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The Stereochemistry of the Bis Complexes of Cobalt(III) with Iminodiacetic Acid and Methyliminodiacetic Acid

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The acid and potassium salts of the bis cobalt(III) complexes with iminodiacetic acid (IDA) and methyliminodiacetic acid (MIDA) were prepared and characterized. Both ligands formed a facial *trans* isomer (with respect to the nitrogens) while IDA formed a *cis* isomer. Because of steric repulsions in the *cis* isomer, 80% of the IDA complex obtained at steam bath temperature was *trans*. Low temperature favored more of the *cis* isomer. The pmr spectrum of the *trans* isomers gave one AB acetate pattern unambiguously confirming the facial configuration. When the amine protons, NCH_3 groups, or acetate protons are in the region *trans* to the IDA nitrogen as they are in the *trans* complexes, they are deshielded. In the *cis* complex the amine and acetate protons are shielded. Splitting is seen in the low-field portions of the AB patterns in the IDA complexes due to coupling with the amine protons. The visible absorption spectra follow the concepts of crystal field theory with the *trans* isomers being split and shifted twice as much as the *cis* isomer.

Introduction

Complexes of cobalt(III) with iminodiacetic acid (IDA) have been previously prepared by two different groups of workers. Mori and co-workers[1] obtained the violet *cis*-K[Co(IDA)$_2$] and Tsuchida and co-workers[2] obtained both the *cis* isomer and a brown *trans* isomer. The assignment of *cis* and *trans* was made by comparison of the visible spectra of these compounds with those of known compounds. The three possible geometric isomers for the bis complexes are shown in Figure 1. Tsuchida[2] assigned structure II to the *trans* isomer on the basis of the more favorable bond angles on the nitrogen atom when the IDA is in the facial configuration. We have studied the stereochemistry of mixed complexes of cobalt(III) with diethylenetriamine (dien) and IDA utilizing visible and proton nmr spectra and find that IDA does strongly prefer the facial configuration, although it will coordinate in a meridional fashion if forced.[3] We here wish to report nmr spectra of the bis complexes of IDA and of methyliminodiacetic acid (MIDA) which indicate unequivocally that both ligands favor the facial configuration in these complexes. The equilibrium distribution and visible spectra of the IDA complexes are explained in terms of the steric interactions found in the mixed complexes.[3]

Experimental Section

Preparation of Complexes.—*cis*- and *trans*-K[Co(IDA)$_2$] were prepared using the method of Tsuchida.[2] The *trans* preparation gave pure complex on cooling but mixtures were obtained from the *cis* preparation. The *cis* isomer was purified by crystallization from a saturated solution on addition of an equal volume of ethanol. The approximate solubilities at 25° are 0.060 g of *cis*-K[Co(IDA)$_2$] per ml of H_2O, 0.039 g of *trans*-K[Co(IDA)$_2$] per ml of H_2O. Several attempts were made to obtain the meridional *trans* isomer (isomer III) by elution of a mixture of the isomers from a Dowex 2-X8 anion-exchange resin in the chloride form using NH_4Cl eluting agent. The *trans* isomer eluted first followed by the *cis*. In no case was there any evidence for a second *trans* isomer. Although the existence of this isomer is not ruled out, it is felt that it could at the most represent only a small portion of the total amount of *trans* isomer present.

trans-K[Co(MIDA)$_2$] was prepared in an analogous fashion to the *trans*-IDA isomer using the appropriate amount of MIDA. *Anal.* Calcd for $K[Co(C_5H_7NO_4)_2]\cdot{}^1/_2H_2O$: C, 30.23; H, 3.81; N, 7.05. Found: C, 30.34; H, 3.82; N, 7.48. No *cis* isomer of MIDA was obtained using the analogous *cis*-IDA preparation. This was verified by its absence on elution from anion-exchange resin.

The acid salts of the various isomers were prepared by passing solutions of the potassium salts through Dowex 50W-X8 resin in the acid form. The approximate solubilities at 25° are 0.16 g of *cis*-H[Co(IDA)$_2$] per ml of H_2O, 0.034 g of *trans*-[HCo(IDA)$_2$] per ml of H_2O. *Anal.* Calcd for *cis*-$H[Co(C_4H_5NO_4)_2]\cdot H_2O$: C, 28.23; H, 3.85; N, 8.24. Found: C, 28.23; H, 3.67; N, 8.17. Calcd for *trans*-$H[Co(C_4H_5NO_4)_2]\cdot 4H_2O$: C, 24.37; H, 4.86; N, 7.11. Found: C, 24.22; H, 4.85; N, 7.21. Calcd for *trans*-$H[Co(C_5H_7NO_4)_2]\cdot 2H_2O$: C, 31.10; H, 4.96; N, 7.26. Found: C, 30.95; H, 4.88; N, 7.33.

Proton Magnetic Resonance Spectra.—Spectra of the complexes in D_2O were recorded on a Varian A-60 spectrometer at about 35°, the internal temperature of the instrument. An internal reference of NaTMS (sodium 2,2-dimethyl-2-silapentane-5-sulfonate) was utilized. When dissolved in deuteriochloroform, TMS resonates 0.05 ppm from NaTMS in D_2O. All resonances occurred to the low-field side of NaTMS and are arbitrarily made positive. Solutions were prepared and measured such that the spectrum was obtained within 10 min of the initial mixing. In acidic *cis*-H[Co(IDA)$_2$] exchange of the amine protons began almost immediately and was essentially complete 1 week later. In neutral *cis*-K[Co(IDA)$_2$] exchange was complete in the first 10 min. For *trans*-H[Co(IDA)$_2$] the amine proton exchange was not nearly as rapid and several months time was required for complete proton exchange.

Electronic Absorption Spectra.—Spectra were recorded at room temperature using a Cary Model 11 spectrophotometer for $10^{-2}M$ solutions in 1-cm cells.

Analyses.—The C, H, and N analyses were done by the Spang Microanalytical Laboratory, Ann Arbor, Mich.

Discussion of Results

Distribution of Isomers of Iminodiacetic Acid.—The methods of preparation which were developed by the Japanese workers[2] for the complexes of IDA maximized the yields of each isomer. When the reaction was carried out at high temperatures the *trans* isomer was obtained on cooling the solution, while a low-temperature oxidation gave the *cis* isomer. It was of interest

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[1] M. Mori, M. Shibata, E. Kyuno, and F. Maryama, *Bull. Chem. Soc. Japan*, **35**, 75 (1962).

[2] J. Hidaka, Y. Shimura, and R. Tsuchida, *ibid.*, **35**, 567 (1962).

[3] J. I. Legg and D. W. Cooke, *Inorg. Chem.*, **5**, 594 (1966).

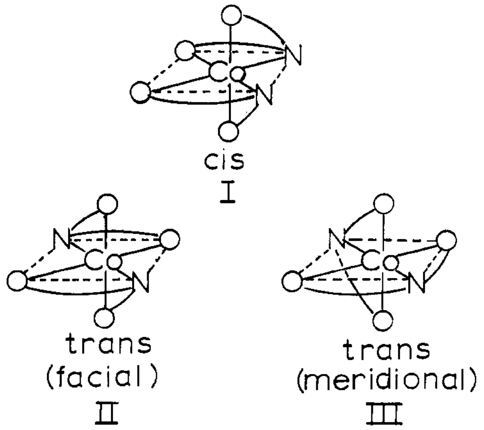

Figure 1.—The three possible geometric isomers of $[Co(IDA)_2]^-$ (only the coordination sites are shown).

to explain this difference and to obtain the equilibrium distribution of isomers to see if it was related to that found for the mixed isomers of cobalt(III) with dien and IDA or MIDA.[3] Solutions of the acid salts were quite stable to isomerization but potassium salt solutions isomerized rapidly on heating or on standing for a period of several months. The addition of base also increased the rate of isomerization with no apparent decomposition. (Further studies are being carried out on the temperature and base dependence of the isomerization process.) Solutions of the potassium salt of either the *cis* or *trans* isomer on heating on a steam bath (80°) for 0.5 hr gave identical visible spectra. These spectra when analyzed using the extinction coefficients of the pure compounds indicated 21% *cis* and 79% *trans*. It was observed that the solubility of the *trans* isomer was considerably less than that of the corresponding *cis* isomer. Molecular models show that this low solubility is probably related to intermolecular hydrogen bonding possible in the *trans* crystal between the amine protons on one molecule and the carboxyl groups on a neighbor. This lower solubility together with the equilibrium preference of the *trans* isomer accounts for the obtention of pure *trans* isomer from the high-temperature preparation. When samples of the potassium salts reached equilibrium at room temperature either slowly by standing for 3 months or more rapidly in buffered solution in the pH range 9–11, the mixtures analyzed for a higher percentage of *cis* (28%). Presumably the lower temperature synthesis would favor the *cis* isomer to an even greater extent and would account for the success of the low-temperature preparation.

The equilibrium distribution of isomers is in agreement with that observed for the mixed isomers with dien and IDA.[3] No meridional *trans* isomer was found in the bis complex, in agreement with the small amount of meridional *trans* found in the mixed isomers. This fact can be related to the strain found in IDA and MIDA in the meridional configuration. Statistical calculations assuming only the facial isomer would predict 33% *trans* and 67% *cis* for the bis complexes. The absence of any *cis* isomer with MIDA and the dominance of the *trans* isomer in IDA indicate the presence of steric interactions between the amine groups in the *cis* isomers which are confirmed by the nmr and visible spectra. This same steric interaction was found in the mixed complexes, which gave only 33% facial *cis*, agreeing with the 28% *cis* found here.

Proton Nuclear Magnetic Resonance Spectra.—The pmr spectra of the acid salts of the IDA and MIDA complexes are tabulated in Table I and the spectra of the IDA complexes are given in Figures 2 and 3. The tables and figures as presented show the spectra at the time of mixing and after such time as the amine protons have completely exchanged with D_2O. Except for the broad amine proton resonances, the spectra are seen to be quite sharp because complexation fixes the chelate rings. The acetate protons are in different chemical environments and symmetrical AB quartets due to two spin-coupled protons are observed as found in similar complexes.[3–5] No coupling is observed due to the ^{59}Co nucleus. The spectrum for *trans*-$H[Co(MIDA)_2]$ is similar to that for the *trans*-IDA after amine proton exchange with the additional peak due to the NCH_3 protons. The spectra for the potassium salts of MIDA and *cis*-IDA are identical with those of the corresponding acid salts after amine proton exchange. The spectrum of *trans*-$K[Co(IDA)_2]$ on mixing is a composite of the two spectra of *trans*-$H[Co(IDA)_2]$ which gradually changes on long standing to a spectrum identical with the NH proton exchanged spectrum. If acid is added to *cis*-$K[Co(IDA)_2]$ a similar composite of the two *cis* spectra is observed.

We have earlier discussed the expected pmr signals for IDA and MIDA in configurations analogous to the *cis* and *trans* facial and *trans* meridional cases.[3] In Figure 4 the orientation of *trans* IDA in each configuration is shown. In the *trans* facial configuration the plane of symmetry through the two nitrogen atoms and bisecting each ligand results in a single AB quartet splitting pattern. In both the *cis* facial and *trans* meridional isomers the lack of symmetry in the complex ion places the protons in each acetate in slightly different chemical environments and two overlapping AB patterns should result. Such patterns were observed in the mixed dien complexes of cobalt(III) with IDA and MIDA. In *trans*-$[Co(dien)(IDA)]^+$, with IDA in the meridional configuration, the small differences in chemical shifts result in two AB patterns with very intense central peaks. The corresponding MIDA complex has two normally spaced AB patterns. Thus the single AB patterns observed for the bis *trans* complexes with IDA and MIDA confirm unequivocally that the *trans* isomers are indeed in the facial configuration.

Having established the facial configuration of the *trans* complexes on the basis of the number of AB patterns observed, it is of interest to consider the trends in the chemical shifts of these patterns. These

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(4) J. I. Legg and D. W. Cooke, *Inorg. Chem.*, **4**, 1576 (1965).

(5) R. J. Kula, D. T. Sawyer, S. I. Chan, and C. M. Finley, *J. Am. Chem. Soc.*, **85**, 2930 (1963); R. J. Day and C. N. Reilley, *Anal. Chem.*, **36**, 1073 (1964); J. L. Sudmeier and C. N. Reilley, *ibid.*, **36**, 1698 (1964).

TABLE I

RESONANCE FREQUENCY ASSIGNMENTS AND INTEGRATION VALUES FROM THE PMR SPECTRA OF THE ACID SALTS[a]

(I) *trans* ISOMERS

	trans-H[Co(IDA)$_2$]				*trans*-H[Co(MIDA)$_2$]	
Assignment	Res freq,[b] ppm	No. of H's[b]	Res freq,[c] ppm	No. of H's[c]	Res freq, ppm	No. of H's
>NH	9.00					
>NCH$_2$COO$^-$	4.65		4.59	1.4	4.45	0.9
	4.53	0.75				
	4.37	1.3	4.30	2.6	4.16	3.2
	4.23	1.3				
	3.75 3.72	2.6	3.73	2.7	3.96	3.0
	3.45 3.42	1.3	3.44	1.3	3.68	1.2
>NCH$_3$					3.17	5.7

(II) *cis*-H[Co(IDA)$_2$]

	Res freq,[b,d] ppm	Res freq,[b,d] ppm	No. of H's[b]	Res freq,[c,d] ppm	Res freq,[c,d] ppm	No. of H's[c]
>NH	7.77					
>NCH$_2$COO$^-$	4.49 4.36		1.0	4.42		1.2
	4.19 4.05	4.25 4.12	1.9	4.12	4.18	2.0
		3.96 3.84	1.5		3.89	1.4
	3.39		2.2		3.38	2.2
	3.09 3.07		1.5		3.08	1.2

[a] All frequencies on low-field side of NaTMS (NaTMS = 0). Each integration represents an average of at least three values. [b] Before N–H proton exchange. [c] After N–H proton exchange. [d] The two overlapping patterns are given in different columns.

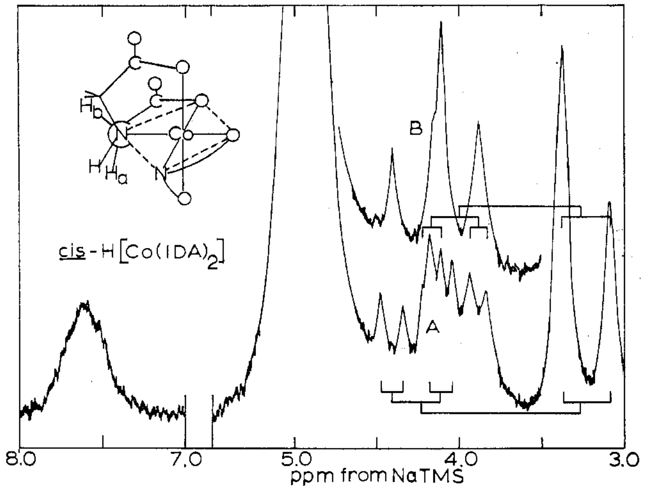

Figure 2.—The pmr spectrum of *cis*-H[Co(IDA)$_2$] (complex oriented looking down the N–C bond): A, before amine proton exchange; B, after amine proton exchange.

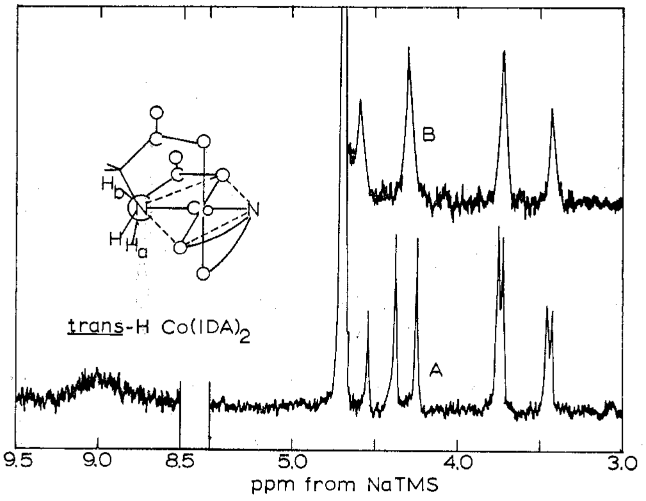

Figure 3.—The pmr spectrum of *trans*-H[Co(IDA)$_2$]: A, before amine proton exchange; B, after amine proton exchange.

have been calculated according to Jackman[6] and are summarized in Table II. We have earlier studied two different series of similar complexes[3,4] and have found that certain trends in these shifts can be related to the magnetic anisotropy of the C–N bond similar to that found by Bothner-By and Naar-Colin[7] for C–C single bonds. A proton located along the C–N bond axis is deshielded while one perpendicular to the bond axis is shielded. Designating the protons as in Figure 4, each H_b proton is in the shielded region of the C–N bond associated with the other H_b proton and is at higher fields than the H_a proton which is in the deshielded region. In the *trans* complexes, the replacing of the amine proton with CH_3 in MIDA furnished a second anisotropic region which places the H_a proton in a somewhat more shielded environment and the H_b proton in a less shielded one. The shielding of H_a by 0.17 ppm and the deshielding of H_b by 0.25 ppm compares with the corresponding values of 0.10 and 0.25 ppm found in the mixed complexes.

The *cis* complex is observed to have its chemical shifts at somewhat higher fields that the *trans* complex.

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(6) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1964, p 89.

(7) A. A. Bothner-By and C. Naar-Colin, *J. Am. Chem. Soc.*, **80**, 1728 (1958).

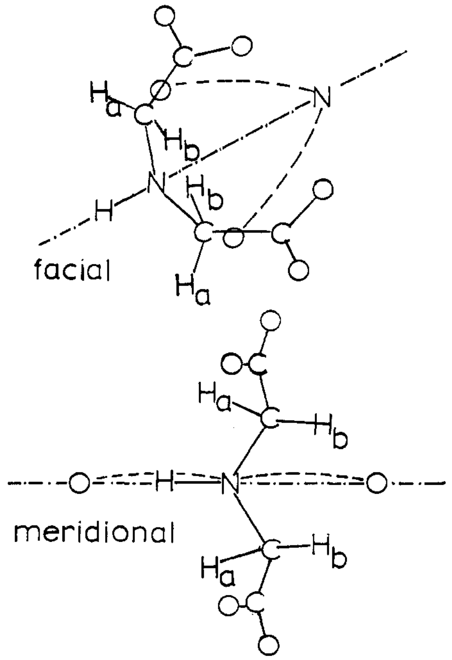

Figure 4.—Orientation of *trans*-IDA in facial and meridional configurations: plane of symmetry of IDA, — · · — · · — · · (second ligand represented only by dotted lines).

Table II

Chemical Shifts Observed for the Bis Complexes Compared to the Analogous Mixed Complexes[a,b]

	Proton chemical shifts		
	N–H	Acetate[c]	
Complex	or CH_3	δ_A	δ_B
trans-$[Co(IDA)_2]^-$	9.0	4.42	3.61
s-*cis*-$[Co(dien)(IDA)]^+$		4.29	3.45
trans-$[Co(MIDA)_2]^-$	3.17	4.25	3.86
s-*cis*-$[Co(dien)(MIDA)]^+$	2.99	4.19	3.69
cis-$[Co(IDA)_2]^-$	7.7	4.24	3.26
		4.00	3.27
u-*cis*-$[Co(dien)(IDA)]^+$	7.0	4.45	3.47
		4.35	3.41

[a] Calculated according to Jackman.[4] [b] Values in ppm. [c] Proton coupling constants (J_{AB}) vary from 16 to 18 cps.

The replacement of IDA or MIDA with dien in the *trans* complexes (as tabulated in Table II) also results in a general over-all shielding (although the acetate protons are deshielded in the *cis*-dien complexes). This shielding is similar to the results of Clifton and Pratt,[8] who studied acidopentaammine- and bis(ethylenediamine)cobalt(III) complexes and found that amine protons *cis* to acido species resonate at lower fields than those *trans* to acido species. The change from the *trans* bis complex to the *cis* or the replacement of IDA with dien would result in less acido groups in the *cis* position. Clifton and Pratt explain their results by stating that when the amine is *cis* to an acido group, intramolecular hydrogen bonding together with possible magnetic anisotropy of the ligand causes the shift to lower fields. When the acid group is *trans*, a lowered inductive effect causes a shift to higher fields. Our data is consistent with the Clifton–Pratt suggestion that magnetic anisotropy (in this case associated with the region of the cobalt–carboxylic acid bond) gives a partial contribution to the over-all effects. Protons in the Co–O–C plane appear to be deshielded while those above or below this plane seem to be shielded. This anisotropy would explain the shifts discussed above.

The additional splitting in the low-field components of the acid salts of IDA is the same as that found in u-*cis*-$[Co(dien)(IDA)]^+$, which has been shown to be due to H–N–C–H coupling of the amine proton with the acetate protons.[3] The disappearance of this splitting after the amine protons have completely been deuterated confirms this assignment. The rate of the amine proton exchange is slower in acid salt solutions than in those of the potassium salts as expected. The exchange is also slower for the *trans* salts and is similar to that observed by Clifton and Pratt[8] and Basolo and Pearson[9] for *trans* amine groups. The lower solubility of the *trans* isomer may also contribute to this slower exchange. If sufficient *trans* isomer was used in order to get a good nmr signal, some of the sample was not dissolved. This suspended salt would be in equilibrium with dissolved salt and the amine signal would be expected to be much slower to disappear.

Karplus[10] has shown that the coupling constants between two protons on adjacent carbon atoms depends on the dihedral angle between the protons. We have found that the coupling through tetrahedrally bound nitrogen is similar to that through a tetrahedral carbon.[3] Models indicate that the H–N–C–H_a angle is approximately 0° and H–N–C–H_b is approximately 100°, which should theoretically result in constants of 8 and <1 cps, respectively. The constants obtained are 7.5 and 1.0 cps, respectively, for the protons assigned as H_a and H_b, in agreement with the theory and with the constants found in the mixed complex, thus showing that the proton assignments are correct.

Visible Absorption Spectra.—The visible absorption spectra of the acid salts of IDA are identical with those of the potassium salts as tabulated by Tsuchida.[2] The spectra of the acid and potassium salts of *trans*-$[Co(MIDA)_2]^-$ are identical and are similar to those of *trans*-$[Co(IDA)_2]^-$. The acid salt spectra are tabulated for comparison in Table III. We have earlier applied the concepts of crystal field theory[11] to systems[3,4] having the general formulation $[Co(amine)_4(carboxylic\ acid)_2]^+$. For systems with the general formulation $[Co(amine)_2(carboxylic\ acid)_4]^-$ the shifts and splittings will be the same except that the shifts will be to higher energies because amine is a stronger ligand than is carboxylic acid.[12] Thus the *cis* isomer has a broadened peak in the band I region which should be shifted to higher energies than the first band in the parent compound $[Co(acid)_6]^{3-}$. The *trans* isomer has band Ia at higher energy than the *cis* band and a low-intensity

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[8] P. Clifton and L. Pratt, *Proc. Chem. Soc.*, 339 (1963).

[9] F. Basolo and R. G. Pearson, *Progr. Inorg. Chem.*, **4**, 381 (1962).

[10] M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).

[11] C. J. Ballhausen and C. K. Jørgensen, *Kgl. Danske Vedenskab. Selskab, Mat. Fys. Medd.*, **29**, (14) (1955); W. J. Moffitt and C. J. Ballhausen, *J. Inorg. Nucl. Chem.*, **3**, 178 (1956); H. Yamatera, *Bull. Chem. Soc. Japan*, **31**, 95 (1958).

[12] Y. Shimura and R. Tsuchida, *ibid.*, **29**, 311 (1956).

TABLE III

THE VISIBLE ABSORPTION SPECTRA OF THE BIS COMPLEXES

	Spectral bands ($\bar{\nu}$)			Dt',	Dq(amine),
	I_a	I_b	II	cm^{-1}	$cm^{-1} \times 10^{-3}$
cis-$H[Co(IDA)_2]\cdot H_2O$	1.779[a]	2.008	2.618	−152	2.0
	(145)[b]	sh (38)[c]	(131)		
trans-$H[Co(IDA)_2]\cdot 4H_2O$	1.602	2.008	2.740	382	2.6
	sh (11)[c]	(57.5)	(58.5)		
trans-$H[Co(MIDA)_2]\cdot 2H_2O$	1.607	1.969	2.717	304	2.5
	sh (11)[c]	(59.2)	(67.5)		

[a] All $\bar{\nu}$ in $cm^{-1} \times 10^{-4}$. [b] Extinction coefficients (ϵ) in parentheses; those of shoulders are estimated. [c] The wavelengths for the shoulders are determined assuming a symmetrical-shaped curve for the main peaks.

shoulder somewhat lower than the *cis*. The theory also predicts that the less symmetric *cis* isomer should have a more intense spectrum than the *trans* isomer,[13] as is observed.

Wentworth and Piper[14] have discussed the splitting patterns found in terms of a splitting parameter Dt' related to the Dq of the ligands involved. In this case

$$Dt' = 4/7(Dq(\text{amine}) - Dq(\text{carboxylic acid}))$$

where

$$Dt'(trans) = 4/35(\text{band Ib} - \text{band I(acid)})$$
$$Dt'(cis) = 8/35(\text{band Ia} - \text{band I(acid)})$$

The approximate values of Dt' and Dq(amine) as tabulated in Table III are calculated using approximately a Dq(acid) of 2200 cm^{-1} found for the mixed complexes with dien and IDA and a value of C of 3800 cm^{-1} to give a band I(acid) of 18,200 cm^{-1}. The lower value of Dq(amine) for the *trans*-MIDA complex compared to *trans*-IDA is in agreement with the lower stability on N-alkyl substitution as observed with similar substituted amine carboxylic acid compounds.[4] The low value found for the *cis* complex is expected because of the amine repulsions indicated in the equilibrium distribution and the nmr measurements.

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(13) S. Yamada and R. Ysuchida, *Bull. Chem. Soc. Japan*, **26**, 15 (1953).
(14) R. A. D. Wentworth and T. S. Piper, *Inorg. Chem.*, **4**, 709 (1965).

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The Mechanism of the Replacement of Heterocyclic Amines from Some Aminotrichlorogold(III) Complexes

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A series of complexes of the type $[AuCl_3am]^0$, where am is a heterocyclic nitrogen base, has been prepared and the kinetics of the reactions with chloride, azide, and nitrite ions in methanol at 25° have been studied. In each case the first step is the replacement of the organic base, and the kinetics of this substitution follow the normal square-planar rate law: rate = $(k_1 + k_2[Y^-])$[complex]. k_1, the rate constant for the bimolecular solvolysis of the complex, is not very sensitive to the nature of the substrate, but the dependence of k_2 upon the natures of the substrate and the entering group indicates that the nucleophilic discrimination ability of Au(III) in these complexes is good and is influenced markedly by the nature of the leaving group. A linear free energy relationship is observed between the basicity of the leaving group and the rate constant for its replacement by chloride, but this simple behavior is not followed by azide and nitrite, and the more complicated relationship is discussed in terms of polarizability and π bonding in the transition state.

Introduction

Kinetic studies of the mechanism of the substitution reactions of square-planar complexes have been confined exclusively to complexes of d^8 transition metal ions. Nearly all of the systematic investigations have been carried out with complexes of Pt(II) and little has been reported about analogous complexes of other metals. It is of interest to compare the reactions of Au(III) complexes with those of Pt(II) in order to assess the relative importance of two possible factors that might be working in opposition to one another. On one hand it has been suggested[1] that the tendency to form stable trigonal-bipyramidal five-coordinate complexes of low-spin d^8 metal ions decreases as the oxidation state increases, *i.e.*, Cr(−II) > Mn(−I) > Fe(0) > Co(I) > Ni(II) > Cu(III), with a similar relationship for the isovalent elements of the second and third transition series. This argument should be equally valid when applied to the five-coordinate transition state for bimolecular substitution in a square-planar complex and would suggest that the bimolecular transition state is less readily formed by Au(III) than it is by Pt(II). On the other hand, the increased nuclear charge of Au(III) might attract the electron pair of the incoming nucleophile more strongly and thereby provide compensation. Under these circumstances the five bonds in the transition state are less likely to be equivalent and the three nonchanging bonds might be more covalent than the other two. A third point of interest is the extent to which the increased effective nuclear charge has made the nonbonding d electrons insensitive to electrophilic attack and thereby reduced the "biphilicity" of the process.

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(1) R. S. Nyholm, *Proc. Chem. Soc.*, 273 (1961); R. S. Nyholm and M. L. Tobe, *Experientia, Suppl.*, **9**, 112 (1965).