Contribution from the Department of Chemistry and the
Radiation Laboratory,[1] University of Notre Dame, Notre Dame, Indiana

Infrared Spectra of Complexes of Metal Halides with Esters of Amino Acids

By M. PAULITA SPRINGER and COLUMBA CURRAN

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The infrared spectra of bis complexes of methyl and ethyl glycinate with dihalides of platinum, palladium, copper, zinc, cobalt, and cadmium and of DL-methyl-α-alaninate with dihalides of palladium and copper in the solid state indicate the formation of only nitrogen-to-metal bonds by the organic ligands. The zinc, cadmium, and cobalt complexes appear to be tetrahedral. Mono complexes were isolated of all three esters with cadmium bromide, of the latter two esters with cupric chloride, and of ethyl glycinate with nickel(II) chloride (hydrate); shifts in the carbonyl peaks in the spectra of these solid mono complexes and of the bis complexes of methyl and ethyl glycinate with nickel chloride indicate chelation. The NH_2 stretching and bending frequencies were observed to decrease and the NH_2 rocking frequencies to increase with increasing strengths of the nitrogen-to-metal bonds. Spectral evidence is presented for chelation of neutral glycine with copper in bis-(glycine)-copper(II) trichlorocuprate(I).

Esters of α-amino acids are potential chelating agents; coordination of both the nitrogen and carbonyl oxygen atoms with a metal atom results in a five-membered ring. This chelation is expected to be accompanied by decreases in the frequencies of the NH_2 and C═O stretching vibrations and therefore to be revealed by infrared absorption spectra of the solid complexes.

Infrared spectra of complexes of metal halides with methyl anthranilate,[2] an ester of an arylamino acid, and with ethyl picolinate[3] have been obtained previously in this laboratory. The former have the disadvantages of six-membered rings and destabilization by the blocking of resonance. The latter have the advantages of planar ligands and no intramolecular hydrogen bonds in the free esters; their spectra, however, are more complex and much less informative than those of complexes of esters of α-amino acids.

Complexes of metal halides with esters of amino acids previously isolated include dichlorobis-(methyl glycinate)-platinum(II) and dichlorobis-(ethyl glycinate)-platinum(II), which were prepared by esterifying bis-(glycinato)-platinum(II) in acid solutions of methanol and ethanol.[4] Bielig and Bayer[5] reported the spectrum from 2 to 9 μ of a solid which they designated as dihydroxybis-(L-ethyl leucinate)-iron(III) chloride dihydrochloride. The carbonyl peak of the ester was not shifted with reference to the free ester, indicating no chelation; the 3-μ region of the spectrum was obscured by the broad absorption band of the hydroxyl groups.

Klotz and co-workers[6] have concluded from the visible absorption spectrum of a water solution of methyl glycinate and the copper(II) ion in a 2:1 ratio that only nitrogen-to-copper bonds are formed. A similar conclusion was reached by Li and co-workers[7] from the magnitudes of the formation constants of nickel(II) and copper(II) complexes with ethyl glycinate. Kroll[8] and Bender and Turnquest[9] concluded from experiments on the acceleration of hydrolysis of ethyl glycinate by copper(II) and heavy metal ions that the ester molecules chelate with these ions.

The present investigation is concerned with solid complexes of methyl glycinate, ethyl glycinate, and methyl-α-alaninate with halides of cobalt(II), nickel(II), copper(II), zinc, cadmium, palladium(II), and platinum(II).

Experimental

Preparation and Purification of Compounds. Methyl Glycinate, Ethyl Glycinate, and Methyl DL-α-Alaninate were obtained from the hydrochlorides (Nutritional Biochemicals Co. products) by the methods of Fischer[10] and Viscontini[11]; the boiling points of the esters were, respectively 65° (45 mm.), 57° (25 mm.), and 64° (52 mm.). White crystals of a condensation product, 2,5-diketopiperazine, began to separate from methyl glycinate after about 10 hr., from the ethyl ester after 2 days, and condensation products of methyl DL-α-alaninate appeared after 3 days. The N-deuterated esters of glycine were prepared by dissolving 0.15 g. of the hydrochloride in 5 ml. of warm 99.5% deuterium oxide, permitting this solution to stand for 30 min., and proceeding to the ester by the method of Fischer. Infrared spectra showed that deuteration was not quite complete.

The metal complexes were prepared as indicated later. With the exceptions noted, each complex was collected on a sintered glass disk, washed with small amounts of fresh solvent and anhydrous ether, and dried at room temperature in a vacuum desiccator over phosphoric anhydride for a minimum of 6 hr. The bromide of cadmium was used because of the low solubility of the chloride in methanol and ethanol.

Dichlorobis-(methyl glycinate)-zinc was prepared by mixing dropwise with stirring equal volumes (5 ml.) of anhydrous ether solutions containing 0.003 mole of zinc chloride and 0.006 mole of methyl glycinate. A white precipitate formed immediately. An identical compound was obtained by using an excess of zinc chloride or absolute ethanol as the solvent. **Dichlorobis-(ethyl glycinate)-zinc** was prepared in the same manner.

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[1] The Radiation Laboratory is operated by the University of Notre Dame under contract with the Atomic Energy Commission.

[2] M. A. G. Hill and C. Curran, Abstracts, 132nd National Meeting of the American Chemical Society, New York, N. Y., Sept., 1957, p. 14N.

[3] M. R. Brennan and C. Curran, Abstracts, 139th National Meeting of the American Chemical Society, St. Louis, Mo., March, 1961, p. 8R.

[4] G. Wallin, *Ofvers. Akad. Stockholm*, **49**, 21 (1892).

[5] H. J. Bielig and E. Bayer, *Ber.*, **88**, 1158 (1955).

[6] I. M. Klotz, I. L. Faller, and J. M. Urquhart, *J. Phys. Chem.*, **54**, 18 (1950).

[7] J. M. White, R. A. Manning, and N. C. Li, *J. Am. Chem. Soc.*, **78**, 2367 (1956).

[8] H. Kroll, *ibid.*, **74**, 2036 (1952).

[9] M. L. Bender and B. W. Turnquest, *ibid.*, **79**, 1889 (1957).

[10] E. Fischer, *Ber.*, **34**, 444 (1901).

[11] M. Viscontini, *Compt. rend.*, **221**, 445 (1945).

Anal. Calcd. for $ZnCl_2(C_3H_7NO_2)_2$: Zn, 20.79; Cl, 22.55. Found: Zn, 20.73; Cl, 22.53. Calcd. for $ZnCl_2(C_4H_9NO_2)_2$: Zn, 19.09; Cl, 20.70. Found: Zn, 18.87; Cl, 20.66.

Partially deuterated complexes were prepared by mixing ether solutions of the deuterated ester with ether solutions of zinc chloride. The ether used in this preparation was dried over freshly cut sodium and then shaken with several drops of heavy water.

Dichlorobis-(methyl glycinate)-cobalt(II) was prepared by mixing dropwise with stirring ethanol solutions (3 ml.) containing 0.003 mole of anhydrous cobalt(II) chloride and 0.007 mole of methyl glycinate. Blue crystals separated as the solution was stirred. **Dichlorobis-(ethyl glycinate)-cobalt(II) and dibromobis-(ethyl glycinate)-cobalt(II)** were prepared similarly, using halide–ester ratios of 1:2. Attempts to prepare mono complexes were unsuccessful.

Anal. Calcd. for $CoCl_2(C_3H_7NO_2)_2$: Co, 19.13; Cl, 23.02. Found: Co, 18.94; Cl, 23.16. Calcd. for $CoCl_2(C_4H_9NO_2)_2$: Co, 17.54; Cl, 21.10. Found: Co, 17.75; Cl, 21.10. Calcd. for $CoBr_2(C_4H_9NO_2)_2$: Co, 13.87; Br, 37.60. Found: Co, 14.26; Br, 37.76.

Dibromobis-(methyl glycinate)-cadmium was prepared by the dropwise addition of a solution of 0.003 mole of anhydrous cadmium bromide in 10 ml. of methanol and a solution of 0.007 mole of methyl glycinate in 4 ml. of methanol to 2 ml. of the same solvent with stirring. White crystals formed after several minutes. **Dibromobis-(ethyl glycinate)-cadmium** was prepared in a similar manner. **Dibromo-(methyl glycinate)-cadmium** was obtained by mixing methanol solutions containing equivalent quantities of the bromide and ester, and **dibromo-(ethyl glycinate)-cadmium and dibromo-(methyl α-alaninate)-cadmium** were prepared similarly using ethanol as the solvent.

Anal. Calcd. for $CdBr_2(C_3H_7NO_2)$: Cd, 31.11; Br, 44.23. Found: Cd, 31.35; Br, 35.34. Calcd. for $CdBr_4(C_3H_7NO_2)_2$: Cd, 24.96; Br, 35.48. Found: Cd, 25.00; Br, 35.34. Calcd. for $CdBr_2(C_4H_9NO_2)$: Cd, 29.94; Br, 42.5. Found: Cd, 29.95; Br, 42.18. Calcd. for $CdBr_2(C_4H_9NO_2)_2$: Cd, 23.49; Br, 33.40. Found: Cd, 23.53; Br, 33.09. Calcd. for $CdBr_2(\alpha\text{-}C_5H_9NO_2)$: Cd, 29.94; Br, 42.58. Found: Cd, 29.96; Br, 42.36.

Dichlorobis-(methyl glycinate)-nickel(II) was prepared by the dropwise addition of a solution of 0.008 mole of methyl glycinate in 2 ml. of absolute ethanol to a solution of 0.004 mole of dried nickel(II) chloride in 10 ml. of the same solvent. The bright green solution was evaporated under reduced pressure to a volume of about 2 ml. and a light green powder separated as the solution was stirred. **Dichlorobis-(ethyl glycinate)-nickel(II)** was prepared similarly except that the light green crystals separated slowly without evaporation of the solution. **Dichloro-(ethyl glycinate)-nickel(II) monohydrate** was prepared similarly using a halide–ester ratio of 1:1. The solution was evaporated under reduced pressure to a green gum and 2 ml. of warm *n*-propyl alcohol was added. Yellow-green crystals separated over a period of several days. Attempts to prepare pure complexes of methyl α-alaninate were unsuccessful.

Anal. Calcd. for $NiCl_2(C_3H_7NO_2)_2$: Ni, 19.05; Cl, 23.04. Found: Ni, 19.97; Cl, 22.81. Calcd. for $NiCl_2(C_4H_9NO_2)_2$: Ni, 17.47; Cl, 21.11. Found: Ni, 17.59; Cl, 21.12. Calcd. for $NiCl_2(C_4H_9NO_2)H_2O$: Ni, 23.41; Cl, 28.28; C, 19.16; H, 4.42. Found: Ni, 23.73; Cl, 28.16; C, 19.40; H, 4.42.

Dichlorobis-(methyl glycinate)-palladium(II) was prepared by mixing dropwise with stirring water solutions (3 ml.) of a mixture of 0.002 mole of anhydrous palladium(II) chloride and 0.004 mole of sodium chloride and 0.004 mole of methyl glycinate. Yellow-orange crystals separated as the solution was stirred. **Dichlorobis-(ethyl glycinate)-palladium(II) and dichlorobis-(methyl α-alaninate)-palladium(II)** were prepared similarly. Attempts to prepare the mono complexes were unsuccessful and in the case of methyl α-alaninate the use of potassium chloride in the place of sodium chloride resulted in the hydrolysis of the ester and the formation of the reddish salt, potassium dichloro-(α-alaninato)-palladium(II). Almost complete deuteration of the bis complexes was accomplished by using heavy water in the foregoing procedures. Allowing the light complexes to stand in heavy water for several days resulted in a negligible deuteration.

Anal. Calcd. for $PdCl_2(C_3H_7NO_2)_2$: Pd, 29.99; Cl, 19.93. Found: Pd, 29.82; Cl, 19.89. Calcd. for $PdCl_2(C_4H_9NO_2)_2$: Pd, 27.80; Cl, 18.47. Found: Pd, 27.73; Cl, 18.22. Calcd. for $PdCl_2(\alpha\text{-}C_4H_9NO_2)_2$: Pd, 27.80; Cl, 18.47. Found: Pd, 27.48; Cl, 18.47.

Dichlorobis-(methyl glycinate)-platinum(II) and dichlorobis-(ethyl glycinate)-platinum(II) were prepared similarly to the palladium complexes except that potassium tetrachloroplatinate(II) was used, and the light yellow complexes formed very slowly as the solution was stirred for 3 hr. Deuterated complexes were obtained by the use of heavy water in the preparations. Mono complexes of all three esters were not obtained and no bis complex of methyl α-alaninate was obtained. Mixing water solutions of potassium tetrachloroplatinate(II) and methyl α-alaninate resulted in the hydrolysis of the ester and the formation of the yellow salt, potassium dichloro-(α-alaninato)-platinum(II).

Anal. Calcd. for $PtCl_2(C_3H_7NO_2)_2$: C, 16.23; H, 3.18; Cl, 15.96. Found: C, 16.25; H, 3.22; Cl, 16.00. Calcd. or $PtCl_2(C_4H_9NO_2)_2$: Pt, 41.33; Cl, 15.05. Found: Pt, 41.31; Cl, 15.07.

Dichlorobis-(methyl glycinate)-copper(II) was prepared by mixing dropwise with stirring ethanol solutions (1.5 ml.) of 0.003 mole of anhydrous copper(II) chloride and 0.006 mole of methyl glycinate. A blue precipitate formed almost immediately in the green solution. **Dibromobis-(methyl glycinate)-copper(II) and dichlorobis-(ethyl glycinate)-copper(II)** were prepared similarly. These complexes decompose in several weeks. Two forms of **dichlorobis-(methyl α-alaninate)-copper(II)** were isolated. Using a halide–ester ratio of 1:2 a blue-green complex was obtained. A bright blue complex was obtained by using a halide:ester ratio of 3:7. Both complexes are stable. **Dichloro-(ethyl glycinate)-copper(II)** was prepared by mixing dropwise with stirring a solution of 0.020 mole of anhydrous copper(II) chloride in 10 ml. of methanol and a solution of 0.016 mole of ethyl glycinate in 2 ml. of methanol. Silky blue-green crystals separated from the brown solution as the mixture was evaporated under reduced pressure. **Dichloro-(methyl α-alaninate)-copper(II)** was prepared similarly using a halide:ester ratio of 5:4. The bright green complex formed immediately. Both complexes decompose slowly.

Anal. Calcd. for $CuCl_2(C_3H_7NO_2)_2$: Cu, 20.32; Cl, 22.68. Found: Cu, 20.90; Cl, 22.62. Calcd. for $CuBr_2(C_4H_9NO_2)_2$: Cu, 14.79. Found: Cu, 15.04. Calcd. for $CuCl_2(C_4H_9NO_2)_2$: Cu, 18.65; Cl, 20.81. Found: Cu, 18.74; Cl, 21.17. Calcd. for $CuCl_2(\alpha\text{-}C_4H_9NO_2)_2$ (blue-green): Cl, 20.81. Found: Cl, 20.80. Calcd. for $CuCl_2(\alpha\text{-}C_4H_9NO_2)_2$ (blue): Cu, 18.65; Cl, 20.81. Found: Cu, 18.48; Cl, 20.74. Calcd. for $CuCl_2(C_4H_9NO_2)$: C, 20.22; H, 3.82; Cu, 26.74; Cl, 29.85. Found: C, 20.08; H, 3.74; Cu, 26.31; Cl, 29.81. Calcd. for $CuCl_2(\alpha\text{-}C_4H_9NO_2)$: Cu, 26.74; Cl, 29.85. Found: Cu, 26.54; Cl, 29.55.

Bis-(glycine)-copper(II) trichlorocuprate(I) was prepared by adding 0.010 mole of bis-(glycinato)-copper(II) monohydrate to a mixture of 0.02 mole of concentrated hydrochloric acid and 0.01 mole of copper(I) chloride in 5 ml. of water. The mixture was heated on a water bath until the copper(I) chloride dissolved. The gray-green powder separated in almost quantitative yield as the solution was cooled. The complex was not washed. Partial deuteration was obtained by adding a small amount of the complex to heavy water, heating to effect solution, and cooling.

Anal. Calcd. for $[Cu^{II}(C_2H_5NO_2)_2][Cu^{I}Cl_3]$: C, 12.57; H, 2.63; Cu, 33.12; Cl, 27.73. Found: C, 12.77; H, 2.73; Cu, 32.80; Cl, 27.74.

Dichlorobis-(*n*-butylamine)-zinc was prepared by mixing dropwise with stirring ether solutions (30 ml.) of 0.01 mole of anhydrous zinc chloride and 0.02 mole of Eastman White Label *n*-butylamine. The complex separated in shiny white waxy plates.

TABLE I

ABSORPTION MAXIMA (CM.$^{-1}$) ASSOCIATED WITH N–H AND C=O VIBRATIONS

	NH$_2$ stretching			NH$_2$ bending	NH$_2$ rocking	C=O stretching
Methyl glycinate	3390 w[a]	3322 w		1604		1743 s
Methyl glycinate HCl						1748 s
$CoCl_2(megly)_2$	3302 m	3250 m	3155 w	1592 m	618; 599	1737 s
$NiCl_2(megly)_2$	3295 s	3252 m	3175 m	1604 mw	639	1742 w; 1692 s
$CuCl_2(megly)_2$	3284 s	3236 s	3170 mw	1575 m	711 (?)	1756 s; 1714 (s)
$ZnCl_2(megly)_2$	3306 s	3252 s	3160 w	1596 m	620; 599	1737 s
$CdBr_2(megly)_2$	3311 s	3268 m	3165 w	1630 m; 1588 sh	579	1732 s
$CdBr_2(megly)$	3317 m	3263 m	3145 w	1586 ms	584; 555 sh	1715
$PdCl_2(megly)_2$	3275 m	3215 m	3150 m	1586 ms	730	1739 s
$PtCl_2(megly)_2$	3257 m	3205 m	3135 m	1589; 1578 m	760	1749 s
Ethyl glycinate	3392 w	3322 w		1608 w		1740 s
Ethyl glycinate HCl						1754 s
$CoCl_2(etgly)_2$	3289 s	3252 m	3165 w	1597 m	612; 593	1730 s
$NiCl_2(etgly)_2$	3306 m	3257 m		1596 m	610; 573 sh	1685 s
$NiCl_2(etgly) \cdot H_2O$	3311 s	3257 m		1596 m	613; 568	1686 s
$CuCl_2(etgly)_2$	3300 m	3263 w	3170 w	1607 w; 1570 m	708 (?)	1748 s; 1700 s
		3236 m	3125 w			
$CuCl_2(etgly)$	3284 m	3236 w	3125 w	1577 m	662 (?)	1740 w; 1658 s
$ZnCl_2(etgly)_2$	3295 s	3257 m	3165 w	1600 m	620; 601	1730 s
$CdBr_2(etgly)_2$	3317 s	3270 m	3165 w	1594 m	593; 578	1727 s
$CdBr_2(etgly)$	3317 s	3257 m	3135 w	1584 s	594; 557 sh	1701 s
$PdCl_2(etgly)_2$	3279 m	3226 m		1585 m	704	1751 s
Methyl α-alaninate	3382 w	3311 w		1605 w		1737 s
Methyl α-alaninate HCl						1749 s
$CuCl_2(me\text{-}\alpha\text{-}alan)_2$	3279 m	3205 m	3135 m	1590 m	717 (?)	1742 s; 1715 s
						1727 (blue form)
$CuCl_2(me\text{-}\alpha\text{-}alan)$	3279 m	3200 m	3135 m	1587 mw	662 (?)	1731 w; 1638 s
$CdBr_2(me\text{-}\alpha\text{-}alan)_2$	3289 m	3242 m	3150 w	1584 m	572	1708 s; 1691 s
$PdCl_2(me\text{-}\alpha\text{-}alan)_2$	3311 m	3227 m	3145 w			1742 s
	3279 m					
$[Cu(glyH)_2][CuCl_3]$	3226 m	3081 m		1584 m		1659 s

[a] s, strong; m, medium; w, weak; sh, shoulder.

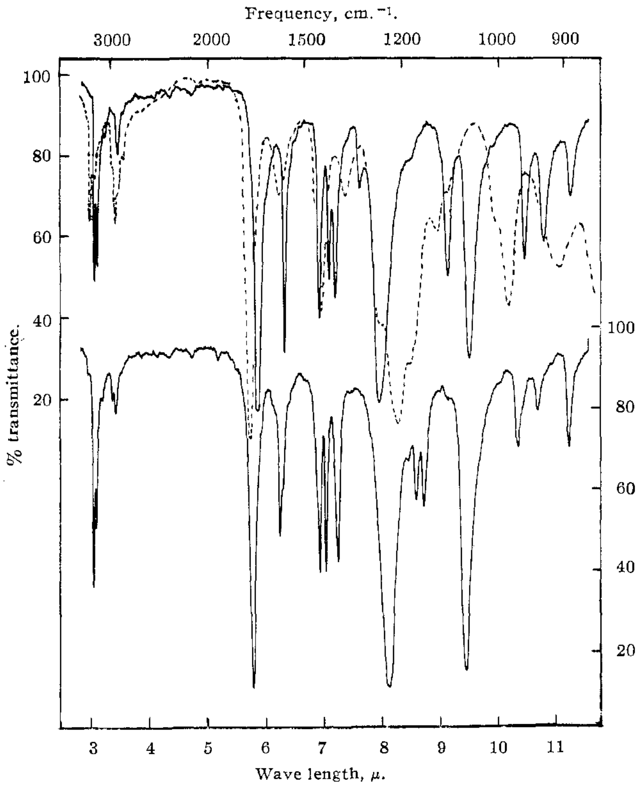


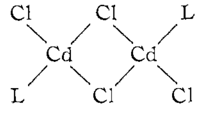
Fig. 1.—Infrared spectra in KBr disks. Upper curves: -------- methyl glycinate; ——— dibromo-(methyl glycinate)-cadmium. Lower curve: dibromobis-(methyl glycinate)-cadmium.

Anal. Calcd. for $ZnCl_2(C_4H_{11}N)_2$: Zn, 23.14; Cl, 25.10. Found: Zn, 22.86; Cl, 25.12.

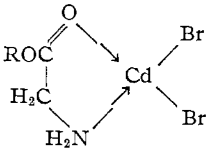
Infrared Spectra.—Spectra were obtained with a Perkin-Elmer Model 12 spectrophotometer, using calcium fluoride, sodium chloride, and cesium bromide prisms. Spectra were obtained of the esters as liquid films and of the complexes in potassium bromide disks. The positions of the absorption maxima in the spectra of the disks were checked with Nujol and hexachlorobutadiene mulls.

Discussion of Results

The absorption maxima attributed to the NH$_2$ and C=O vibrations in the spectra of the esters and complexes are listed in Table I. Typical spectra of an ester, a 1:1 complex, and 2:1 complex are illustrated in Fig. 1. The spectra of all the complexes investigated show decreases in the NH$_2$ stretching frequencies compared to the liquid esters, indicating the formation of nitrogen-to-metal bonds. The 1:1 complexes (with cadmium bromide, cupric chloride, and nickel chloride) are expected to be chelated; this chelation is evidenced by the decrease in the carbonyl stretching frequency in each complex relative to the free ester. Cadmium chloride has been observed to form tetrahedral 1:1 complexes of the type



with a variety of ligands; the decreases in carbonyl frequency observed in the spectra of the 1:1 complexes of all three esters with cadmium bromide indicate that the complexes are of the type



and are probably tetrahedral. The sharp water peak at 3478 cm.$^{-1}$ in the spectrum of dichloro-(ethyl glycinate)-nickel(II) monohydrate suggests that the water molecule occupies one of the octahedral coordination sites in this complex and that there are no $O-H\cdots X$ hydrogen bonds. The water was not removed by heating to 140° under vacuum. All three esters showed a tendency to chelate with cobalt(II), but the 1:1 solid complexes could not be obtained pure.

$C=O$ Stretching Vibration.—The shifts in the carbonyl stretching frequency on coordination are expected to be greater the greater the strengths of the O–M bonds. The observed shifts for the 1:1 complexes are in the order Cu > Ni > Cd. The decreases in the carbonyl frequency on formation of the 2:1 complexes with nickel chloride, 51 and 55 cm.$^{-1}$, respectively, for the methyl and ethyl glycinate complexes, are attributed to the formation of chelated octahedral complexes. This is substantiated by the reaction of these complexes with potassium thiocyanate in the solid state. The spectra of the reaction mixtures reveal (a) no changes in the N–H stretching frequencies of the coordinated NH_2 groups, (b) $C=O$ stretching frequencies corresponding to those of the free esters (approximately), and (c) bridged thiocyanate groups (NCS absorption at 2118 cm.$^{-1}$, compared to 2080 cm.$^{-1}$ for unbridged Ni–NCS bonding), indicating that the thiocyanate groups displace both the chlorine atoms and the carbonyl groups from coordination sites around the nickel atoms. For all other 2:1 complexes of the esters with metal halides, spectra indicate the formation of only nitrogen-to-metal bonds.

The slight decreases in the carbonyl stretching frequency observed for methyl and ethyl glycinate on the formation of 2:1 complexes with zinc chloride, cadmium bromide, and cobalt chloride may be associated with intermolecular hydrogen bonding; the amino groups are much more positive in character in the complexes than in the free esters. The slight increases in frequency observed for the platinum complexes are probably due to the electron demand of the coordinated nitrogen atom. The carbonyl frequencies of the esters are increased by 5, 14, and 12 cm.$^{-1}$, respectively, on the formation of the hydrochlorides of methyl and ethyl glycinates and DL methyl α-alaninate, indicating that the inductive pull $O=C-C-N^+$ of electrons is more effective than hydrogen bonding in changing the carbonyl frequency. The N—Pt dative bond is expected to be the most polar (to have the greatest covalent character) of all the nitrogen-to-metal bonds and therefore to be the most effective in increasing the carbonyl stretching frequency.

The carbonyl absorption is split into two peaks of nearly equal intensity in the spectra of the bis complexes of all three esters with cupric chloride and in the complex of ethyl glycinate with palladium chloride. (Dichlorobis-(methyl α-alaninate)-copper(II) was also obtained in the form of a bright blue solid giving a spectrum with a single carbonyl peak.) The cause of this splitting is not known; there are no evident combinations or overtones which could result in Fermi resonance. It may be associated with coupling between $C=O$ vibrations of separate molecules in the same unit cell.

NH_2 Stretching Vibrations.—The similarity in the absorption profiles in the 3-μ region for the bis complexes of the glycine esters with zinc, cobalt, and cadmium halides suggests that these complexes have similar configurations. A tetrahedral arrangement is indicated by the blue color of the cobalt complexes. This configuration is expected for zinc complexes and the ease of displacement of bromine by thiocyanate ions observed in the solid state reactions with the cadmium complexes also indicates a tetrahedral configuration. Octahedral cadmium complexes with bridged halogen atoms react relatively slowly with solid potassium thiocyanate.[12] The spectra of the reaction mixtures reveal that the dithiocyanatobis-(glycine ester)-cadmium complexes contain Cd–NSC–Cd bridges and are therefore octahedral.

The shifts in the high frequency N–H peak of methyl glycinate on formation of the bis complexes are in the order Pt > Pd > Cu > Ni > Co > Zn > Cd. This corresponds to the stability sequence usually observed for complexes of divalent ions in solution.[13] Somewhat larger shifts are observed for the antisymmetric N–H frequency of ethyl glycinate on complex formation with zinc and cobalt than with copper and nickel. It may be that in the tetrahedral complexes of the former two metals $CO\cdots HN$ hydrogen bonding is stronger than in the square or tetragonal complexes, thus lowering the N–H frequencies.

The third, relatively weak peak in the 3-μ region of the spectrum of each of the complexes has a frequency slightly less than twice that of the NH_2 bending vibration, suggesting that it is an overtone, its intensity enhanced and its frequency lowered by Fermi resonance with an NH_2 stretching mode. The spectra of the deuterated complexes also have three absorption peaks in the N–D stretching region. It is recognized that this third peak may also have its source in intra- or intermolecular coupling between NH_2 stretching vibrations.

NH_2 Bending Vibration.—The absorption maxima in the 1620–1570 cm.$^{-1}$ region of the spectra of the complexes disappear on deuteration, indicating that

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[12] M. D. Glonek, M. R. Petra, and C. Curran, in "Advances in the Chemistry of the Coordination Compounds," S. Kirschner, Ed., The Macmillan Company, New York, N. Y., 1961, p. 260.

[13] H. Irving and R. J. P. Williams, *J. Chem. Soc.*, 3192 (1953).

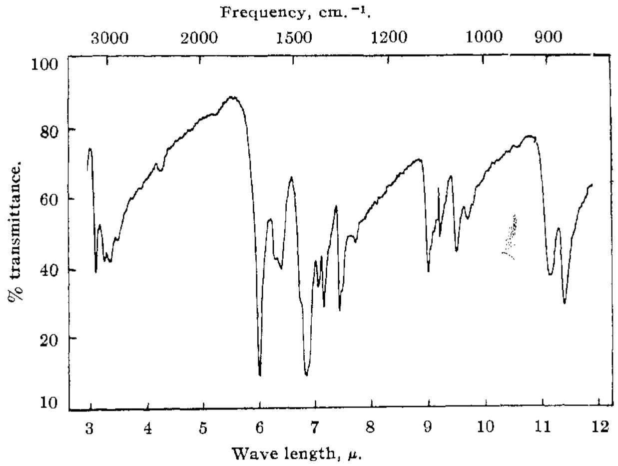

Fig. 2.—Infrared spectrum of bis-(glycine)-copper(II) trichlorocuprate(I) in KBr.

they are associated with the NH_2 bending vibration. The frequency of this vibration in solid dimethylammonium tetrachlorocuprate, in which hydrogen bonding is relatively weak, is 1572[14] compared to the value 1600 cm.$^{-1}$ observed in this laboratory for methylamine in carbon tetrachloride solution, indicating that the formation of a fourth bond by the nitrogen results in a decrease in the NH_2 bending vibration. The data of Table I reveal that with the exception of the nickel chloride complexes, the frequency of this vibration in each ester is decreased on complex formation. The decreases are small compared to those of the NH_2 stretching vibrations, but they are in the general order of the expected nitrogen-to-metal bond strengths; the lowest observed frequency, 1577 cm.$^{-1}$, is that for dichlorobis-(ethyl glycinate)-platinum(II).

Absorption peaks corresponding to NH_2 wagging vibrations have not been identified by deuteration of these complexes. The wagging vibration has been assigned to absorption maxima in the 1050-cm.$^{-1}$ region in the spectra of complexes of methylamine with metal halides,[15] and in the 1000–1190-cm.$^{-1}$ region in the spectra of aniline complexes.[16]

NH_2 Rocking Vibration.—The rocking frequencies are more difficult to identify than are the NH_2 bending frequencies. The values listed in Table I for the zinc, palladium, and platinum complexes disappeared on deuteration; values for the cobalt, cadmium, and nickel complexes were assigned by analogy. The peaks assigned to NH_2 rocking frequencies correspond to isotopic ratios of 1.24–1.27, slightly lower than the usual ratios obtained for this vibration, about 1.3; the low values are probably due to coupling between the CH_2 and NH_2 rocking vibrations, which lowers the frequencies of the latter. As a check on the assignment of the rocking frequencies of the zinc complexes, the less complicated spectrum of dichlorobis-(butylamine)-zinc was obtained. A doublet with maxima at 649 and 625 cm.$^{-1}$ was observed, compared to the values 620–599 cm.$^{-1}$ in Table I. The assigned rocking frequencies are in the range of those reported by Powell and Sheppard[17] for ethylenediamine complexes; their values are slightly higher than ours, as expected for the chelated cations. As indicated in Table I, the identification of the rocking frequencies in the copper complexes is uncertain.

The order of increasing rocking frequencies in these ester complexes is essentially the same as the order of decreasing N–H stretching frequencies. This increasing rocking frequency with increasing nitrogen-to-metal bond strength was also noted by Powell and Sheppard. Sacconi and Sabatini have noted a correlation between the NH_2 rocking frequencies and the M–N stretching frequencies in complexes of hydrazine with metal halides.[18]

The Ester Bands.—The spectra of esters of carboxylic acids as well as of ethers containing the =C—O—R grouping have a prominent band in the 1270–1150-cm.$^{-1}$ region and a less intense band between 1120 and 1130 cm.$^{-1}$.[19] These have been attributed to vibrations involving chiefly the C–O–R group and are commonly referred to as ester I and ester II bands. The ester I band in methyl glycinate is at 1210 cm.$^{-1}$. The frequency increases to an average of 1235 cm.$^{-1}$ in the complexes containing only nitrogen-to-metal dative bonds, and to 1259 and 1271 cm.$^{-1}$ in the chelated cadmium and nickel complexes. The ester II band in methyl glycinate is at 986 cm.$^{-1}$. It increases to an average of 1060 cm.$^{-1}$ in the complexes in which the ester acts as a monodentate ligand, and on chelation a new additional band appears at 1101 and 1125 cm.$^{-1}$ in the spectra of cadmium and nickel complexes, respectively.

Ethyl glycinate absorbs at 1200 and 1023 cm.$^{-1}$. The high frequency peak is shifted to an average of 1235 cm.$^{-1}$ on the formation of nitrogen-to-metal bonds, and to between 1236 and 1278 cm.$^{-1}$ on chelation. Chelation also results in a new absorption at 1303 ± 4 cm.$^{-1}$. The low frequency ester peak is increased to an average of 1060 cm.$^{-1}$ on nitrogen-to-metal bond formation, and chelation results in a new absorption at 1100–1126 cm.$^{-1}$.

The bis complexes of methyl and ethyl glycinate with copper(II) are anomalous; their spectra are similar to the chelated complexes in the region of the ester I and ester II bands. Chelation of methyl α-alaninate with cadmium and copper(II) results in characteristic absorption maxima at 1321 and 1340 cm.$^{-1}$, respectively.

Chelation by Neutral Glycine.—The spectrum of bis-(glycine)-copper(II) trichlorocuprate(I) is illustrated in Fig. 2 and some of the absorption maxima are listed in Table I. The positions of the two high frequency peaks are very nearly equal to the N–H stretching

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(14) M. P. Springer and C. Curran, paper presented at the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, March, 1961.

(15) M. St. A. Radzikowski and C. Curran, Preprints of Symposium on Molecular Structure and Spectroscopy, Tokyo, Japan, Sept., 1962, p. A319.

(16) M. A. J. Jungbauer and C. Curran, Abstracts, 140th National Meeting of the American Chemical Society, Chicago, Ill., Sept., 1961, p. 6T.

(17) D. B. Powell and N. Sheppard, *J. Chem. Soc.*, 1112 (1961).

(18) L. Sacconi and A. Sabatini, *Nature*, **186**, 549 (1960).

(19) A. R. Katritsky, J. M. Lagowski, and J. A. T. Beard, *Spectrochim. Acta*, **16**, 954, 964 (1960).

frequencies in *trans*-bis-(glycinato)-platinum(II), 3231 and 3083 cm.$^{-1}$, indicating that the NH_2 groups are coordinated to copper(II) in a *trans* arrangement.

The third high frequency peak in Fig. 2 is attributed to the O–H stretching vibration. It is much weaker, less broad, and at a higher frequency than the corresponding absorption by dichlorobis-(glycine)-platinum(II), in which intra- and intermolecular C=O · · ·H—O hydrogen bonds are important.

The frequency of the carbonyl peak, 1659 cm.$^{-1}$, compares with 1658 cm.$^{-1}$ in chelated dichloro-(ethyl glycinate)-copper(II), 1711 cm.$^{-1}$ in dichlorobis-(glycine)-platinum(II) in which only the nitrogen atoms of the glycine molecules are coordinated, and with about 1605 cm.$^{-1}$ for the antisymmetric O=C—O stretching vibration in bis-(glycino)-copper(II) monohydrate. The 1659 cm.$^{-1}$ peak in the spectrum of bis-(glycine)-copper(II) trichlorocuprate(I) indicates the presence of C=O —Cu bonds. This is the only complex known to the authors containing chelated neutral glycine ligands. We were unable to prepare similar complexes by adding other metal halides and hydrogen chloride to solutions of metal glycinates.

CONTRIBUTION FROM THE MELLON INSTITUTE,
PITTSBURGH 13, PENNSYLVANIA

Some Reactions of Bis-(iron tricarbonyl nitrosyl)-mercury

BY R. B. KING

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Reaction between $Hg[Fe(CO)_3NO]_2$ and tris-(dimethylamino)-phosphine yields the complexes $[(Tdp)_2Fe(CO)_2NO][Fe(CO)_3NO]$ and $(Tdp)_2Fe(NO)_2$, depending on the reaction conditions. Reaction between $Hg[Fe(CO)_3NO]_2$ and bis-(trifluoromethyl)-dithietene yields a nitrosyl derivative of stoichiometry $C_4F_6S_2FeNO$. Reaction between $Hg[Fe(CO)_3NO]_2$ and triphenylphosphine yields the substitution product $Hg[Fe(CO)_2(NO)P(C_6H_5)_3]_2$.

The compound $Hg[Fe(CO)_3NO]_2$, described recently by Hieber and Beutner,[1] was prepared and characterized independently in this laboratory prior to appearance of the original report. In the present paper substitution reactions of $Hg[Fe(CO)_3NO]_2$ are described.

Experimental

In general infrared spectra were taken in potassium bromide pellets and recorded on a Perkin-Elmer Model 21 double beam machine with sodium chloride optics. In addition, the metal carbonyl and nitrosyl regions of the infrared spectra of selected compounds were taken in halocarbon oil mulls and recorded on a Perkin-Elmer Model 112 single-beam machine with CaF_2 optics. Microanalyses and molecular weight determinations (Mechrolab vapor pressure osmometer in benzene solution) were performed by Dr. A. Bernhardt, Mikroanalytisches Laboratorium, Max-Planck-Institut für Kohlenforschung, Mülheim (Ruhr), Germany, and Schwarzkopf Microanalytical Laboratory, Woodside, New York. Melting points were taken in capillaries and are uncorrected.

Materials.—Triphenylphosphine was purchased from Metal and Thermit Co., Rahway, New Jersey. Tris-(dimethylamino)-phosphine[2,3] and bis-(trifluoromethyl)-dithietene[4] were prepared by published procedures.

Bis-(iron tricarbonyl nitrosyl)-mercury.—The procedure which we used for the preparation of $Hg[Fe(CO)_3NO]_2$ was very similar to that of Hieber and Beutner[1] involving the reaction between the anion $[Fe(CO)_3NO]^-$ and aqueous mercury(II) cyanide. Material recrystallized from dichloromethane was used for these reactions. It was found necessary to store $Hg[Fe(CO)_3NO]_2$ in a refrigerator.

Reaction between $Hg[Fe(CO)_3NO]_2$ and Triphenylphosphine.[4a]—Upon stirring a solution of 1.35 g. (2.5 mmoles) of $Hg[Fe(CO)_3NO]_2$ and 2.62 g. (10 mmoles) of triphenylphosphine in 50 ml. of thiophene-free benzene at room temperature for several hours, a fine yellow-orange precipitate gradually formed. After 22 hr. this precipitate was filtered, washed with 50 ml. of dichloromethane, and dried to give 1.72 g. (68% yield) of $Hg[Fe(CO)_2(NO)P(C_6H_5)_3]_2$, which on heating turned brown above 200°. The compound $Hg[Fe(CO)_2(NO)P(C_6H_5)_3]_2$ is a yellow-orange powder considerably more stable than the unsubstituted $Hg[Fe(CO)_3NO]_2$. Like $Hg[Co(CO)_3P(C_6H_5)_3]_2$,[5] $Hg[Fe(CO)_2(NO)P(C_6H_5)_3]_2$ is very sparingly soluble in organic solvents.

Anal. Calcd. for $C_{40}H_{30}N_2P_2HgFe_2O_6$: C, 47.3; H, 3.5; N, 2.8; P, 6.1; Hg, 19.8. Found: C, 46.9; H, 3.0; N, 3.0; P, 5.8; Hg, 19.7.

Infrared Spectrum.—C–H bands too weak to be unequivocally observed; metal carbonyl bands at 1980 (w), 1950 (m), and 1905 (s) cm.$^{-1}$; metal nitrosyl bands at 1712 (s) and 1705 (s) cm.$^{-1}$; other bands at 1475 (w), 1430 (w), 1375 (vw), 1263 (vw), 1175 (vw), 1090 (w), 1025 (vw), 992 (vw), 745 (w), 705 (w), and 691 (m) cm.$^{-1}$.

Preparation of $[(Tdp)_2Fe(CO)_2NO][Fe(CO)_3NO]$.—A mixture of 1.5 g. (2.77 mmoles) of $Hg[Fe(CO)_3NO]_2$, 2.5 ml. (~2.5 g., 15.4 mmoles) of tris-(dimethylamino)-phosphine, and 40 ml. of thiophene-free benzene was refluxed ~6 hr. under nitrogen with magnetic stirring. After cooling to room temperature the reaction mixture was filtered by gravity. Solvent was removed from the orange filtrate at ~30 mm. The resulting orange crystalline residue was recrystallized twice from mixtures of dichloromethane and hexane and washed with pentane to give 0.34 g. (19% yield) of orange crystals of $[(Tdp)_2Fe(CO)_2NO][Fe(CO)_3NO]$, which on heating gradually turned black above ~135°.

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(1) W. Hieber and H. Beutner, *Z. anorg. allgem. Chem.*, **320**, 101 (1963).

(2) To minimize confusion and the use of several types of brackets tris-(dimethylamino)-phosphine will be abbreviated as Tdp in formulas.

(3) A. B. Burg and P. J. Slota, Jr., *J. Am. Chem. Soc.*, **80**, 1107 (1958).

(4) C. G. Krespan, *ibid.*, **83**, 3434 (1961).

(4a) NOTE ADDED IN PROOF.—Since this paper was accepted, the compound $Hg[Fe(CO)_2(NO)P(C_6H_5)_3]_2$ has been described independently by Hieber and Klingshirn [W. Hieber and W. Klingshirn, *Z. anorg. allgem. Chem.*, **323**, 292 (1963)]. They also described several other $Hg[Fe(CO)_2(NO)PR_3]_2$ compounds.

(5) W. Hieber and R. Breu, *Ber.*, **90**, 1259 (1957).