen bonding. Specifically, these interactions involve the hydroxyl groups of the protonated oxime ligand and (1) the Cl ligand in Co(dmgH)(dmgH$_2$)-(Cl)$_2$, (2) the S-bonded thiocyanate of Co(dmgH)-(dmgH$_2$)(SCN)(NCS), (3) the cyano ligand of Co-(dmgH)(dmgH$_2$)(SCN)(CN), and (4) one of the cyano ligands of Co(dmgH)(dmgH$_2$)(CN)$_2$.

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$_2$ represents neutral dimethylglyoxime (CH$_3$C(=NOH)C(=NOH)CH$_3$). This symbolism differs from that used in ref 4 and 11c.

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(11) See, for example: (a) D. F. Shriver in "Structure and Bonding", C. K. Jorgensen, Ed., Springer-Verlag, New York, N.Y. 1966, p 32; (b) D. A. Dows, A. Haim, and W. K. Wilmarth, *J. Inorg. Nucl. Chem.*, **21**, 33 (1961); (c) A. L. Crumbliss and P. L. Gaus, *Inorg. Nucl. Chem. Lett.*, **10**, 485 (1974).

(12) While examples of such low-frequency values for ν_{CN} of coordinated thiocyanate are relatively uncommon, they are not unprecedented. See for example: (a) M. Wada and R. Okawara, *J. Organomet. Chem.*, **8**, 261 (1967); (b) A. Miezis, *Acta Chem. Scand., Ser. A*, **28**, 415 (1974); (c) S. Fronaeus and R. Larsson, *Acta Chem. Scand.*, **16**, 1447 (1962).

(13) L. G. Marzilli, *Inorg. Chem.*, **11**, 2504 (1972).

(14) Both cyano–thiocyanato complexes, [AsPh$_4$][Co(dmgH)$_2$(CN)(SCN)] and Co(dmgH)(dmgH$_2$)(CN)(SCN), were found to contain S-bonded coordinated thiocyanate in solution and the solid state. Our inability to prepare the corresponding N-bonded isomer is consistent with the idea that in cobalt(III) complexes a π bonding ligand trans to coordinated thiocyanate will result in S bonding being favored, while a purely σ bonding ligand will result in N-bonded thiocyanate.[15] Consequently, the trans cyano ligand favors S-bonded thiocyanate in these complexes.

(15) See, for example: W. Beck and W. P. Fehlhammer, *MTP Int. Rev. Sci., Inorg. Chem., Ser. One, 1972*, **2**, 253 (1972).