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Infrared Absorption Spectra of Metal–Amino Acid Complexes.
IV. The Infrared Spectra and Configurations of Metal–Isoleucine Chelates[1b]

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The infrared spectra of DL-isoleucine and some metal–isoleucine chelates have been investigated from 4000 to 270 cm.$^{-1}$ and detailed assignments for the observed bands have been made. The characteristics of the spectra of geometrical isomers of the planar chelates are discussed, with particular emphasis on the spectral region 600 to 270 cm.$^{-1}$. From the variations in the frequencies of the metal–nitrogen stretching vibrations and the NH_2 stretching and rocking vibrations it is concluded that the relative covalent character of the metal–nitrogen bonds varies in the order Pt(II) > Pd(II) > Cu(II).

Introduction

The relative complexity of the spectra of *cis* isomers of planar glycine chelates as compared to the *trans* compounds in the sodium chloride region of the spectrum has been observed in previous infrared spectroscopic studies.[2,3] Rosenberg[3] has proposed that this increased complexity for *cis*-bis(glycino)platinum(II) in the 3 and 6 μ regions may be due to (1) the higher symmetry of the *trans* isomer in which some vibrations may be inactive in the infrared, (2) nonequivalent metal–nitrogen bonds in the *cis* isomer due to an unsymmetrical positioning of the chelate groups, or (3) differences in hydrogen bonding in the two isomers.

In a recent investigation of metal–glycine chelates[4] a more specific criterion, based on the different symmetries of the chelate rings, was suggested for distinguishing the geometrical isomers using their infrared spectra. In the approximate range 500–270 cm.$^{-1}$ only the metal–nitrogen antisymmetric stretching vibration is infrared active for *trans* isomers, but both antisymmetric and symmetric stretching vibrations are active for the *cis* chelates. Using an approximate normal coordinate analysis the frequency separation of the two vibrations can be calculated and the isomers distinguished. The present study was undertaken in order to determine the applicability of this approach to a more complicated system, *i.e.*, metal–isoleucine chelates.

Experimental

Preparation of Compounds. Bis(DL-isoleucino)copper(II) monohydrate was prepared by the method of Neuberg, *et al.*[5] The bright blue crystals were dried over calcium chloride. A violet solid, presumably the anhydrous complex, is obtained on heating this product at 100° *in vacuo*, but it immediately reverts to the blue monohydrate on exposure to the atmosphere.

Anal. Calcd. for $Cu(C_2H_5CH_3CHCHNH_2COO)_2 \cdot H_2O$: C, 42.15; H, 7.67; N, 8.20. Found: C, 42.19; H, 7.17; N, 8.34.

cis-**Bis(DL-isoleucino)palladium(II)** precipitated immediately upon mixing a hot solution (150 ml.) containing 3.28 g. (0.025 mole) of DL-isoleucine with a concentrated solution containing 1.63 g. (0.005 mole) of K_2PdCl_4. The fine cream crystals were washed several times with boiling water and were dried at 110° *in vacuo*.

Anal. Calcd. for $Pd(C_2H_5CH_3CHCHNH_2COO)_2$: C, 39.30; H, 6.60; N, 7.64. Found: C, 39.17; H, 6.59; N, 7.80.

The configuration of this compound was shown to be *cis* according to the Kurnakov reaction[6] using a variation of the procedure outlined by Volshtein and Velikanova[7]; 0.8 g. of *cis*-bis(DL-isoleucino)palladium(II) was mixed with 5 ml. of 1:1 hydrochloric acid at room temperature. The yellow crystals of dichlorobis(DL-isoleucine)palladium(II) which formed were washed with 1:1 hydrochloric acid and water and were dried *in vacuo;* 0.2 g. of this dichloro compound was then dissolved in 4 ml. of an aqueous solution containing 0.2 g. of thiourea. The solution was boiled for 10 sec. and immediately cooled. The addition of concentrated hydrochloric acid produced a bright orange precipitate which was washed with 1:1 hydrochloric acid, alcohol, and ether and was dried at 80° for 3 hr.

The presence of four moles of thiourea in this reaction product confirms a *cis* configuration for the original chelate.

Anal. Calcd. for $[Pd(H_2NCSNH_2)_4]Cl_2$: C, 9.97; H, 3.35; N, 23.26. Found: C, 10.55; H, 3.76; N, 23.17.

A second crop of crystals was obtained by concentrating the filtrate from the separation of the *cis*-palladium complex. The solid was mixed with 200 ml. of water at 80° for 1 hr. and the mixture was filtered while hot. Concentration and cooling the filtrate yielded yellow plates of bis(DL-isoleucino)palladium(II) which were dried at 110° *in vacuo*. The infrared spectrum of this product is significantly different from that of the *cis* chelate.

Anal. Calcd. for $Pd(C_2H_5CH_3CHCHNH_2COO)_2$: C, 39.30; H, 6.60; N, 7.64. Found: C, 39.89; H, 6.96; N, 7.78.

Attempts to obtain a thiourea derivative of this complex were unsuccessful.

trans-**Bis(DL-isoleucino)platinum(II)** was prepared by mixing a solution containing 5.24 g. (0.04 mole) of DL-isoleucine dissolved in 36 ml. of 1 *M* KOH with a concentrated solution containing 4.16 g. (0.01 mole) of K_2PtCl_4. On heating the solution at 70° for 15 min. a white precipitate formed which was isolated *immediately*, washed several times with cold water, and dried *in vacuo*.

Anal. Calcd. for $Pt(C_2H_5CH_3CHCHNH_2COO)_2$: C, 31.65; H, 5.31; N, 6.15. Found: C, 32.55; H, 5.37; N, 6.32.

Application of the Kurnakov reaction confirms a *trans* configuration for this complex since only two moles of thiourea is

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[1] (a) The Radiation Laboratory of the University of Notre Dame is operated under contract with the U. S. Atomic Energy Commission. This is document COO-38-347. (b) Abstracted in part from the Ph.D. thesis of R. J. Hooper, Notre Dame, 1962, and supported in part by NIH grants HE-02218 and GM-10855. (c) To whom requests for reprints should be addressed.

[2] A. J. Saraceno, I. Nakagawa, S. Mizushima, C. Curran, and J. V. Quagliano, *J. Am. Chem. Soc.*, **80**, 5018 (1958).

[3] A. Rosenberg, *Acta Chem. Scand.*, **10**, 840 (1956).

[4] T. J. Lane, J. A. Durkin, and R. J. Hooper, *Spectrochim. Acta*, **20**, 1013 (1964).

[5] C. Neuberg, H. Lustig, and I. Mandl, *Arch. Biochem.*, **26**, 77 (1950).

[6] N. S. Kurnakov, *J. Russ. Phys. Chem. Soc.*, **25**, 585 (1893).

[7] L. M. Volshtein and N. S. Velikanova, *Zh. Neorgan. Khim.*, **2**, 2383 (1957); *Chem. Abstr.*, **52**, 19,662*b* (1958).

present in the reaction product. The thiourea derivative was prepared using exactly the same procedure outlined above for the palladium compound, with the exception that it was necessary to warm the mixture of chelate and 1:1 HCl in a water bath for 1 min. in order to obtain the dichlorobis(DL-isoleucine)-platinum(II).

Anal. Calcd. for $[\mathrm{Pt(H_2NCSNH_2)_2(C_2H_5CH_3CHCHNH_2COOH)_2]Cl_2}$: C, 24.71; H, 5.04; N, 12.35. Found: C, 24.86; H, 5.26; N, 12.24.

Recrystallization from bis(DL-isoleucino)platinum(II) and attempts to prepare the complex by other methods resulted in the formation of a monohydrate which retains the water of crystallization at 140° *in vacuo*. The presence of this water of crystallization was confirmed by a broad absorption band at 3481 cm.$^{-1}$ in the infrared spectrum.

Anal. Calcd. for $\mathrm{Pt(C_2H_5CH_3CHCHNH_2COO)_2 \cdot H_2O}$: C, 30.44; H, 5.53; N, 5.92. Found: C, 30.88; H, 5.46; N, 6.20.

The configuration of this monohydrate is also *trans* since the infrared spectrum of its thiourea derivative is identical with that obtained from the anhydrous platinum chelate.

Deuteration of Compounds.—The amino acid was deuterated by recrystallization from 99.5% deuterium oxide. The N-deuterated chelates were prepared by prolonged mixing of the pure compounds with D_2O in a sealed tube at 70–80°.[8]

Absorption Measurements.—The infrared spectra were obtained using a Perkin-Elmer Model 221 infrared spectrophotometer equipped with a grating from 4000 to 1420 cm.$^{-1}$ and with sodium chloride and cesium bromide prisms in the regions 1420–650 and 650–270 cm.$^{-1}$, respectively. Samples were prepared by the potassium bromide disk technique[9] and all spectra were checked using Nujol mulls. Wave-number calibration was accomplished by comparison with polystyrene and atmospheric water vapor standard peaks. The amplifier balance in the instrument was checked in regions of strong atmospheric water vapor absorption by obtaining "blank" spectra before and after each sample recording.

Results

The observed absorption frequencies for DL-isoleucine and N-deuterated DL-isoleucine are listed in Table I. Frequencies for the metal complexes are given in Table II. Spectra in the region 650–270 cm.$^{-1}$ are shown in Fig. 1.

Discussion

(I) Assignment of the Observed Frequencies.

(A) DL-Isoleucine.—Detailed assignments for DL-isoleucine and the N-deuterated acid are given in Table I. The assignments for DL-isoleucine were accomplished by comparing the spectrum with that of N-deuterated DL-isoleucine and by a comparison with the spectra of some thoroughly studied simpler molecules: glycine,[10] DL-alanine,[11] isobutane,[12,13] and isopentane.[14]

At frequencies lower than 500 cm.$^{-1}$ absorption bands due to skeletal deformation vibrations are expected to appear and the assignment of these bands is considered in detail. The skeletal deformation vibrations can be separated into two types: (1) Those due primarily to the $\begin{smallmatrix}\mathrm{C}\\ \mathrm{C-C}\end{smallmatrix}\!\!>\!\mathrm{C-C}$ portion of the skeleton, and (2) those due to the $\mathrm{C-C}\!<\!\begin{smallmatrix}\mathrm{C}\\ \mathrm{N}\end{smallmatrix}$ portion of the skeleton. For DL-valine, $\mathrm{(CH_3)_2CHCH(NH_3^+)COO^-}$, which has a spectrum very similar to that of DL-isoleucine, $\mathrm{(C_2H_5)(CH_3)CHCH(NH_3^+)COO^-}$, in this region observed absorption bands at 473, 425, and 363 cm.$^{-1}$ are assigned to deformation vibrations of the $\begin{smallmatrix}\mathrm{C}\\ \mathrm{C}\end{smallmatrix}\!\!>\!\mathrm{C-C}$ portion of the skeleton on the basis of a normal coordinate analysis of metal–valine chelates.[15] A corresponding similarity of spectra is evident when comparing the more simple hydrocarbons which are structurally similar to the $\begin{smallmatrix}\mathrm{C}\\ \mathrm{C}\end{smallmatrix}\!\!>\!\mathrm{C-C}$ and $\begin{smallmatrix}\mathrm{C}\\ \mathrm{C-C}\end{smallmatrix}\!\!>\!\mathrm{C-C}$ portions of these amino acids. The skeletal deformation vibrations of isobutane, $\mathrm{(CH_3)_3CH}$, are observed at 438 cm.$^{-1}$ ($\mathrm{CC_3}$ symmetric deformation) and 370 cm.$^{-1}$ ($\mathrm{CC_3}$ degenerate deformation)[12,13] and two Raman lines at approximately the same frequencies are observed for isopentane, $\mathrm{(C_2H_5)(CH_3)_2CH}$.[13,16] In

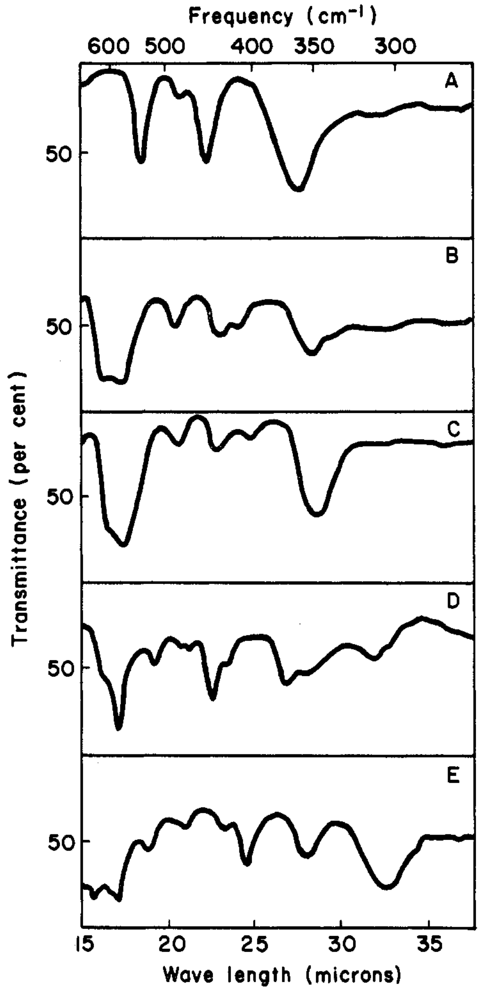

Fig. 1.—Infrared absorption spectra of DL-isoleucine and metal–isoleucine chelates in the CsBr region: A, DL-isoleucine; B, *trans*-Pt(II) (anhydrous); C, *trans*-Pd(II); D, *cis*-Pd(II); E, *cis*-Cu(II)·H_2O.

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(8) W. R. Harp and R. C. Eiffert, *Anal. Chem.*, **32**, 794 (1960).

(9) M. M. Stimson and M. J. O'Donnell, *J. Am. Chem. Soc.*, **74**, 1805 (1952).

(10) S. Suzuki, T. Shimanouchi, and M. Tsuboi, *Spectrochim. Acta*, **19**, 1195 (1963).

(11) K. Fukushima, T. Onishi, T. Shimanouchi, and S. Mizushima, *ibid.*, **15**, 236 (1959).

(12) H. Takahashi, *Nippon Kagaku Zasshi*, **83**, 799, 980 (1962).

(13) N. Sheppard, *J. Chem. Phys.*, **16**, 690 (1948).

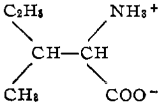
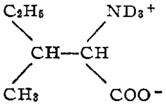
(14) R. S. Rasmussen, *ibid.*, **16**, 712 (1948).

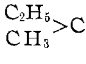
(15) I. Nakagawa, R. J. Hooper, J. L. Walter, and T. J. Lane, to be published.

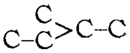
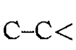
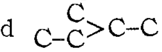
(16) M. R. Fenske, W. G. Braun, R. V. Wiegard, D. Quiggle, R. H. McCormick, and D. H. Rank, *Ind. Eng. Chem., Anal. Ed.*, **19**, 766 (1947).

TABLE I

INFRARED FREQUENCIES (CM.$^{-1}$) AND ASSIGNMENTS FOR DL-ISOLEUCINE AND N-DEUTERATED DL-ISOLEUCINE[a]

		Assignments
3131 s, b		NH_3^+ stretching
2583 s, b		
2533 sh		
2962 s	2964 s	C–H stretching
2928 sh	2932 m	
2878 s	2878 m	
2130 w, b	2307 sh	
	2235 s	ND_3^+ stretching
	2035 s	
	1982 s	
1621 sh		NH_3^+ degenerate deformation
1596 s, b	1582 s, vb	COO^- antisymmetric stretching
1493 s, b		NH_3^+ symmetric deformation
1464 sh	1461 s	CH_3 degenerate deformation
1444 sh	1450 sh	
1417 s, b	1418 s, b	COO^- symmetric stretching
1362 s		
1349 s	1351 s, b	CH_2 bending, C–H bending
1327 s	1324 s	
1311 s	1311 s	
1282 sh	1278 w	CH_2 wagging and twisting, C–H bending
1282 sh	1252 m	
	1240 sh	
1184 m	1179 s	CH_3 rocking, C–C stretching, C–N stretching, with NH_3^+ rocking for DL-isoleucine; with ND_3^+ degenerate and symmetric deformations for N-deuterated DL-isoleucine
1131 m	1165 s	
1091 sh	1145 sh	
1075 w, b	1098 w, b	
1042 w, b	1983 sb	
993 w	1024 w	
961 w	999 w	
917 w, b	982 sh	
	951 w	
	930 w	
890 w	885 sh	
874 m	872 w	
827 w	858 w	
808 sh	829 m[b]	
798 m	799 m	COO^- scissors
774 m	780 m	CH_2 rocking
	757 m	ND_3^+ rocking
691 m	657 m, b	COO^- wagging
681 sh		
540 s	522 s	COO^- rocking
486 w	489 w	Skeletal deformations[c]
450 s	440 s	
366 vs, b	338 vs, b	

[a] s, strong; m, medium; w, weak; sh, shoulder; b, broad; v, very. [b] ND_3^+ rocking overlap. [c]  $\begin{smallmatrix}C_2H_5\\CH_3\end{smallmatrix}\!>\!CH-C$ portion of the skeleton.

addition, Raman lines corresponding to skeletal deformations of DL-alanine, $(CH_3)(NH_3^+)CHCOO^-$, are observed at 340 and 260 cm.$^{-1}$,[17] which indicates that the skeletal deformation frequencies of the  $\begin{smallmatrix}C\\C-C\end{smallmatrix}\!>\!C-C$ portion of the molecule should be higher than those of the  $C-C<\begin{smallmatrix}C\\N\end{smallmatrix}$ part. In view of these data the observed bands at 486, 450, and 366 cm.$^{-1}$ in the spectrum of DL-isoleucine are assigned to mixed  $\begin{smallmatrix}C\\C-C\end{smallmatrix}\!>\!C-C$ vibrational modes analogous to those observed for DL-valine.

(B) **Metal–Isoleucine Chelates.**—Detailed assignments for the metal complexes are given in Table II. In this table and in subsequent paragraphs configurations for some of the complexes are stated without proof in order to avoid ambiguities in the discussion. The reasons for concluding that a given complex has a particular configuration are summarized in the next section.

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(17) K. Fukushima, *Nippon Kagaku Zasshi*, **79**, 370 (1958).

TABLE II

INFRARED FREQUENCIES (CM.$^{-1}$) AND ASSIGNMENTS FOR METAL–ISOLEUCINE CHELATES[a]

trans-$\mathrm{PtR_2}$[b]	*trans*-$\mathrm{PdR_2}$	*cis*-$\mathrm{PdR_2}$	*cis*-$\mathrm{CuR_2 \cdot H_2O}$	Assignments
		3284 s	(3291 s	$\mathrm{NH_2}$ stretching
3215 s, b	3250 s, b	3215 s	3244 s, b)[c]	
3115 s, b	3115 s, b	3139 s	3160 m	
		3100 sh		
2961 s	2962 s	2961 s	2962 s	C–H stretching
2932 m	2934 m	2933 m	2933 m	
2875 m	2876 m	2876 m	2876 m	
	1658 sh			
1656 s, b	1644 s, b	1640 sh	1622 s, vb[c]	$\mathrm{COO^-}$ antisymmetric stretching
		(1628 s		
1615 sh	1607 sh	1586 s)	1600 s	$\mathrm{NH_2}$ scissors
	1461 sh	1461 m	1461 m	$\mathrm{CH_3}$ degenerate deformation
1460 m	1451 m	1453 sh	1452 sh	
1389 sh	1388 sh	1385 sh	1382 sh	$\mathrm{CH_3}$ symmetric deformation
1369 s	1365 s, b	1366 s	1390 s	$\mathrm{COO^-}$ symmetric stretching
			1371 sh	$\mathrm{CH_2}$ bending
1340 s	1339 sh	1338 s	1346 m	$\mathrm{CH_2}$ wagging and twisting, CH bending
1323 s	1317 s	1323 sh	1332 sh	
1297 m	1294 sh	1293 s	1305 w	
1271 sh	1270 sh	1266 sh	1271 sh	
1247 sh	1255 w, b	1250 sh	1255 vw	
		1219 w	1215 w	
1184 m, b	1170 sh	1176 sh	1147 m	$\mathrm{CH_3}$ rocking, C–C stretching, C–N stretching, $\mathrm{NH_2}$ wagging and twisting
	1162 m	1148 s	1124 m	
	1132 m	1122 sh	1094 w	
1089 w	1091 w	1096 vw	1066 sh	
1036 w	1035 w	1037 w	1037 sh	
999 w	1006 w	1003 w	1009 vw	
969 w	969 w	964 w	993 w	
942 w, b	947 w	947 w	962 w	
			944 sh	
	927 sh	935 w	924 sh	
889 sh	902 sh	905 w	901 w	
884 w	886 w	884 w	882 w	
814 sh	830 m	830 m	830 sh	
		820 m	811 sh	
831 m	721 w, b	(729 w	633 s	$\mathrm{NH_2}$ rocking
		702 m)		
776 w	778 m	778 w	777 w	$\mathrm{CH_2}$ rocking
745 w, b	807 m	807 sh	800 m	$\mathrm{COO^-}$ scissors
681 vw			(700 sh	
618 s	596 sh	610 sh	688 m, b)[d]	$\mathrm{COO^-}$ wagging
			591 sh	
580 s	570 s	(587 s	(575 s	$\mathrm{COO^-}$ rocking
		524 w)	528 w)	
		(482 sh	(482 sh	
494 m	488 m	474 w)	473 w)	Skeletal deformation
439 m	439 m	445 s	411 s	Skeletal deformation
419 w	406 w	429 w	431 w	M–N antisymmetric stretching
356 m	352 s	376 m	308 s, b	Skeletal deformation
		356 m, b	357 m, b	M–N symmetric stretching
		316 w		Chelate ring deformation?

[a] s, strong; m, medium; w, weak; sh, shoulder; b, broad; v, very. [b] $\mathrm{R^-}$ = isoleucinate ion. [c] $\mathrm{H_2O}$ vibration overlap. [d] $\mathrm{NH_2}$ rocking overlap.

Most of the absorption bands at frequencies higher than 500 cm.$^{-1}$ were assigned to vibrations similar to those of the ligand by direct comparison of the spectra. The stretching and deformation vibrations of the coordinated $\mathrm{NH_2}$ groups were identified on the basis of data obtained for corresponding N-deuterated complexes.

In the region 500 to 270 cm.$^{-1}$ bands due to metal–nitrogen stretching vibrations are expected to appear[4,15,18] in addition to the skeletal deformation vibrations observed in the spectrum of the ligand.

For the *trans*-platinum and palladium complexes the spectra in this region contain, in addition to the vibrations observed for the ligand, one weak band at approximately 400 cm.$^{-1}$ (see Fig. 1) which is attributed to the metal–nitrogen antisymmetric stretching vibration. This vibration has also been observed at

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[18] T. Shimanouchi and I. Nakagawa, *Spectrochim. Acta*, **18**, 89 (1962).

approximately 400 cm.$^{-1}$ for the platinum and palladium complexes of glycine[4] and DL-valine.[15] Additional support for this assignment is obtained using the results of an approximate normal coordinate analysis. Approximate bond-stretching force constants and frequencies for the metal–nitrogen stretching vibrations were calculated as outlined in ref. 4, on the basis of a five-body problem in which only the nitrogen and oxygen atoms coordinated to the metal ion are included. A simple valence force potential field was used. For the *trans*-platinum and palladium chelates approximate bond-stretching force constant values of 1.27 and 1.07 were obtained using the metal–nitrogen antisymmetric stretching frequencies of 419 and 406 cm.$^{-1}$, respectively. For the palladium chelate this force constant value results in a calculated metal–nitrogen symmetric stretching frequency at 360 cm.$^{-1}$, and a band is observed at 356 cm.$^{-1}$ in the spectrum of the *cis* isomer, for which this symmetric stretching vibration is infrared-active.[19] The observed band at 356 cm.$^{-1}$ in the spectrum of the *cis*-palladium complex is therefore assigned to the metal–nitrogen symmetric stretching vibration.

The medium band at 376 cm.$^{-1}$ is attributed to a skeletal deformation vibration (observed at 352 cm.$^{-1}$ in the *trans* complex) and the weak band at 429 cm.$^{-1}$ is assigned to the metal–nitrogen antisymmetric stretching vibration (observed at 406 cm.$^{-1}$ in the *trans* isomer). The frequency shift for these vibrations is probably due to differences in vibrational mixing for the *trans* and *cis* isomers. Additional absorption bands below 500 cm.$^{-1}$ in the spectrum are due to skeletal deformation vibrations, with the exception of the peak at 316 cm.$^{-1}$, for which there is no analogous absorption in the spectrum of DL-isoleucine. This band is tentatively assigned to a deformation vibration of the metal–nitrogen bonds, which is presumably inactive in the *trans* isomer. Skeletal deformation vibrations have been observed at about 320 cm.$^{-1}$ for cobaltic ammine complexes.[18]

Assignments for the copper chelate are accomplished by a direct comparison of the spectrum with that of the *cis*-palladium complex since the two spectra are very similar (see Table II and Fig. 1). However, an approximate normal coordinate analysis[4] shows that the separation of the antisymmetric and symmetric metal–nitrogen stretching frequencies should be approximately 70 cm.$^{-1}$ for the copper compound. Therefore, the observed band at 357 cm.$^{-1}$ is assigned to the metal–nitrogen symmetric stretching vibration and the band at 308 cm.$^{-1}$ is assigned to a skeletal deformation vibration.

(II) **Configurations of the Complexes.**—As described in a previous section, on the basis of chemical evidence a *trans* configuration has been demonstrated for the platinum complex and a *cis* configuration for the first of two palladium complexes isolated.

The *trans* configuration for the platinum compound is supported by (1) the appearance of only one additional absorption band, as compared to the spectrum of the ligand, in the region 500–270 cm.$^{-1}$, and (2) the simplicity of the spectrum in the sodium chloride region, particularly in the regions where the coordinated NH_2 groups absorb. The spectra of the platinum complex and the second palladium complex isolated are almost identical, especially in the important regions noted above. Therefore, on the basis of the similarity of the spectra, it is concluded that this palladium complex is *trans*.

The increased complexity of the spectrum, as compared to those for the *trans* complexes, is consistent with a *cis* configuration for the other palladium chelate. In addition to the appearance of the metal–nitrogen symmetric stretching vibration previously noted, four N–H stretching bands are observed as compared to only two for the *trans*-palladium complex. The NH_2 scissors and rocking vibrations and, probably, the carboxylate rocking vibration, for which only one band is observed in the *trans* isomer, appear as doublets in the *cis* compound.

An interesting change has been noted in the spectrum on the formation of bis(DL-isoleucino)platinum(II) monohydrate. The two bands at 3215 and 3115 cm.$^{-1}$ in the spectrum of the anhydrous platinum chelate are split in the monohydrate, giving a total of four N–H stretching bands. This observation alone would indicate a *cis* configuration for the monohydrate, but no splitting is observed for bands due to deformation vibrations of the NH_2 groups and there is no band which can be attributed to the metal–nitrogen symmetric stretching vibration in the low-frequency region. Except for the NH_2 stretching bands the spectrum is simple and is almost identical with that for the anhydrous compound. Thus, from a consideration of the entire spectrum it can be concluded that the monohydrate is *trans*, which is confirmed by the results of the Kurnakov reaction, as described previously.

As previously noted, the spectrum of bis(DL-isoleucino)copper(II) monohydrate is similar to that for the *cis*-palladium complex. In the N–H stretching region three bands are observed and, although the compound is a hydrate which is a possible complicating factor, the relative intensities and profile of the bands in this region are very similar to that for bis(glycino)copper(II) monohydrate, for which a *cis* configuration has been demonstrated.[20] In addition, two bands due to the NH_2 rocking vibration are observed. Of primary interest is the CsBr region of the spectrum in which there is a complex absorption pattern, including an extra band which can be assigned to the metal–nitrogen symmetric stretching vibration. In the absence of data for the anhydrous complex, this observation should not be considered conclusive evidence for

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(19) On the basis of the frequency separation for the metal–nitrogen stretching vibrations alone, there are two possible choices for the antisymmetric frequency in the *trans* chelate. If the antisymmetric frequency is taken as 352 cm.$^{-1}$, the symmetric stretching vibration should appear at 313 cm.$^{-1}$ and a new band is observed at 316 cm.$^{-1}$ for the *cis* complex. However, assignment of the band at 406 cm.$^{-1}$ to the metal–nitrogen antisymmetric stretching vibration is much more reasonable when the spectra of the *trans* chelate and the ligand are compared.

(20) K. Tomita, *Bull. Chem. Soc. Japan*, **34**, 280, 286 (1961).

the *cis* configuration since vibrations due to coordinated water molecules may appear in the CsBr region.[21] However, in view of the remarkable similarity of the spectra of the copper and *cis*-palladium complexes and the absence of extensive differences in the spectra of the anhydrous platinum chelate and the corresponding monohydrate, it is proposed that the copper complex is *cis*.

(III) The Metal–Nitrogen Bonds.—The N–H stretching frequencies of the coordinated NH_2 groups increase from platinum through copper, which indicates that the covalent character of the metal–nitrogen bonds varies in the order Pt(II) > Pd(II) > Cu(II).[22] This order is supported by a consideration of the relative values for the metal–nitrogen stretching frequencies and masses of the metal ions (and by the approximate bond-stretching force constant values for the platinum and palladium complexes). In addition, the NH_2 rocking frequencies follow the above order, as was the case for glycine and DL-valine chelates.[4,15]

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Synthesis of Nitroammine- and Cyanoamminecobalt(III) Complexes with Potassium Tricarbonatocobaltate(III) as the Starting Material

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A series of cobalt(III) complexes with the general formula $[Co(NO_2)_n(NH_3)_{6-n}]^{3-n}$ (n = 1–5) was synthesized with a solution of potassium tricarbonatocobaltate(III) as the starting material. The distinctive feature of the method employed in the systematic synthesis is that the amounts of the reagents going into the reactions are stoichiometrically fixed for the products wanted. Of those complexes potassium pentanitroamminecobaltate(III) is to be regarded as a new compound. Two other complexes, cyanopentaamminecobalt(III) chloride and tricyanotriamminecobalt(III), belonging to the cyanoammine series $[Co(CN)_n(NH_3)_{6-n}]^{3-n}$, were also prepared. Very recently the former was prepared by others, but the latter is a new compound. These three complexes were characterized by their absorption spectra in the visible and ultraviolet regions.

Introduction

When cobalt(II) ion is oxidized by hydrogen peroxide in the presence of an alkali bicarbonate, a green coloration occurs. This is known as the "Field–Durant reaction"[2,3] and has been used for cobalt analysis. We attempted to use this reaction for a new synthesis of cobalt(III) complexes; the attempts were first directed to production of the green solution on a preparative scale, and success was attained when potassium bicarbonate was employed instead of the sodium salt which had been used before on an analytical scale. Isolation of the complex as potassium tricarbonatocobaltate trihydrate and synthesis of a carbonatoammine series of cobalt(III) complexes were accomplished.[4] Afterward the method was extended to the synthesis of carbonatoethylenediamine, oxalatoammine, and oxalatoethylenediamine complexes.[5] An important feature of these methods is the successive substitution of carbonate ions by the desired ligands. Furthermore, the green solution of the tricarbonatocobaltate(III) was used for the preparation of some new compounds such as potassium carbonatoammoniatriacetatocobaltate(III),[6] potassium carbonatoethylenediaminediacetatocobaltate(III),[7] and potassium tungstocobaltate(III).[8]

Recently a closely resembling method was reported by Bauer and Drinkard,[9] who used sodium tricarbonatocobaltate(III) trihydrate as the starting material and obtained several new cobalt(III) complexes of easily oxidizable ligands as well as some of the known symmetrical complexes.

In the present paper, systematic preparation of the cobalt(III) complexes containing nitro and ammonia groups as ligands is reported as well as preparation of two other complexes belonging to the cyanoammine series. Most of the former complexes are very familiar substances, but as far as we are aware pentanitromonoamminecobaltate(III), $K_2[Co(NO_2)_5NH_3]$, was never obtained before. The cyanoammine series is much less familiar, and the only known member other than hexacyanocobaltate was pentacyanomonoammine[10] until quite recently. However, the preparation of the complexes $[CoCN(NH_3)_5]X_2$ with X = Cl, Br, NO_3, ClO_4, or $^1/_2SO_4$ has been reported by Siebert.[11]

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