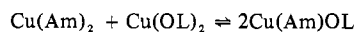


$\log X$, as defined by equilibrium 6 (calculation with eq 7). Generally, one would expect to observe negative values for $\Delta \log K$ (eq 5), since usually it holds that $K^{\text{Cu}}_{\text{CuL}} > K^{\text{Cu}}_{\text{CuOL}}$ (cf. Table I). The method using equilibrium 6 for characterization is somewhat more "objective," as the value expected for X can be deduced from statistical arguments: $X = 4$, i.e., $\log X = 0.6$.¹⁷

$$\Delta \log K = \log K^{\text{Cu(Am)}}_{\text{Cu(Am)OL}} - \log K^{\text{Cu}}_{\text{Cu(OL)}} = \log K^{\text{Cu(OL)}}_{\text{Cu(OL)Am}} - \log K^{\text{Cu}}_{\text{Cu(Am)}} \quad (5)$$



$$X = \frac{[\text{Cu(Am)OL}]^2}{[\text{Cu(Am)}_2][\text{Cu(OL)}_2]} \quad (6)$$

$$\log X = 2 \log \beta^{\text{Cu}}_{\text{Cu(Am)OL}} - (\log \beta^{\text{Cu}}_{\text{Cu(Am)}_2} + \log \beta^{\text{Cu}}_{\text{(OL)}_2}) \quad (7)$$

By using the results of Tables I and II, the values for $\Delta \log K$ (eq 5) and $\log X$ (eq 7) were calculated. These data are listed in Table III, together with some results taken from the literature. The $\Delta \log K$ values observed by Martell, *et al.*,^{3,18} for the 2,2'-bipyridyl-copper(II)-pyrocatecholate system (+0.36)^{3,18} and the 1,10-phenanthroline-copper(II)-pyrocatecholate system (+0.31)¹⁸ are in excellent agreement with the present results. The same is true for the 2,2'-bipyridyl-copper(II)-tiron system (+0.03)^{18,19} and the 1,10-phenanthroline-copper(II)-tiron system (-0.14).¹⁸

A comparison of the data of the mixed-ligand systems containing 2,2'-bipyridyl and a ligand with O as donor atoms, 1-4 in Table III, demonstrates unequivocally that the electron density in the ligand OL has a significant influence on the stability of the ternary Cu^{2+} complexes: electron-withdrawing substituents lower the stability (tiron, 2; cf. also ref 7) and electron-donating "substituents" (the naphthalene derivative, 4) increase it.²⁰ The systems containing 1,10-phenanthroline (5-8) instead of 2,2'-bipyridyl reveal the same picture but even more pronounced: while the difference between the lowest and highest values of $\log X$ for the 2,2'-bipyridyl systems is about 0.8 log unit, the same difference for the systems with 1,10-phenanthroline is about 1.5 log units. Hence, Cu(phen)^{2+} is somewhat more sensitive toward the electron distribution on the ligand with O as donor atoms as is Cu(bipy)^{2+} .

However, as a first approximation one may still say that the stability-increasing effect of 1,10-phenanthroline is of the same order as the one due to 2,2'-bipyridyl. Ternary complexes containing an aromatic amine are significantly more stable as the ones containing an aliphatic amine (cf. 1, 5, and 9).² A comparison of the systems 1, 5, 9, and 10 shows not only the influence of the π systems of the ligand with N donors but, additionally, the one of the ligand with O donors (cf. also ref 5).²¹

The discriminating qualities toward the second ligand to be coordinated have unequivocally been demonstrated for the Cu^{2+} -2,2'-bipy complex. This means, if an aqueous

solution contains a ligand with N and another one with O as donor atoms, both ligands having the same coordination tendency toward Cu(aq)^{2+} , the latter ligand is preferably bound to Cu(bipy)^{2+} .⁴ The same qualities may be surmised for Cu(phen)^{2+} . In fact, the systems 11 and 12 of Table III give good evidence for such behavior: the ternary complexes formed with "mixed" ligands containing N and O as donor atoms are remarkably less stable than the ones formed with ligands having only O as donor atoms (5-8).

Registry No. 2,2'-Bipyridyl, 366-18-7; 1,10-phenanthroline, 66-71-7; pyrocatechol, 120-80-9; tiron, 149-45-1; pyrogallol 1-methyl ether, 934-00-9; 6,7-dihydroxynaphthalene-2-sulfonate, 135-53-5.

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Enhanced Acidity of Protic Chelate Complexes

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The acidity of protic ligands is an important characteristic of many coordination complexes. In connection with redox studies to be reported elsewhere, we have obtained additional evidence in support of enhanced acidities for protic *chelate* complexes relative to their monodentate analogs. An interpretation of the data appears to require the recognition of at least one influence which previously has not been considered in regard to the acidity of protic complexes.

Experimental Section

Preparation of Complexes. Glycolatobis(ethylenediamine)cobalt(III) perchlorate was prepared by the method used for the glycinate analog.¹ *cis*-[Co(en)₂Cl₂]Cl (2.0 g) and freshly prepared Ag₂O (0.81 g) were ground periodically with 4 ml of H₂O in a mortar for 1 hr. AgCl was removed by filtration and washed with portions of boiling water until the combined filtrate and washings totaled 10-12 ml. NaOOCCH₂OH (0.9 g) was added and the solution evaporated on a steam bath until a thick crust formed. After cooling to room temperature the mixture was filtered and the precipitate washed twice with absolute ethanol. The solid was dissolved in 10 ml water to which 10 ml of saturated NaClO₄ solution was added to precipitate the perchlorate salt. Recrystallization was effected by dissolving the salt in the minimum amount of water and adding solid NaClO₄ to make the solution ~4 M in perchlorate. The solution was cooled to 0° and the precipitate was filtered, washed twice with absolute ethanol and twice with diethyl ether, and dried overnight under vacuum; yield 1.3 g. *Anal.* Calcd for [Co(en)₂(OOCCH₂O)]ClO₄: C, 20.45; H, 5.15; N, 15.0; Co, 16.7. Found: C, 20.36; H, 5.12; N, 15.7; Co, 16.6.

2-Aminoethanolbis(ethylenediamine)cobalt(III) perchlorate was

(17) R. DeWitt and J. I. Watters, *J. Amer. Chem. Soc.*, **76**, 3810 (1954); S. Kida, *Bull. Chem. Soc. Jap.*, **29**, 805 (1956).

(18) G. F. Condiak and A. E. Martell, *J. Inorg. Nucl. Chem.*, **31**, 2455 (1969).

(19) The value $\Delta \log K = +0.87$, as observed in ref 3, is certainly too high.

(20) 2,3-Dihydroxynaphthalene is too insoluble to be studied. The influence of the methoxy substituent (3) is obviously too weak to be significant.

(21) For a general discussion of the factors governing the stability of mixed-ligand complexes cf. ref 4 and R. Griesser and H. Sigel, *Inorg. Chem.*, **10**, 2229 (1971).

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(1) M. D. Alexander and D. H. Busch, *Inorg. Chem.*, **5**, 1590 (1966).

prepared from the bromide salt.² To a solution of *cis*-[Co(en)₂(Cl)(NH₂CH₂CH₂Br)]Cl₂ (9.35 g in 1000 ml of H₂O) was added 1 M LiOH (36 ml). After 2 hr the solution was adjusted to pH 1–2 with 7 M HBr and reduced to dryness on the rotary evaporator. The orange solid was heated to 90° for 10 min in 150 ml of 2 M HBr and charged onto a cation-exchange column of Bio-Rad 50W-X2 (200–400 mesh) resin (H⁺ form). Fractions elutable with 200 ml each of 1 and 2 M HBr were discarded and the orange band eluted with 3.5 M HBr was collected. The product obtained by rotary evaporation to dryness (4.3 g) was dissolved in 100 ml of 1 M HClO₄ and concentrated to 4–5 ml at 70° under reduced pressure on the rotary evaporator. Absolute ethanol (100 ml) was added and the slurry was filtered. The orange solid was recrystallized twice from warm (80°) 0.01 M HClO₄ by the addition of LiClO₄ followed by cooling. The absence of [Co(en)₂(H₂O)(NH₂CH₂CH₂OH)](ClO₄)₃ was established by the failure of the compound to anate in boiling 3 M HBr and the spectral properties agreed with the reported values.² *Anal.* Calcd for [Co(en)₂(NH₂CH₂CH₂OH)](ClO₄)₃: C, 13.38; H, 4.30; N, 13.00. Found: C, 13.34; H, 4.53; N, 13.14.

Lactatobis(ethylenediamine)cobalt(III) perchlorate was prepared by dissolving Co(H₂O)₆(ClO₄)₂ (18.3 g) in 125 ml of water, adding ethylenediamine (6.0 g) with stirring, and drawing air through the solution for 12 hr. Aqueous lactic acid (70%) (5.0 g), 20 ml of water, and NaOH pellets (2.0 g) were added and the solution was evaporated to ~100 ml at 100° with stirring under a gentle stream of nitrogen. The solution was cooled to ambient temperature and filtered, and the solids were washed with 10 ml of water. The combined filtrate and washings were evaporated as before to 50 ml, cooled to ambient temperature, filtered, washed successively with water, absolute ethanol, and diethyl ether, and dried *in vacuo*; yield 4.75 g. *Anal.* Calcd for [Co(en)₂(OOCCH(CH₃)O)]ClO₄: C, 22.90; H, 5.52; N, 15.27; Co, 16.11. Found: C, 22.86; H, 5.52; N, 15.14; Co, 15.82.

1,2-Ethanediolatobis(ethylenediamine)cobalt perchlorate was prepared by combining *trans*-[Co(en)₂Cl₂]Cl (10 g), Ag₂O (15 g), NaOCH₂CH₂OH (4.0 g), and ~75 ml of dry ethylene glycol in a nitrogen-flushed flask, stirring for 20 min under nitrogen flow, diluting with an equal volume of water, adding excess NaClO₄, and filtering. The solid was dissolved in the minimum amount of water, filtered, reprecipitated by adding NaClO₄, filtered, washed with 1:1 ethanol-water, ethanol, and diethyl ether, and dried *in vacuo*. *Anal.* Calcd for [Co(en)₂(OCH₂CH₂O)]ClO₄: C, 21.28; H, 5.95; N, 16.54. Found: C, 21.18; H, 5.73; N, 16.40.

Extensive characterization studies involving visible, ultraviolet, infrared, and proton magnetic resonance spectroscopy, ion-exchange chromatography, conductance behavior, and reactivity patterns are consistent with the formulations presented and will be discussed elsewhere with other related complexes.

Determination of pK_a Values. Except for the aminoethanol complex, for which independent confirmation was available, the pK_a values for the complexes at 0.1 M ionic strength were determined by at least two of the following techniques: (1) spectrophotometric titration with perchloric acid, (2) determination of the pH at the midpoint of a titration with perchloric acid, and (3) determination of the pH at the midpoint of a back-titration with sodium hydroxide, the complex having been previously dissolved in a known excess of perchloric acid.

Results and Discussion

The results are summarized with those from other reports in Table I. The acidities of the four chelate complexes containing alcohol functions (entries V, VI, VII, and XI) are dramatically higher than those reported or expected for monodentate analogs. A presumably related acidity enhancement has been observed for Pt(en)₃⁴⁺ (pK_a = 5.5) relative to Pt(NH₃)₆⁴⁺ (pK_a = 7.9).³ This enhancement has been attributed to a diminished relative stability of the conjugate acid in the chelate system as a result of its decreased solvation.⁴ The data in Table I permit a more detailed evaluation of this effect.

(2) D. A. Buckingham, C. E. Davis, and A. M. Sargeson, *J. Amer. Chem. Soc.*, **92**, 6159 (1970).

(3) (a) L. G. Sillen and A. E. Martell, "Stability Constants," The Chemical Society, London, 1964; (b) A. A. Grinberg and Kh. I. Gildengershel, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, **479** (1948).

(4) (a) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, p 184; (b) C. F. Weick and F. Basolo, *Inorg. Chem.*, **5**, 576 (1966).

It is evident from comparing entries I vs. II and IX vs. X that chelation which does not involve the acidic site has little effect on the acid strength. Alkyl substitution at the amine which is *cis* to the acidic group similarly has little effect (entry III). Methyl substitution on the oxygen of the acidic group does increase the acid strength but only by 0.6 pK_a unit (entry IV). (Since the acidity of CH₃OH (pK_a = 15.9)⁵ is slightly less than that of H₂O (pK_a = 15.74), it could be argued reasonably that the increase is due to a solvation effect of the type mentioned above.)

From these observations it is reasonable to expect that *cis*-Co(en)₂(NH₃)(HOCH₃)³⁺ will have a pK_a on the order of 5.4 or higher. It seems unlikely that the introduction of a methylene chelating linkage between the amine and alcohol functions of this complex will affect the solvation energetics sufficiently to account for the observed acidity enhancement to pK_a = 3.5 (entry V). This contention is supported by the observation that methyl substitution at the methylene adjacent to the acidic group results in no acidity enhancement (entries VI and VII).

We suggest that the enhancement arises not only from the solvation changes which occur on substitution at the acidic site but also from a modification of the influence of the amine (or other polar) function(s) on the acidic group in the chelate complex. The greater acidity enhancement observed with Co(en)₂(HOCH₂CH₂OH)³⁺ (entry XI), which should undergo a solvation change on deprotonation similar to Co(en)₂(H₂NCH₂CH₂OH)³⁺, is consistent with this proposal.

The influence which we propose as being partially responsible for the observed acidity enhancement is closely related to the *polar substituent effects* which have been extensively analyzed for organic compounds.⁶ The influence of a polar substituent is believed to arise from (1) an inductive effect which operates *via* the successive polarization of adjacent bonds and/or (2) an electric field effect which is operative throughout the region between the polar and reactive groups.⁶ Inductive effects are considered to attenuate rapidly along a saturated bond network leaving the electric field as the dominant source of substituent effects,⁶ at least when the intervening bond network is extended.

In the chelate complexes provision is made for any inductive effect that can operate through the relatively short bonding network between the polar and acidic functions. Moreover, consideration should be given to a modification of the electric field influence as the result of the methylene chelate linkage excluding solvent water from a region which it occupies in the monodentate analogs. The extent of any such modification depends on the degree to which the *effective* dielectric constant between the polar and acidic groups is diminished through introduction of the chelate linkage. An assessment of any such diminution requires a knowledge of the extent to which the water excluded by the chelate linkage is dielectrically saturated in the monodentate complexes.

Ritson and Hasted suggested that significant dielectric lowering extends beyond the first coordination sphere for divalent and trivalent ions.⁷ However, Reynolds and Lumry

(5) P. Ballinger and F. A. Long, *J. Amer. Chem. Soc.*, **82**, 795 (1960).

(6) For summaries of current views in this area see (a) M. J. S. Dewar, R. Golden, and J. M. Harris, *J. Amer. Chem. Soc.*, **93**, 4187 (1971); (b) E. J. Grubbs, R. Fitzgerald, R. E. Phillips, and R. Petty, *Tetrahedron*, **27**, 935 (1971); (c) C. F. Wilcox and C. Leung, *J. Amer. Chem. Soc.*, **90**, 336 (1968); (d) S. Ehrenson, *Progr. Phys. Org. Chem.*, **2**, 195 (1964); (e) C. D. Ritchie and W. F. Sager, *ibid.*, **2**, 323 (1964), and references therein.

(7) D. M. Ritson and J. B. Hasted, *J. Chem. Phys.*, **16**, 11 (1948).

Table I. Acidity and Spectral Values for Some Protic Species (25°)[†]

Entry	Metal complexes	pK _a (I)	$\bar{\nu}_1, \bar{\nu}_2, \text{kK}$	$\delta(\text{O}-\text{CH}_n), \text{ppm}$	Ref
Ia	Co(NH ₃) ₅ OH ₂ ³⁺	6.2 (0.3)	20.4, 29.0		a
Ib	Co(NH ₃) ₅ OH ²⁺		19.7, 27.0		a
IIa	cis-Co(en) ₂ (NH ₃)OH ₂ ³⁺	6.0 (1.0)	20.7, 29.4		b, c
IIb	cis-Co(en) ₂ (NH ₃)(OH) ²⁺		20.2, 27.8		c, d
III	cis-Co(en) ₂ (NH ₂ CH ₂ CH ₂ Br)OH ₂ ³⁺	6.2 (?)			e
IVa	Co(NH ₃) ₅ (HOCH ₃) ³⁺	5.6 (0.1)	20.2, 28.8	3.58	f
IVb	Co(NH ₃) ₅ (OCH ₃) ²⁺		19.6, 27.0	3.05	f
Va	Co(en) ₂ (NH ₂ CH ₂ CH ₂ OH) ³⁺	3.5 (0.1)	20.6, 29.1	3.60	g
		3.5 (0.1)			h
		3.6 (?)			e
Vb	Co(en) ₂ (NH ₂ CH ₂ CH ₂ O) ²⁺		20.4, 28.8	3.19	g
VIa	Co(en) ₂ (OOCCH ₂ OH) ²⁺	3.3 (0.1)	20.0, 28.8	4.26	g
VIb	Co(en) ₂ (OOCCH ₂ O) ⁺		19.3, 27.8	3.90	g
VIIa	Co(en) ₂ (OOCCH(CH ₃)OH) ²⁺	3.4 (0.1)			g
VIIb	Co(en) ₂ (OOCCH(CH ₃)O) ⁺				g
VIIIa	cis-Co(en) ₂ (O ₃ CH)OH ₂ ²⁺	5.3 (?)			i
VIIIb	cis-Co(en) ₂ (OOCCH ₃)OH ₂ ²⁺		20.1, 27.8		j
VIIIc	cis-Co(en) ₂ (OOCCH ₃)OH ⁺		19.5, 27.4		j
IX	cis-Co(NH ₃) ₄ (H ₂ O) ³⁺	6.0 (1.0)			k
Xa	cis-Co(en) ₂ (H ₂ O) ₂ ³⁺	6.1, 8.2 (1.0)	20.3, 28.2		l
Xb	cis-Co(en) ₂ (OH) ₂ ⁺		19.4, 27.1		l
XIa	Co(en) ₂ (HOCH ₂ CH ₂ OH) ³⁺	2.6, 5.8 (0.1)	20.0, 28.2	3.68	g
XIb	Co(en) ₂ (OCH ₂ CH ₂ O) ⁺		19.1, 26.2	3.00	g

Entry	Organic ions	pK _a (I)	Entry	Organic ions	pK _a (I)	Ref
XIIa	CH ₃ (CH ₂) ₂ NH ₃ ⁺	11.0 (1.0)	XIIb	H ₂ N(CH ₂) ₂ NH ₂ ²⁺	7.5, 10.2 (1.0)	m
XIIIa	$\begin{array}{c} \text{CH}_2 - \text{CH}_2 \\ \diagdown \quad \diagup \\ \text{H}_2\text{C} \quad \text{NH}_2^+ \\ \diagup \quad \diagdown \\ \text{CH}_2 - \text{CH}_2 \end{array}$	11.1 (0.10)	XIIIb	$\begin{array}{c} \text{CH}_2 \quad \text{CH}_2 \\ \diagdown \quad \diagup \\ \text{H}_2\text{N} \quad \text{NH}_2^{2+} \\ \diagup \quad \diagdown \\ \text{CH}_2 \quad \text{CH}_2 \end{array}$	5.6, 9.7 (0.10)	m, n, o
XIVa	$\begin{array}{c} \text{CH}_2 - \text{CH}_2 \\ \diagdown \quad \diagup \\ \text{H}_2\text{C} - \text{CH}_2 - \text{CH}_2 - \text{NH}^+ \\ \diagup \quad \diagdown \\ \text{CH}_2 - \text{CH}_2 \end{array}$	10.8 (0.10)	XIVb	$\begin{array}{c} \text{CH}_2 - \text{CH}_2 \\ \diagdown \quad \diagup \\ \text{HN} - \text{CH}_2 - \text{CH}_2 - \text{NH}^{2+} \\ \diagup \quad \diagdown \\ \text{CH}_2 - \text{CH}_2 \end{array}$	3.0, 8.8 (0.10)	m, p, q
XV	HOCH ₂ CH ₂ NH(CH ₃) ₂ ⁺	9.3 (0.05)				r
XVI	$\begin{array}{c} \text{O} \\ \diagdown \quad \diagup \\ \text{CH}_2 - \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{N}^+ - \text{H} \\ \diagdown \quad \diagup \\ \text{CH}_2 \end{array}$	7.4 (0.02)				s

^a R. G. Splinter, S. J. Harris, and R. S. Tobias, *Inorg. Chem.*, **7**, 897 (1968). ^b R. D. Cannon and J. E. Earley, *J. Amer. Chem. Soc.*, **88**, 1872 (1966). ^c F. Basolo, *ibid.*, **72**, 4393 (1950). ^d M. D. Alexander and C. A. Spillert, *Inorg. Chem.*, **9**, 2344 (1970). ^e Reference 2. ^f R. B. Jordan, A. M. Sargeson, and H. Taube, *Inorg. Chem.*, **5**, 1091 (1966). ^g This work. ^h V. V. Udorenko and L. G. Reiter, *Russ. J. Inorg. Chem.*, **15**, 958 (1970). ⁱ R. B. Jordan and D. J. Francis, *Inorg. Chem.*, **6**, 1605 (1967). ^j V. Carunchio, G. Illuminati, and G. Ortaggi, *ibid.*, **6**, 2168 (1967). ^k Reference 3a. ^l J. Bjerrum and S. E. Rasmussen, *Acta Chem. Scand.*, **6**, 1265 (1952). ^m Reference 9. ⁿ R. Paoletti, M. Ciampolini, and E. Vacca, *J. Phys. Chem.*, **67**, 1065 (1963). ^o R. G. Bates and V. E. Bower, *J. Res. Nat. Bur. Stand.*, **57**, 153 (1956). ^p R. Paoletti, J. H. Stern, and A. Vacca, *J. Phys. Chem.*, **69**, 3759 (1965). ^q Th. Landis, Dissertation, ETH, Zurich, 1969. ^r D. J. Almer and R. C. Lansbury, *J. Chem. Soc.*, 3169 (1961). ^s H. K. Hall, *J. Phys. Chem.*, **60**, 63 (1956). [†] I is the ionic strength; δ is the chemical shift downfield from external TMS.

concluded that significant dielectric saturation is unlikely in the second shell around Fe(H₂O)₆³⁺ since the interaction energy (~15 kcal/mol of second-sphere water) is insufficient to hold those molecules rigidly aligned.⁸ Thus, a relatively high effective dielectric constant may be retained in the second coordination sphere of the monodentate complexes considered here. To the extent that this is the case, the methylene linkage would provide for a lower dielectric constant which should attenuate less effectively any electric field operating between the polar and acidic functions in the chelates. In this context it is interesting to note that the acidity enhancements are comparable for conjugate acids with considerable variations in net charge (4+ to 2+).

Similar effects appear to be operative in certain organic systems, although no strictly comparable examples exist. Schwarzenbach's thorough analysis⁹ requires the inclusion of a decreasing dielectric constant between the polar and acidic functions along the series XIIb-XIVb in order to account for the acidity behavior. A similar effect is probably

responsible, along with others, for the acidity enhancement of entry XVI over XV.

Finally, we note that the spectral data collected in Table I provide no basis for understanding the uniform acidity enhancements in terms of a diminished loss of ligand field stabilization on deprotonation of the chelate complexes. It is difficult to evaluate any contribution to the enhancements from a relaxation in chelate ring strain on deprotonation. However, no evidence for such strain is apparent from the electronic or pmr spectra. Further indications against important contributions from this factor are provided by similar enhancements for two different types of chelate ring skeletons (V vs. VI) whereas systems expected to be similar in conformational energetics (V vs. XI) are enhanced to differing degrees in line with that expected from a polar substituent effect.

Registry No. [Co(en)₂(OOCCH₂O)]ClO₄, 26743-66-8; [Co(en)₂(NH₂CH₂CH₂OH)](ClO₄)₃, 38641-62-2; [Co(en)₂(OOCCH(CH₃)O)]ClO₄, 38673-80-2; *trans*-[Co(en)₂Cl₂]Cl, 14040-33-6; [Co(en)₂(OCH₂CH₂O)]ClO₄, 38641-64-4; Co(en)₂(NH₂CH₂CH₂O)²⁺, 38641-65-5; Co(en)₂(OOCCH₂OH)²⁺,

(8) W. L. Reynolds and R. W. Lumry, "Mechanisms of Electron Transfer," Ronald Press, New York, N. Y., 1966, p 21.

(9) G. Schwarzenbach, *Pure Appl. Chem.*, **24**, 307 (1970).

38731-30-5; $\text{Co(en)}_2(\text{OOCCH}(\text{CH}_3)\text{OH})^{2+}$, 38641-66-6; $\text{Co(en)}_2(\text{HOCH}_2\text{CH}_2\text{OH})^{3+}$, 38673-81-3.

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Hydrogen-1, Nitrogen-15, and Cobalt-59 Chemical Shifts in Several Cobalt(III) Complexes

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Nuclear magnetic resonance (nmr) is a useful method in studying the structure of transition metal complexes and gives valuable information on the second coordination sphere. Here we report the ^1H , ^{15}N , and ^{59}Co chemical shift data for several cobalt(III) complexes in D_2O - D_2SO_4 solutions. The results are interpreted in terms of changes in the properties of the complexes with the change in the second coordination sphere.

Experimental Section

cis- and *trans*- $\text{Co}(\text{gly})_3$ were prepared according to the method of Mori, *et al.*² However, since the *cis* form of $\text{Co}(\text{gly})_3$ was more difficult to synthesize, we have made only the *trans* isomer of ^{15}N -enriched $\text{Co}(\text{gly})_3$. $\text{Co}(\text{en})_3\text{Cl}_3$ was prepared by a standard method³ and recrystallized from aqueous ethanol. The preparation of $[\text{Co}(^{15}\text{NH}_3)_3\text{Cl}](\text{ClO}_4)_2$ was described previously.⁴

Proton nmr spectra were recorded at 100 MHz with a Varian HA-100 spectrometer. ^{59}Co nmr spectra were recorded on a Varian VF-16 spectrometer at 12.0 MHz using concentrated $\text{Co}(\text{NH}_3)_6\text{Cl}_3$ as an external standard in a coaxial tube. Measurements of ^{15}N chemical shifts using the proton resonance with H_2SO_4 as an internal lock signal were made by the "spin-tickling" technique which is described elsewhere.⁴

The cryoscopic measurement on *cis*- $\text{Co}(\text{gly})_3 \cdot \text{H}_2\text{O}$ was carried out by using the procedure described by Hammett and Deyrup⁵ using an apparatus described by Newman, *et al.*⁶

Results and Discussion

The proton nmr spectrum of $[\text{Co}(\text{en})_3]^{3+}$ (en = ethylenediamine) is probably the most widely studied among those of all cobalt(III) complexes.^{7,8} In acidified D_2O solutions, the proton exchange is slow and the NH protons show two distinct signals at both low and high acid concentrations (Figure 1),

which are not resolved at 60 MHz.⁹ The origin of the two NH peaks was attributed to either different conformers¹⁰ or different (axial and equatorial) configurations in the same conformer.⁹ In a recent review,⁷ Beattie presented a detailed analysis of the proton nmr spectrum of the methylene group in a number of transition metal complexes with ethylenediamine, including $[\text{Co}(\text{en})_3]^{3+}$. He concluded that the ligands undergo rapid inversion between δ and λ conformations, and the observed (time-averaged) chemical shift difference between the two diastereotopic methylene protons arises from a preference for the δ conformation, which has a lower free energy than the λ conformation for the Λ conformation. A similar argument is applicable to the NH_2 group. However, another factor that is not important for the methylene protons now may be operative. Because of the proximity of the NH protons to three of the Co-N bonds in the two other ligands, the interaction with the neighboring rings may be important in determining their chemical shifts. In both the δ and the λ conformations, one of the NH bonds is more or less parallel to the C_3 axis of the complex, and the other NH bond is more or less perpendicular to the C_3 axis. Their interactions with the two other rings are different and they do not convert to each other during the inversion of the ring. Therefore, the nonequivalence due to the total chirality of the complex is probably a major factor in determining the proton chemical shift difference for the NH_2 group, although it is less important for the methylene protons.

The two protons in the NH_2 group in $[\text{Co}(\text{en})_3]^{3+}$ are in a complicated spin system. Appreciable spin-spin interactions with nitrogen, cobalt, the adjacent methylene protons, and each other are expected. However, because of the effect of quadrupolar relaxation, no spin-spin splittings were observed in the nmr spectrum of the NH_2 protons. In D_2O - D_2SO_4 solutions, the NH proton signal of $[\text{Co}(\text{en})_3]^{3+}$ moves downfield with the increase in D_2O content because of an increase in hydrogen bonding.⁹ A more careful examination of the spectra at 100 MHz (Figure 1) suggests that the two NH signals shift differently with the change in the solvent composition. The peak that has a larger change (labeled e in Figure 1) can be assigned to the proton with the NH bond roughly parallel to the C_3 axis of the complex, because it is sterically less hindered and therefore more susceptible to hydrogen-bond formation with D_2O . The proton with the NH bond roughly perpendicular to the C_3 axis (labeled a in Figure 1) is more crowded because of two other protons in the neighboring NH_2 groups and is less affected by the change in the solvent composition, because the formation of the second coordination sphere with D_2O via hydrogen bond is less favorable. Therefore, the overlapping of the two NH signals at intermediate acid concentration is due to a coincidence in the chemical shifts. Variable-temperature studies show that the coalescence of the two signals is not due to chemical exchange. For example, in a solution with a ratio of $\text{D}_2\text{O}:\text{D}_2\text{SO}_4 = 4$, the two NH proton signals coalesce at room temperature; at 100° , the width of the peak increases by about 30%. This can be explained either by the increase of the chemical shift difference between the two NH protons or by the decrease in the ^{59}Co quadrupole relaxation rate but is inconsistent with an exchange mechanism. A previous calculation⁹ on the activation energy of ring inversion based upon the proton nmr spectra of the NH_2 group for $[\text{Co}(\text{en})_3]^{3+}$

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