bands in the visible region of the spectrum is larger for the *cis* isomer[20] tends to confirm the assignment being suggested; the area under the *cis* curve is ~5% greater than the area under the *trans* curve.

The Equilibrium, *cis*-$Cr(OH_2)_4Cl_2^+$ = *trans*-$Cr(OH_2)_4Cl_2^+$.—Measurement of the absorbancies of all of the eluent portions at the two wave lengths, 450 and 635 mμ, allows the calculation of the total amount of each isomeric dichlorochromium(III) ion in the quenched equilibrated mixture. Such measurements in two experiments give (*trans*)/(*cis*) = $0.5_6 \pm 0.0_3$; this is the value of the equilibrium quotient for the isomerization reaction in the molten hydrated salt if the quenching procedure is effective. An estimate of the value of this quotient in solutions of *I* (the ionic strength) $\cong$ 4, at temperatures in the range 30–95° can be obtained from the apparent absorbancy index value of the equilibrium mixture of the two isomers.[8] The value so determined is 0.5 ± 0.2. This value is within experimental error of the value observed in the dithiocyanatotetraaquochromium(III) system.[5] The *cis* and *trans* complexes in the dihydroxobis-(ethylenediamine)-cobalt(III) and the hydroxoaquobis-(ethylenediamine)-cobalt(III) systems are also of comparable stability, (*trans*)/(*cis*) = 0.7 and 1.2, respectively, at 25° in 1 *M* sodium nitrate.[21] Statistical considerations alone suggest a value of 0.25 for this ratio. The observed somewhat greater stability of the *trans* complex in these systems might be rationalized in terms of electrostatic considerations, although the diaquobis-(ethylenediamine)-cobalt(III) system, in which such electrostatic factors might be expected to be less pronounced, has an equilibrium value of (*trans*)/(*cis*) of 0.017.[21]

Taube and Myers[22] report that the oxidation of chromium(II) by iron(III) in 2 *M* hydrochloric acid results in chromium(III) chloride species which are not, exclusively, a mixture of $CrCl^{++}$ and the $CrCl_2^+$ species here identified as the *trans* isomer. The absorbancy data which they report suggests that *cis*-$CrCl_2^+$ is a component of the mixture of chromium(III) chloride species so produced.

MADISON, WISCONSIN

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

Infrared Absorption Spectra of Inorganic Coördination Complexes. XVI. Infrared Studies of Glycino-Metal Complexes[1,2]

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The assignment of infrared bands of glycino-metal complexes, based on the study of normal vibrations of glycine, mercuric amidohalides and 1,2-dichloroethane has been made. Significant differences in the spectra of geometrical isomers of Pt(II) and Co(III) have been observed. An interesting dehydration effect has been found to occur for the spectrum of bis-(glycino)-zinc(II) monohydrate.

Previous work on the infrared spectra of some glycino-metal complexes dealt primarily with the nature of the metal-to-ligand bond.[4,5] Recently, calculations of normal vibrations of molecules closely related to these complexes, and assignments of the spectra of glycine and deuterated glycine have also been reported.[6–9] In the present investigation the infrared spectra of several glycino-metal complexes are reported in the 2-15μ region together with a detailed assignment of the observed bands. Assignment of the observed bands for the coördination compounds has been made on the basis of the study of normal vibrations of glycine, mercuric amido halides and 1,2-dichloroethane. Studies on the nature of the metal-to-ligand bond and *cis*–*trans* isomerism are further discussed in relation to the spectra observed for the metal complexes.

Experimental

Preparation of Compounds.—*cis*- and *trans*-**Bis-(glycino)-platinum(II)**, $Pt(NH_2CH_2CO_2)_2$, were prepared as described by Pinkard and co-workers[10] and were twice recrystallized from water.

Anal. Calcd. for $Pt(NH_2CH_2COO)_2$: C, 13.99; H, 2.35; Pt, 56.86; N, 8.16. Found: *cis*: C, 14.22; H, 2.36; Pt, 57.04; N, 8.50. *trans*: C, 14.20; H, 2.25; Pt, 56.80; N, 7.93.

Bis-(glycino)-copper(II) monohydrate, $Cu(NH_2CH_2COO)_2 \cdot H_2O$, was prepared as reported by Abderhalden and Schnitzler.[11]

Anal. Calcd. for $Cu(NH_2CH_2COO)_2 \cdot H_2O$: C, 20.91; H, 4.39. Found: C, 21.06; H, 4.39.

Bis-(glycino)-nickel(II) dihydrate, $Ni(NH_2CH_2COO)_2 \cdot 2H_2O$, was prepared according to the directions of Stosick.[12]

Anal. Calcd. for $Ni(NH_2CH_2COO)_2 \cdot 2H_2O$: C, 19.78; H, 4.98; Ni, 24.17; N, 11.54. Found: C, 20.42; H, 5.01; Ni, 24.53; N, 11.48.

Bis-(glycino)-zinc(II) monohydrate, $Zn(NH_2CH_2COO)_2 \cdot H_2O$ was prepared according to the method of Dubsky and Rabas.[13]

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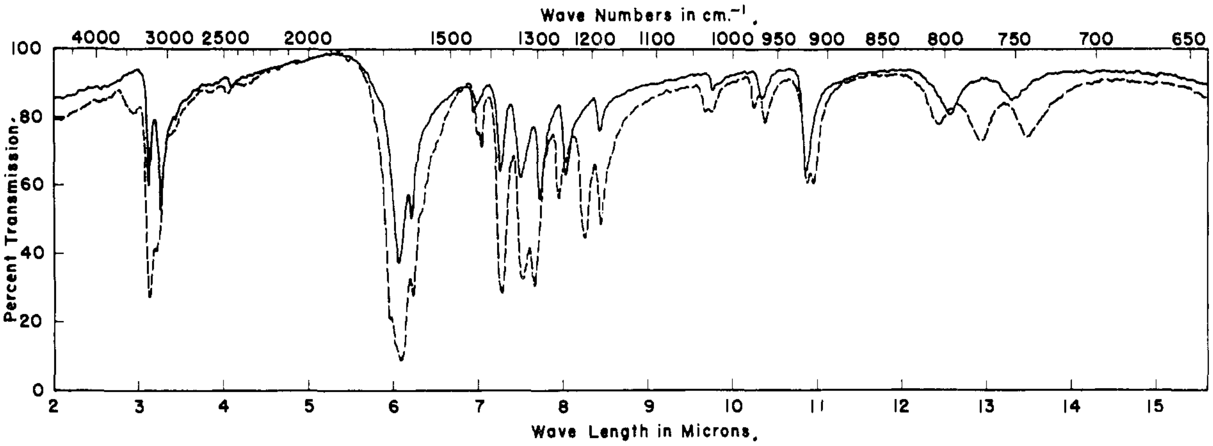

Fig. 1.—Infrared absorption spectra: —, *cis*-bis-(glycino)-platinum(II); ----, *trans*-bis-(glycino)-platinum(II), [Pt($NH_2CH_2COO)_2$].

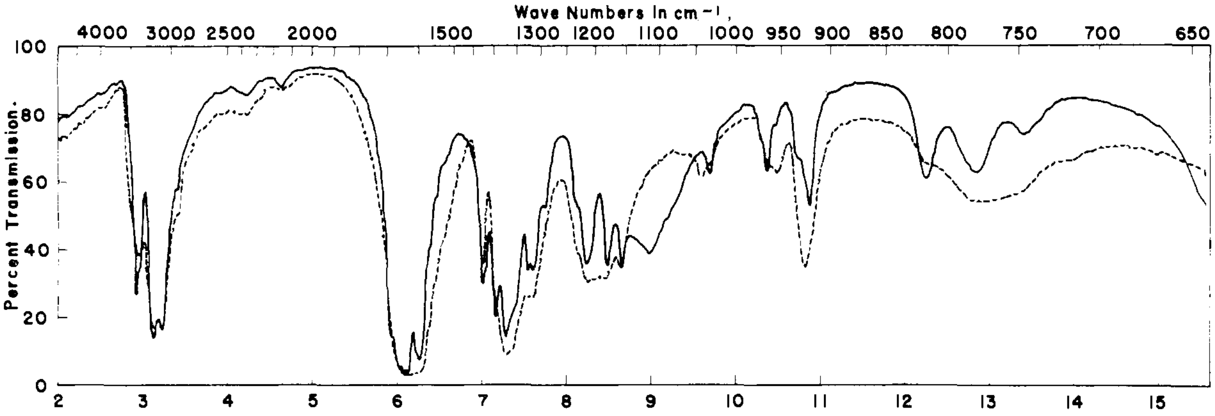

Fig. 2.—Infrared absorption spectra: —, tris-(glycino)-cobalt(III) monohydrate, $Co(NH_2CH_2COO)_3 \cdot H_2O$; ----, tris-(glycino)-cobalt(III) dihydrate, $Co(NH_2CH_2COO)_3 \cdot 2H_2O$.

The compound prepared in our Laboratory was spectroscopically identical with a sample kindly sent to us by Dr. Low.[5]

trans-**Bis-(glycino)-palladium(II)**, $Pd(NH_2CH_2COO)_2$, was prepared by the method of Pinkard and co-workers.[10]

Anal. Calcd. for $Pd(NH_2CH_2COO)_2$: N, 10.99. Found: N, 10.75.

α- and β-Tris-(glycino)-cobalt(III) hydrates were prepared as described by Ley and Winkler.[14] Two forms of the compound are believed to represent geometrical isomers and the more soluble violet form has been assigned the *trans*-configuration.[15,16]

Anal. Calcd. for α-$Co(NH_2CH_2COO)_3 \cdot 2H_2O$: C, 22.72; H, 5.09; N, 13.25. Found: C, 23.00; H, 5.13; N, 13.42. Calcd. for β-$Co(NH_2CH_2COO)_3 \cdot H_2O$: C, 24.09; H, 4.72; N, 14.05. Found: C, 24.26; H, 4.64; N, 13.55.

Absorption Measurements.—All spectra were obtained with a Perkin–Elmer Model 21 recording infrared spectrophotometer employing sodium chloride and calcium fluoride prisms over their regions of greatest resolution. The spectra of the solid complexes were obtained by means of the potassium bromide disk technique[17] and checked by measurements in Nujol mulls.

Results

The experimental results and assignments for *cis*- and *trans*- $Pt(NH_2CH_2COO)_2$ are given in Table I and Fig. 1. The infrared spectra of α- and β-tris-(glycino)-cobalt(III) are shown in Fig. 2. Frequency values for the glycinates of Pd(II) and Co(III) are listed in Table II.

Discussion

General.—The peaks in the 3 μ region for all the glycino-metal complexes reveal that the N–H stretching vibration is considerably changed on formation of the nitrogen-to-metal bond, which is to be expected, if the bond is essentially covalent.[18] The absorption in the 1600 cm.$^{-1}$ region indicates that the resonance in the carboxylate ion (resulting in nearly equivalent carbon-to-oxygen bonds) is preserved in all the metal complexes. Of the complexes studied, *cis*- and *trans*-bis-(glycino)-platinum(II) show the greatest increase in the antisymmetric carboxylate stretching frequency (1640 cm.$^{-1}$) relative to the purely ionic compound, potassium glycinate (1600 cm.$^{-1}$), whereas the corresponding complexes of Ni(II) and Zn(II) show no change (1600 cm.$^{-1}$).[4,5] It is suggested that the

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TABLE I[a]

ASSIGNMENT OF INFRARED FREQUENCIES IN CM.$^{-1}$ OF BIS-(GLYCINO)-PLATINUM(II) COÖRDINATION COMPOUNDS

Type of vibration	*trans*-$Pt(NH_2CH_2CO_2)_2$	*cis*-$Pt(NH_2CH_2CO_2)_2$
	.....	1678(sh)
	1656(sh)	1658(sh)
(COO)A	1640(s)	1639(s)
NH_2 bending	1613(s)	1608(s)
CH_2 bending	1441(w)	1438(w)
		1426(w)
(COO^-)S	1381(m)	1377(s)
CH_2 wagging	1333(m)	1332(m)
NH_2 wagging	1295(s)	1300(m)
	.....	
	.....	1259(w)
CCN out-of-phase stretching	1247(m)	1213(m)
CH_2 twisting	1186(w)	1186(m)
NH_2 twisting	1025(w)	1035(w)
		1027(w)
	.....	
		977(w)
CH_2 rocking	964(w)	963(w)
CCN in-phase stretching	921(s)	919(s)
		913(m)
NH_2 rocking	796(m)	798(m)
	.....	774(m)
OCO^- wagging	752(w)	743(m)

[a] Abbreviations: s = strong; m = medium; w = weak; sh = shoulder. A = antisymmetric; S = symmetric.

TABLE II[a]

OBSERVED INFRARED FREQUENCIES IN CM.$^{-1}$ OF METAL-GLYCINE COMPLEXES

α-$Co(NH_2CH_2CO_2)_3 \cdot 2H_2O$	β-$Co(NH_2CH_2CO_2)_3 \cdot H_2O$	*trans*-$Pd(NH_2CH_2CO_2)_2$
3390m	3400s	.....
3175vs	3200vs	3210s
3090vs	3095vs	3090s
2930vw	2930vw	2930vw
2350vw	2350vw	2310vw
....	2150vw	2130vw
1636vs	1644vs	1645vs
....	1593vs	1617s
1426m	1428s	1447w
....	1395sh	1408w
1370vs	1372s	1377m
1333sh	1326m	1324m
....	1318m	1292m
1194m	1214m	1217m
1177m	1178w	1176m
1155m	1155w	1134w
....	1095w	1028m
1038w	1032vw	.....
950w	964m	963m
921s	920s	914s
....	815m	.....
774m	777m	779m
....	746w	730m

[a] Abbreviations: s = strong; m = medium; w = weak; sh = shoulder; v = very.

higher carboxylate stretching frequency found for the Pt(II) chelates is associated with a greater amount of covalent character in the metal-to-oxygen bond. Nevertheless, from a comparison with the C=O frequency of esters[4] it can be concluded that even in the case of the platinum(II) isomers, the bond between the central metal atom and the carboxylate group is for the most part ionic. The fact that in the Zn(II) and Ni(II) complexes the antisymmetric carboxylate stretching frequency has hardly shifted, as compared with potassium glycinate,[4,5] indicates that zinc(II) and nickel(II) form bonds of greatest ionic character with the carboxylate group.

As can be seen from Tables I and II significant differences exist in the spectra of the isomers of the complexes of Pt(II) and Co(III). It is to be noted that the spectra of *cis*-bis-(glycino)-platinum(II) and β-tris-(glycino)-cobalt(III) show a greater number of bands than their corresponding isomers. The well established geometrical isomerism of the bis-(glycino)-platinum(II) complexes is confirmed by their infrared spectra in accord with the selection rules. In the case of α- and β-tris-(glycino)-cobalt(III)isomers, the infrared spectra reveal that the red β-form has the *cis*(1,2,3)-configuration and the violet α-form has the *trans*(1,2,6)-structure. Although neither isomer possesses a center of symmetry, the greater number of bands observed for the β-compound suggests that the configuration of this isomer has a lower over-all order of symmetry as would be expected for a *cis*(1,2,3)-structure. This conclusion is in agreement with the ultraviolet studies of other investigators.[15,16] The similarity of the spectrum of bis-(glycino)-palladium(II) to that of *trans*-bis-(glycino)-platinum(II) confirms a *trans* configuration for the Pd(II) compound. All our attempts to prepare the reported *cis*-bis-(glycino)-palladium(II) isomer[10] yielded a substance which gave an infrared spectrum identical with that of the *trans* isomer.

Assignments.—Detailed assignments for *cis*- and *trans*-bis-(glycino)-platinum(II) are given in Table I.

The frequencies in the 3μ region are not listed because it is evident that these can be assigned to the NH_2 and CH_2 stretching vibrations.[4,5,17,18] Coördination of the glycino ligand to the central metal atom of the complex takes place through the nitrogen atom. Assignments of the other observed infrared frequencies of the isomeric bis-(glycino)-Pt(II) complexes shown in Table I are as follows:

1. In the spectrum of glycine[9] the antisymmetric COO^- vibration was assigned to the strong band at 1600 cm.$^{-1}$. This corresponds to the 1640 cm.$^{-1}$ (*trans*) and 1639 cm.$^{-1}$ (*cis*) bands of the Pt(II) complexes. This increase in frequency on formation of the O–M bond may result from one of the carbon-to-oxygen bonds having more double bond character than the other carbon-to-oxygen bond, although the bond between the central metal ion and the COO^- group is essentially electrostatic.[4,5]

2. The COO^- symmetric stretching vibration of glycine or of sodium glycinate[9] was assigned to a band at 1415 cm.$^{-1}$. The decrease in frequency of the corresponding vibration in the glycino-Pt(II) complexes, 1381 cm.$^{-1}$ (*trans*) and 1377 cm.$^{-1}$ (*cis*) also can be explained on the above assumption that one of the carbon-to-oxygen bonds has more double

bond character and the other more single bond character.

3. The NH_2 bending vibration is assigned to the band 1613 cm.$^{-1}$ (*trans*) and 1608 cm.$^{-1}$ (*cis*) which is higher than the corresponding NH_2 bending vibration at 1543 cm.$^{-1}$ for $HgNH_2Cl$.[6] In glycine the NH_3^+ vibration is also found to have a frequency higher than the corresponding vibration of $Hg(NH_3)_2Cl_2$[19] and therefore the above assignment of the NH_2 bending vibration is reasonable. These bands disappear on deuteration of the NH_2 group.

4. The CH_2 bending vibration is assigned to the bands 1441 cm.$^{-1}$ (*trans*), and 1433, 1426 cm.$^{-1}$ (*cis*). The corresponding vibration of glycine appears at almost the same frequency. The reason only one band appears for the *trans* complex and two for the *cis* arises from the fact that the *trans* form has a center of symmetry. In all the complexes studied two CH_2 bending vibrations are present, but in the *trans* isomer of bis-(glycino)-platinum(II) the vibration symmetric to the center is forbidden in the infrared absorption.

5. The CH_2 wagging vibration is assigned to the band at 1333 cm.$^{-1}$ (*trans*) and 1332 cm.$^{-1}$ (*cis*) and the corresponding vibration of glycine has practically the same frequency.

6. The NH_2 wagging vibration is assigned to the band at 1295 cm.$^{-1}$ (*trans*) and 1300 cm.$^{-1}$ (*cis*). Of these, the band of the *trans* complex is sharper than that of the *cis*. This probably is due to the fact that the former band is a single band, whereas the latter band may be a doublet. This difference is explained similarly as in the case of the CH_2 bending vibration.

7. The NH_2 twisting vibration is considered to be weak in intensity and has a frequency lower than the NH_2 wagging vibration. This vibration may be assigned to the weak bands at 1025 cm.$^{-1}$ (*trans*) and 1035, 1027 cm.$^{-1}$ (*cis*). These bands also disappear on deuteration, as is to be expected.

8. All the CH_2 and NH_2 deformation vibrations mentioned above couple with each other and this is particularly the case for the CH_2 and NH_2 rocking vibrations. In other words, the coupling of these rocking vibrations must be treated similarly to the coupling of the two CH_2 rocking vibrations in the molecule $ClCH_2$–CH_2Cl.[7] It is understandable, therefore, that the coupling of CH_2 and NH_2 rocking vibrations results in two frequencies separated by some 200 cm.$^{-1}$. Thus, these vibrations can be assigned as shown in Table I. It should be noted that the expressions for the types of vibrations in Table I are only approximate. For example, that of CH_2 rocking should be taken to mean CH_2 rocking mixed with NH_2 rocking.

9. It is to be expected that the C–C–N stretching vibrations change considerably on coördination. The in-phase vibration of glycine can be assigned to the 893 cm.$^{-1}$ band and the out-of-phase vibration to the band at 1030 cm.$^{-1}$. In the case of Pt(II) complexes, these can be assigned as shown in Table I.

10. The OCO wagging vibration of glycine was assigned to a band observed at 697 cm.$^{-1}$. The corresponding vibrations of the complexes have been assigned to the bands at 752 cm.$^{-1}$ (*trans*) and 743 cm.$^{-1}$ (*cis*).

By a comparison of the frequency values of glycine and molecules of related structure, detailed assignments can be made in a similar manner for complexes of Pd(II), Cu(II), Ni(II), Zn(II) and Co(III). In many cases confirmation of these assignments was made by deuterating the coördination compounds and observing the bands which decreased in intensity.

It may not be out of place to report here an interesting dehydration effect observed for bis-(glycino)-zinc(II) monohydrate. The infrared spectrum of this substance was reported in a previous paper.[5] Upon dehydration of the monohydrate its spectrum is changed noticeably with respect to the number of peaks, although the essential feature of the spectrum remains unchanged. The original spectrum is obtained by again hydrating the complex.

These observations may be explained on the basis of a change in the configuration of this complex. The X-ray investigation of Low[5] shows that in bis-(glycino)-zinc(II) monohydrate the glycine ligands are arranged in a planar form about the central zinc ion in *trans* position, water molecules occupying *trans* octahedral positions. In this structure, all the vibrations symmetric to the center are forbidden in the absorption and consequently the number of observed peaks will be reduced. Upon dehydration of the complex, the zinc(II) ion is left with a coördination number of four, thereby permitting the usual tetrahedral configuration of Zn(II). This structure, having no center of symmetry would, by the selection rule, have more infrared absorption bands than the structure of the mono hydrate.

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