TABLE III

THE COVALENT CHARACTER OF METAL-HALOGEN BONDS AND THE NET CHARGE ON THE CENTRAL METAL ATOM[a]

Compound	Covalent character	Net charge
K_2PdCl_6	0.57	0.58
K_2PdBr_6	.63	.22
K_2PtCl_6[b]	.56	.64
K_2PtBr_6[b]	.62	.28
K_2PtI_6[b]	.70	− .20
K_2PdBr_4	.40	.40
K_2PtBr_4	.43	.28

[a] Data at liquid nitrogen temperature were used except for K_2PdBr_4, for which those at Dry Ice temperature were employed. See ref. b to Table I.   [b] See ref. 1.

of the metal-ligand bonds in potassium hexahalopalladates(IV) and the corresponding hexahaloplatinates(IV). The same is true with potassium tetrabromopalladate(II) and tetrabromoplatinate-(II). This is quite understandable, because palladium and platinum have electronic configurations similar to each other and almost the same electronegativity.[21]

The covalent character, $1 - i$, amounting to as much as about 60% in potassium hexahalopalladates(IV) and hexahaloplatinates(IV) is considerably greater than about 40% found for potassium tetrabromopalladate(II) and tetrabromoplatinate-

(II). It is interesting to note that charges migrating toward the central metal ion in accordance to the covalent character, $1 - i$, of metal–ligand bonds partially neutralize the formal charge on the central ion so as to reduce it to a fraction of an electronic charge, whether the formal charge is four or two. This conclusion suggests a simple and useful method for the estimation of the covalent character of metal–ligand bonds in complexes involving transition metals.

$$\text{Covalent character} = \frac{\text{Formal charge} - \text{Net charge}}{\text{Coördination number}}$$

where the net charge $= 0—0.6e$. Collet[3] has studied the X-ray absorption spectra of bivalent and quadrivalent platinum complexes and found almost vanishing net charges on these platinum ions.

As mentioned above, the difference between the electronegativities of the central atom and the ligand is an important factor affecting the covalent character of the metal–ligand bonds and in consequence the net charge of the central metal atom. However, for a central metal atom having a number of ligands, also the formal charge, i.e., the charge on the central atom for a hypothetical 100% ionic structure, is an important factor in determining the extent of covalent character.

Infrared Spectra of Aqueous Solutions. I. Metal Chelate Compounds of Amino Acids[1]

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Thirty metal chelate compounds have been prepared from eight amino acids, and their infrared spectra have been measured in aqueous solution as well as in the crystalline state. The nature of the metal-carboxylate coördinate linkages, as well as the relative bond strengths, are deduced from the variation in the antisymmetric and symmetric carboxyl stretching frequencies. It is concluded that the frequency order of the carboxyl stretching vibration in a series of metal chelate compounds of the same ligand can be used as a measure of relative strengths of the metal–oxygen bonds if the comparison is made from data obtained from pure samples in the same physical state.

Introduction

Aqueous infrared spectra were first measured by Gore, et al.,[2] and the application of this technique to the determination of complexes in solution was reported recently.[3]

This paper is the first of a series of reports on infrared spectra of aqueous solutions of metal chelate compounds. The general purpose of this investigation is to obtain microscopic information on the nature of the bonds between metal ions and organic ligands in aqueous solution. In this study the carboxylate stretching frequencies are studied as a guide to the nature and extent of metal–

(2) R. C. Gore, R. B. Barnes and E. Peterson, Anal. Chem., 21, 382 (1949).
(3) L. H. Jones and R. A. Penneman, J. Chem. Phys., 22, 965 (1954); R. A. Penneman and L. H. Jones, ibid., 24, 293 (1956).

oxygen binding of alpha amino acid chelate compounds in aqueous solution.

The antisymmetric carboxyl stretching frequencies of the metal chelate compounds of amino acids have been interpreted in a variety of ways in recent years. For example, Sen, et al.,[4] and Saraceno, et al.,[5] claimed that the metal–oxygen bonds in Cu(II), Ni(II) and Zn(II) glycinates are essentially ionic since their frequencies are almost the same as those of potassium glycinate and sodium acetate. They also concluded that these metals use sp hybrid orbitals in forming linear bonds with the nitrogen atoms of the ligands. On the other hand, Rosenberg[6] concluded that the shift of the carboxyl band to higher frequencies in the order Ni(II) < Cu(II) < Pt(II) is an indication of in-

(4) D. N. Sen, S. Mizushima, C. Curran and J. V. Quagliano, J. Am. Chem. Soc., 77, 211 and 5508 (1955).
(5) A. J. Saraceno, I. Nakagawa, S. Mizushima, C. Curran and J. V. Quagliano, ibid., 80, 5018 (1958).
(6) A. Rosenberg, Acta Chem. Scand., 10, 840 (1956).

creasing covalent character of the metal–oxygen bond. Recently similar arguments have been made by Sawyer and McKinnie[7] for the infrared spectra of the metal chelate compounds of EDTA. It was therefore considered desirable to study further the nature of the metal–oxygen bond of these compounds by measuring infrared frequency shifts as a function of the metal ion.

It should be pointed out that all the previous measurements cited have been made in the crystalline state where the effect of hydrogen bonding on the carboxyl stretching frequency is appreciable. It has been shown[8] that the observed band shifts of the ammine complexes relative to the free ligand in the crystalline state are due to the coöperative effects of coördination and hydrogen bonding. A similar situation may be anticipated for metallic complexes of amino acids since the results of X-ray analysis on $Ni(glycine)_2 \cdot 2H_2O$,[9] $Zn(glycine)_2 \cdot H_2O$ and $Cd(glycine)_2 \cdot H_2O$[10] indicate that two glycine molecules coördinate to the metal atom by forming a *trans* square planar structure, while the other oxygens of the carboxyl group may be coördinated to an adjacent metal ion[10] or are hydrogen-bonded either to the amino group of the neighboring molecule[9] or to a water molecule of the hydrated crystal.[10] Although X-ray data are not available for the other compounds studied here, it was considered probable that such hydrogen bonding would occur whenever possible. Therefore, the observed carboxyl stretching frequencies must be interpreted with caution. Recently Cotton[11] also pointed out the importance of the effect of hydrogen bonding in the infrared spectra of metallic glycinates.

Experimental

Most of the compounds were prepared by standard procedures, and purity was checked by comparing the infrared spectra with published values. The following six compounds have not been reported previously.

Bis-(N-phenylglycino)-copper(II).—An ethanol solution of N-phenylglycine was added to sodium ethylate in ethanol. The sodium N-phenylglycinate thus obtained was dissolved in water and mixed with a solution of cupric chloride. A dark green finely divided crystalline solid precipitated immediately.

Anal. Calcd. for $Cu((C_6H_5)NHCH_2COO)_2$: C, 52.82; H, 4.43; N, 7.70. Found: C, 52.17; H, 4.70; N, 7.75.

Bis-(N-phenylglycino)-nickel(II) Trihydrate.—The same method as that given above for analogous Cu(II) chelate was employed. The product was obtained as a yellow-green finely divided solid.

Anal. Calcd. for $Ni((C_6H_5)NHCH_2COO)_2 \cdot 3H_2O$: C, 46.52; H, 5.37; N, 6.78. Found: C, 46.98; H, 5.65; N, 7.12.

Bis-(N-phenylglycino)-cobalt(II) Dihydrate.—The same method as that given above for the analogous Cu(II) chelate was employed. The product was obtained as a pink finely divided crystalline material.

Anal. Calcd. for $Co((C_6H_5)NHCH_2COO)_2 \cdot 2H_2O$: C, 48.61; H, 5.10; N, 7.09. Found: C, 48.06; H, 5.19; N, 7.25.

(7) P. T. Sawyer and J. M. McKinnie, *J. Am. Chem. Soc.*, **82**, 4191 (1960).

(8) J. Fujita, K. Nakamoto and M. Kobayashi, *ibid.*, **78**, 3295 (1956).

(9) A. J. Stosick, *ibid.*, **67**, 365 (1945).

(10) B. M. Low, F. L. Hirshfeld and F. M. Richards, *ibid.*, **81**, 4412 (1959).

(11) F. A. Cotton, "Modern Coördination Chemistry," Interscience Publishers, Inc., New York, N. Y., 1960, p. 387.
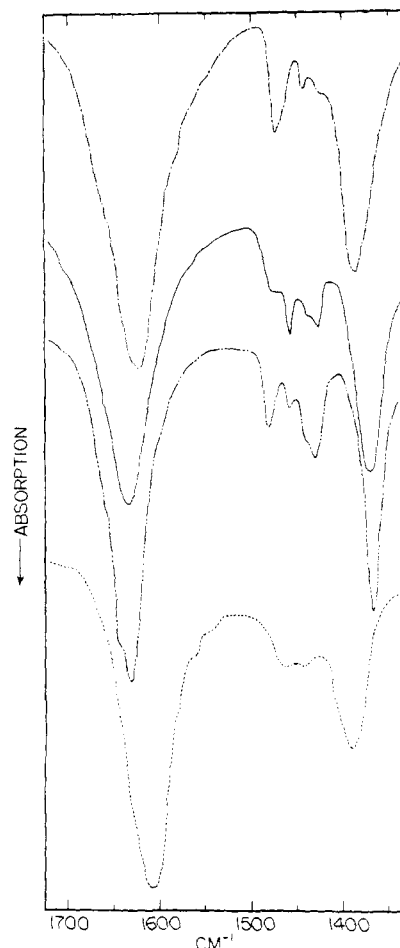
Fig. 1.—Infrared spectra of bis-N-methylglycinato-Cu(II) complex in various phases (curves reproduced photographically from original spectra): ———, hydrous crystal (deuterated); —·—·, anhydrous crystal (deuterated), —··—··, hydrated crystal; ········, D_2O solution.

Bis-(N,N-dimethylglycino)-nickel(II) Dihydrate.—An aqueous solution of N,N-dimethylglycine was added to a suspension of excess nickel carbonate and warmed on a water-bath. After the reaction had subsided, the excess nickel carbonate was filtered off and the solution was condensed and cooled to induce crystallization. The bluish green crystalline solid thus obtained was recrystallized from water.

Anal. Calcd. for $Ni((CH_3)_2NCH_2COO)_2 \cdot 2H_2O$: C, 32.13; H, 6.74; N, 9.38. Found: C, 32.31; H, 6.91; N, 9.65.

Bis-(d,l-isoleucino)-nickel(II) Dihydrate.—d,l-Isoleucene (1/50 mole) was dissolved in 40 ml. of 0.5M NaOH solution and then added to an aqueous solution of 1/100 mole of nickel chloride. The product precipitated as a light blue finely divided crystalline solid.

Anal. Calcd. for $Ni(C_2H_5CH(CH_3)CH(NH_2)COO)_2 \cdot 2H_2O$: C, 40.58; H 7.95; N, 7.89. Found: C, 40.47; H, 8.05; N, 7.58.

Bis-(d,l-valino)-nickel(II) Dihydrate.—The same procedure as that described above for the Ni(II) isoleucine chelate compound was employed. The product was isolated as a light blue crystalline solid.

Anal. Calcd. for $Ni((CH_3)_2CHCH(NH_2)COO)_2 \cdot 2H_2O$: C, 36.68; H, 7.39; N, 8.58. Found: C, 37.46; H, 7.54; N, 8.87.

Bis-(β-alanino)-nickel(II) Dihydrate.—An aqueous solution of 1/100 mole of β-alanine was heated with excess nickel carbonate on a steam-bath for about an hour. After the mixture was filtered and cooled, the product separated as a light blue crystalline solid.

Anal. Calcd. for $Ni(NH_2CH_2CH_2COO)_2\cdot2H_2O$: C, 26.60; H, 5.95; N, 10.34. Found: C, 26.87; H, 5.76; N, 10.92.

Dehydration of Compounds.—All of the substances obtained as hydrates were converted to anhydrous materials by gentle heating. Absence of water was checked by the infrared spectra and lack of reduction of weight of the sample.

Spectral Measurements.—Infrared spectra were measured with a Perkin–Elmer Model 21 infrared spectrophotometer fitted with sodium chloride optics. For measurement in aqueous solutions 0.1 ml. cells of 0.019 mm. thickness of barium fluoride windows were employed. All the aqueous solutions were made with 99.5% D_2O, which was purchased from New England Nuclear Corporation, Boston, Massachusetts. The concentrations employed were approximately 3 to 15% by weight. Spectra of the solids were measured in potassium bromide disks. As examples of the quality of the aqueous infrared spectra obtained by this technique, sample spectra of the carboxyl bands are illustrated in Fig. 1. The accuracy of the wave numbers reported is ±3 cm.$^{-1}$ in this range of the spectrum.

Results and Discussion

Of the various vibrational modes of the amino acids, only the carboxyl stretching frequencies are discussed below since they are usually identified with certainty and are the most sensitive to a change in the strength of the metal–oxygen interaction. It should be noted, however, that in amino acids and their weak metal chelate compounds, the antisymmetric carboxyl stretching frequencies are very close to the NH_3^+ and NH_2 deformation frequencies. In order to avoid any misassignments and frequency errors due to overlapping of these bands, the carboxyl stretching frequencies were obtained from the solids recrystallized from the D_2O solutions whenever possible. Care also was taken to distinguish the symmetric carboxyl stretching bands from the CH_3 degenerate deformation vibration. The purpose of this work is to find the relation between the carboxyl stretching frequencies and the strength of the metal–oxygen interaction. However, the frequencies are also sensitive to the effect of hydrogen bonding on the carboxyl group. Therefore, it is desirable to examine the latter effect before drawing conclusions on the coördinate bonds.

In order to study the effect of hydrogen bonding, the infrared spectra of each compound were measured in aqueous solution, in the hydrated crystalline state and in the anhydrous crystalline state. It was not possible to do so for all cases, since some solid complexes exist only in the anhydrous or hydrated form and since some are not soluble enough to allow infrared measurements of their aqueous solutions. The results of the measurements are given in Table I.

In the anhydrous crystalline state, only the CO—HN or CO—DN type hydrogen bonds are possible. In D_2O solutions, only the CO—DO type bonds are probable, whereas both types may coexist in the hydrous crystalline state. It is hardly possible, however, to compare the strength of hydrogen bonds in various physical states without detailed crystal structure data. Nevertheless, the importance of the hydrogen bonding effect is strikingly demonstrated in Table I, which indicates that the fluctuation of the frequencies by a change of physical state ranges 10 to 30 cm.$^{-1}$ in these compounds.

If the comparison is made in the same physical state, however, Table I always gives the same frequency order for a series of the metals regardless of the kind of the ligand. In other words, the antisymmetric frequencies increase and symmetric frequencies decrease, and the separation between two frequencies increases in this order

$$Ni(II) < Zn(II) < Cu(II) < Co(III) < Pd(II) \approx$$
$$Pt(II) < Cr(III)$$
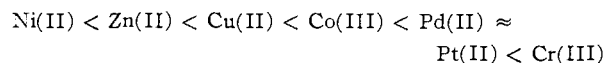
The exception is seen in the glycinato and β-alanino complexes of Ni(II), Zn(II) and Cu(II) in the hydrated solid state. In general, however, these results indicate that in these compounds the effect of coördination is still the major factor in determining the frequency order in a given physical state.

Among the three physical states employed for the measurement of the spectra, aqueous solution is most appropriate for a comparison of the effect of coördination since the effect of hydrogen bonding is alike throughout all the compounds (*i.e.*, the metal chelate molecules or ions are separated so that intermolecular association is minimized, and the chelates are hydrated to a maximum extent because of the availability of solvent molecules). In the solid state the influence of hydrogen bonding would vary from metal to metal in an unpredictable way, since it depends on spacing of water, metal ion and ligand in the crystal lattice as well as on degree of hydration. Since some compounds are not soluble enough to allow infrared measurements, the information obtained from the solid state are still useful for purposes of qualitative comparison.

It is generally recognized that the coördinated bonds are intermediate between purely ionic and purely covalent bonds. In this respect, it is interesting to note that the observed carboxyl stretching frequencies (and their separations) are intermediate between those of crystalline sodium acetate[12] (1578, 1414 cm.$^{-1}$) and those of the acetic acid monomer in the gaseous state[13] (1770, 1284, 1184 cm.$^{-1}$). In crystalline sodium acetate, the carboxylate ion is expected to be almost symmetrical[14]; whereas, in the acetic acid monomer, it is extremely asymmetric because of the presence of the covalent OH bond.

As is seen in Table I, the antisymmetric stretching band shifts to higher frequency, and the symmetric stretching band shifts to lower as the metal is changed in the above order. This result can best be explained if one assumes that the covalent character of the metal–oxygen bond, of a compound of the type indicated by formula I, increases in the order of the metals given above. This behavior results from the fact that an increase of covalent character leads to more asymmetric structure of the carboxyl group and results in an increase in the frequency separation of the two carboxyl bands.

(12) K. Itoh and H. J. Bernstein, *Can. J. Chem.*, **34**, 170 (1956).

(13) W. Weltner, Jr., *J. Am. Chem. Soc.*, **77**, 3941 (1955).

(14) Although no detailed structural data are available on sodium acetate, the X-ray analysis on sodium formate (W. H. Zachariasen, *J. Am. Chem. Soc.*, **62**, 1011 (1940)) definitely indicates that the formate ion is symmetric.

TABLE I

Carboxyl Stretching Frequencies and their Separation in the Metal Chelate Compounds of Various Amino Acids $(Cm.^{-1})$

Compounds[a]	Antisymmetric COO stretching			Symmetric COO stretching			Separation		
	D_2O solution	Hydrated crystal	Anhydrous solid	D_2O solution	Hydrated crystal	Anhydrous solid	D_2O solution	Hydrated crystal	Anhydrous solid
Glycine	1615	..	1595	1411	..	1399	204	..	196
$Ni(NH_2 \cdot CH_2 \cdot COO)_2 \cdot 2H_2O$	1589	1609	1583	1413	1408	1400	176	201	183
$Zn(NH_2 \cdot CH_2 \cdot COO)_2 \cdot H_2O$	1594	1598	1603	1407	1400	1384	187	198	219
$Cu(NH_2 \cdot CH_2 \cdot COO)_2 \cdot H_2O$	1604	1593	1607	..	1387	1366	..	206	241
α-$Co(NH_2 \cdot CH_2 \cdot COO)_3 \cdot 2H_2O$	1624	1625	..	1366	1364	..	258	261	..
β-$Co(NH_2 \cdot CH_2 \cdot COO)_3 \cdot H_2O$	..	1636[b]	..	..	..	..	..	..	..
tr.-$Pd(NH_2 \cdot CH_2 \cdot COO)_2$	..	..	1642[b]	..	..	1373[b]	..	..	269[b]
tr.-$Pt(NH_2 \cdot CH_2 \cdot COO)_2$	..	..	1643[b]	..	..	1374[b]	..	..	269[b]
$Cr(NH_2 \cdot CH_2 \cdot COO)_3 \cdot H_2O$	..	1659⌉ 1649[b] 1639⌋	1658⌉ 1651[b] 1643⌋	..	1381⌉ 1373[b] 1365⌋	1372[b]	..	276[b]	279[b]
α-Alanine	1612	..	1595	1413	..	1406	199	..	189
$Ni\{NH_2 \cdot CH(CH_3) \cdot COO\}_2 \cdot 4H_2O$	1581	1591	1589	1412	1414	1420	169	177	169
$Zn\{NH_2 \cdot CH(CH_3)COO\}_2 \cdot H_2O$	1592	1602	1605	1410	1392	1393	182	210	212
$Cu\{NH_2 \cdot CH(CH_3)COO\}_2 \cdot H_2O$	1601	1606	1620	..	1386	1386	..	220	234
$Co\{NH_2 \cdot CH(CH_3)COO\}_3 \cdot H_2O$	1612	1632[b]	..	..	1383[b]	..	..	249[b]	..
tr.-$Pt\{NH_2 \cdot CH(CH_3)COO\}_2$	..	..	1641 1647[b] 1653	..	..	1382[b]	..	..	265[b]
$Cr\{NH_2 \cdot CH(CH_3)COO\}_3 \cdot H_2O$	..	1656[b]	..	..	1381 1364[b] 1347	..	..	292[b]	..
β-Alanine	1578	..	1570	1405	..	1399	173	..	171
$Ni(NH_2 \cdot CH_2 \cdot CH_2 \cdot COO)_2 \cdot 2H_2O$	..	1607[b]	1560[b]	..	1413[b]	1402[b]	..	194[b]	158
$Cu(NH_2 \cdot CH_2 \cdot CH_2 \cdot COO)_2 \cdot 6H_2O$	1561	1562	1587	1406	1401	1412	155	161	175
dl-Valine	1610	..	1585	1410	..	1416	200	..	169
$Ni\{(CH_3)_2 \cdot CH \cdot CH \cdot NH_2 \cdot COO\}_2 \cdot 2H_2O$	..	1587[b]	1596[b]	..	1408[b]	..	..	179[b]	..
$Cu\{(CH_3)_2 \cdot CH \cdot CH \cdot NH_2 \cdot COO\}_2$	..	..	1619[b]	..	..	1387[b]	..	..	232[b]
dl-Iso-leucine	1613	..	1585	1408	..	1417	205	..	168
$Ni\{CH_3 \cdot CH_2 \cdot CH(CH_3)CH \cdot NH_2 \cdot COO\}_2 \cdot 2H_2O$	..	1591[b]	..	..	1411[b]	..	..	180[b]	..
$Cu\{CH_3 \cdot CH_2 \cdot CH(CH_3)CH \cdot NH_2 \cdot COO\}_2 \cdot H_2O$	..	1623[b]	..	..	1391⌉ 1388[b] 1385⌋	..	..	235[b]	..
N-Methylglycine	1616	..	1614	1408	..	1413	208	..	201
$Ni\{(CH_3)_2NH \cdot CH_2 \cdot COO\}_2 \cdot 2H_2O$	1590	1607	1600	1408	1398	1418	182	209	182
$Cu\{(CH_3)NH \cdot CH_2 \cdot COO\}_2 \cdot 2H_2O$	1606	1635	1624	1390	1369	1386	216	266	238
N-Phenylglycine	..	..	1563[b]	..	..	1380[b]	..	..	183[b]
$Ni\{(C_6H_5)NH \cdot CH_2 \cdot COO\}_2 \cdot 3H_2O$	..	1599[b]	..	..	1389[b]	..	..	210[b]	..
$Co\{(C_6H_5)NH \cdot CH_2 \cdot COO\}_2 \cdot 2H_2O$	..	1602[b]	..	..	1388[b]	..	..	214[b]	..
$Cu\{(C_6H_5)NH \cdot CH \cdot COO\}_2 \cdot$	..	..	1616[b]	..	..	1385 1373[b] 1360	..	..	243[b]
N,N-Dimethylglycine	1623	..	1631	1402	..	1396	221	..	235
$Ni\{(CH_3)_2N \cdot CH \cdot COO\}_2 \cdot 2H_2O$	1606 1598 1590	1599[b]	1606[b]	1410	1405[b]	1430[b]	188	194[b]	176[b]
$Cu\{(CH_3)_2N \cdot CH \cdot COO\}_2 \cdot 3H_2O$	1613	1614[b]	1630[b]	1387	1376[b]	1384 1371[b] 1358	226	238[b]	259[b]

[a] Formulas of the compounds are given for non-deuterated forms. [b] Frequencies obtained from non-deuterated crystals.
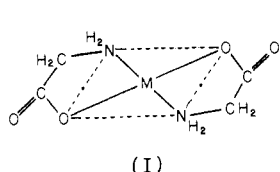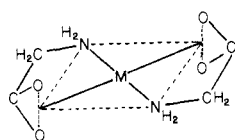
(I)   (II)

Such behavior is not compatible with the theory of symmetrical coördination of the carboxylate ion of α-amino acids advanced recently,[2] represented by formula II. If such were the case, the antisymmetric and symmetric stretching bands would be expected to shift in the same direction with an increase in coördinate bond strength. X-Ray structural data indicate that symmetrical carboxy groups exist in certain metal acetates such as M^{II}-$(CH_3COO)_4 \cdot 2H_2O$ ($M^{II} = Cr$, Cu)[15] and $M_4^{II}O$-$(CH_3COO)_6$ ($M^{II} = Be$, Zn).[16,17] It has been indeed found that for these compounds, both of the carboxyl bands shift in the same direction with a change in the metal, as is shown in Table II. In this case the equivalence of the binding of the two carboxylate oxygens is assured by the symmetry of the crystal lattice and the binding of each carboxyl group to two metal ions.

TABLE II

THE COO STRETCHING FREQUENCIES IN SYMMETRICAL COÖRDINATION

| Compound | Frequencies[b] of COO⁻ bands, cm.⁻¹ | |
	Antisymmetric	Symmetric
Cr(ac)₄·2H₂O[a]	1575	1420
Cu(ac)₄·2H₂O	1605	1425
Be₄O(Ac)₆	1603	1447
Zn₄O(ac)₆	1639	1489

[a] ac, Acetate anion. [b] The above frequencies were obtained in KBr disks.

Finally, it is interesting to note that the order of $Cu(II) > Zn(II) > Ni(II)$ obtained from infrared data in Table I is different from the usual stability order, $Cu(II) > Ni(II) > Zn(II)$.[18] In this connection, it should be pointed out that the order obtained in this work represents the order of the interaction between the carboxyl group and the metal ion and therefore need not be exactly the same as the stability order, which for alpha amino acids actually applies to the reaction

(15) J. N. van Niekerk and F. R. L. Schoening, *Acta Cryst.*, **6**, 227, 501 (1953).

(16) W. H. Bragg and G. T. Morgan, *Proc. Roy. Soc. (London)*, **A104**, 437 (1923).

(17) H. Koyama, Y. Saito and H. Kuroya, *Bull. Chem. Soc. Japan*, **127**, 113 (1954).

(18) D. P. Mellor and L. E. Maley, *Nature*, **159**, 379 (1947); **161**, 436 (1948).
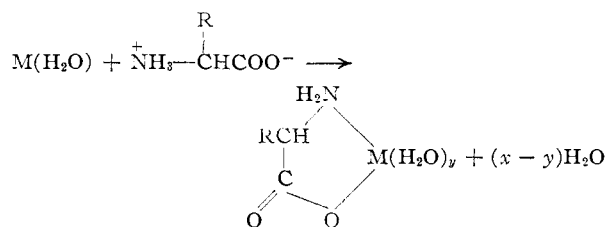
and to successive reactions of the same type. In other words, the stability constants involve combination of the metal ion with both nitrogen and oxygen donor groups. Thus, the infrared measurements follow the relative stabilities of specific bonds, whereas the thermodynamic stability order gives the relative order of energies of interaction for the sum total of all the coördinate bonds formed about the metal ion.

It should also be pointed out that a metal such as Co(III) would interact very strongly with the amino groups and much more weakly with the carboxylate groups, while a metal ion such as Cr(III) would interact somewhat less with nitrogen and relatively more with oxygen. It is seen, therefore, that the order of carboxylate interaction could be Cr(III) > Co(III) and the stability order could easily be Co(III) > Cr(III). The same reasoning would explain why the carboxylate interaction was found to be stronger for Zn(II) than for Ni(II) in disagreement with the usual, or "overall" stability order. In this case, however, there is also the possibility that there is an effect due to a difference in coördination requirements of these two metal ions. X-Ray analysis of Ni(II) glycinate dihydrate[5] shows that two water molecules are tightly bound to the Ni(II) atom, thus giving a tetragonal or distorted octahedral, configuration. (Ni–O distance, 2.08 Å.; Ni–OH₂ distance, 2.12 Å.). On the other hand, the Zn(II) may not be so strongly coördinated to water. Thus one would expect Ni–O (carboxylic group) bonds to be weakened relative to the Zn–O bonds by competitive bond formation with water in the crystalline state and in aqueous solution.

It is apparent from the above discussion that the examination of infrared spectra in aqueous solution, as well as in the solid state, provides valuable microscopic evidence on the nature of the coördinate linkages in compounds of this type—evidence that cannot be obtained from thermodynamic measurements or from other bulk properties of metal ions and complexes in solution.