pected since all of the possible isomeric forms have all vibrations active in the infrared and Raman spectra. Single crystals of the non-needle-like form could be obtained and preliminary single crystal patterns showed the space group to be C^2/C (C_{2H}^6) or C_c (C_s^4). With these space symmetries the available site symmetries (which will be the same as the molecular symmetry) are C_2 (two-fold axis only) or C_i (center of symmetry) for $C^2/_c$ crystal symmetry and C_1 (no symmetry) for C_c crystal symmetry.

Molecular symmetry can, of course, be higher than C_2 or C_i in the liquid or vapor state, but crystal forces do not require it for the solid state, and probably will, in fact, attempt to eliminate any higher symmetry or planes of symmetry as solidification takes place.

Conclusions

The effects of changes in temperature, state and dilution on the infrared and Raman spectra of dichloroacetone can be reasonably explained on the basis of two rotational isomers. The more polar isomer persists in the solid state and is also of lower energy in the liquid. The lower limit for the energy difference in the liquid was found to be 1500 cal./mole. In the gas phase, the less polar species is much more abundant than the other isomer, indicating a reversal in relative stability in going from liquid to gas.

The molecular symmetries of the two isomers have not been determined due to the similarity of the selection rules for the various conceivable isomers.

WASHINGTON 25, D. C.

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

Infrared Absorption Spectra of Inorganic Coördination Complexes.[1a,b] V. The N-H Stretching Vibration in Coördination Compounds

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Coördination with metals by molecules containing H-N bonds results in a marked increase in absorption in the 3 μ region and in a decrease in the frequency of the H-N stretching vibration. The effects of hydration, hydrogen bonding, configuration of the complex and the solvent on the character and position of the absorption peaks in this region have been studied. The shift in the H-N stretching frequency on coördination increases with increasing charge on the complex and with increasing covalent character of the N-M bond. The spectra of salicylaldimine complexes show that the nickel(II) and copper(II) complexes have a *trans* square planar configuration. The N-Ni bond in this complex is revealed to be stronger than the N-Cu bond.

Introduction

Flett[2] has shown that in *para*-substituted anilines delocalization of the unshared pair of nitrogen valence electrons in π-bond formation results in an increase in frequency of the H-N stretching vibration. Both the antisymmetric and symmetric frequencies increase with increasing electron withdrawal of the *para*-substituent, and therefore with increasing double bond character of the nitrogen-to-ring bond. This is not unexpected in the light of the well known increase in frequency of the C-H stretching vibration from ethane to acetylene. In the course of investigation of the infrared spectra of metal coördination compounds in this Laboratory it was observed that the absorption peaks associated with the H-N stretching vibrations of a number of amines shifted to lower frequencies on the formation of nitrogen-to-metal bonds.[3] In this paper are reported the results of a systematic study of this phenomenon. Among the factors investigated were the effects of hydration, hydrogen bonding, configuration of the metal complex, charge on the metal ion and covalent character of the N-M bonds.

Experimental

Preparation and Purification of Compounds.—Bis-(*o*-hydroxyacetophenoneimino)-copper(II) was prepared by a modification of the procedure reported for the preparation of the corresponding nickel complex. Bis-(sarcosino)-zinc(II) dihydrate was prepared in a manner similar to that reported by Dubsky and Rabas[4] for the preparation of the glycine complex. The other compounds listed in Table I were prepared by methods similar to those given in the references listed in the last column of the table. The few compounds in Table II not listed in Table I were supplied by Dr. D. N. Sen.[5] Most of the compounds were dried by heating under reduced pressure in an Abderhalden apparatus for several hours at 110°. Analyses of the compounds are given in Table I.

Absorption Measurements.—Spectra were obtained by means of Perkin-Elmer Infrared Spectrophotometer Model 21, using a calcium fluoride prism. Preparation of the potassium bromide disks were made according to the procedure of Stimson and O'Donnell.[6] Measurements in solution were obtained with 1 cm. quartz cells. The positions and intensities of the absorption maxima of the compounds studied are listed in Tables II and III.

Discussion of Results

A. Intensity of Absorption.—The formation of nitrogen-to-metal bonds by a coördinating group having one or more N-H bonds increases the electron demand of the nitrogen and therefore increases the polarity of the N-H bonds. It is to be expected that the change in the N-H dipole moment during vibration should also increase, resulting in an

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(1) (a) Paper IV in series, THIS JOURNAL, **77**, 5508 (1955). (b) Abstracted from the Ph.D. thesis of G. F. Svatos, Notre Dame, 1954. Presented before the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Pittsburgh, Pa., Feb., 1954. Supported in part under AEC Contract AT(11-1)-38, Radiation Project of the University of Notre Dame.

[2] M. St. C. Flett, *Trans. Faraday Soc.*, **44**, 767 (1948).

[3] J. V. Quagliano, G. F. Svatos and C. Curran, *Anal. Chem.*, **26**, 429 (1954).

[4] J. V. Dubsky and A. Rabas, *Spisy vydávané přírodovědeckou Fakultou Masarykovy Univ.*, No. 123, 3 (1930); *C. A.*, **25**, 2655 (1931).

[5] D. N. Sen, Ph.D. Thesis, University of Notre Dame, 1954.

[6] M. M. Stimson and M. J. O'Donnell, THIS JOURNAL, **74**, 1805 (1952).

increase in total absorption. This effect is illustrated in Fig. 1; the absorption by the NH_2 groups (*ca.* 3300 cm.$^{-1}$) relative to that by the CH_2 groups (*ca.* 2900 cm.$^{-1}$) in ethylenediamine is increased by chelation of this ligand in the complex ethylenediaminedibromoplatinum(II). Other molecules containing nitrogen–hydrogen bonds also show stronger absorption in the 3300 cm.$^{-1}$ region on chelation.

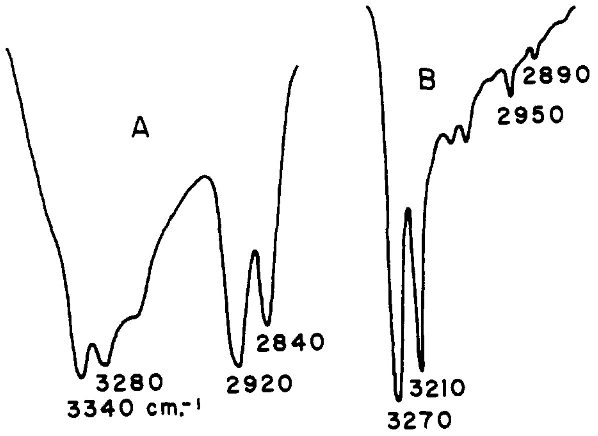

Fig. 1.—Absorption spectra of: A, ethylenediamine, liquid film; B, ethylenediaminedibromoplatinum(II) in KBr disk.

B. Hydration.—The effect of hydration on the position of the N–H absorption peaks varies considerably with the nature of the hydrated compound. From Table IIB it is evident that the addition of water to bis-(diethylenetriamine)-copper(II) chloride and to hexamminecobalt(III) oxalate has practically no effect on the position of the N–H peaks. The N–H absorption peaks in the spectra of the sarcosine complexes of copper(II) and zinc and the salicylaldimine complex of zinc (compounds 20, 24 and 25) undergo marked shifts on hydration (compounds 5, 6 and 7). These shifts indicate that the positions of N–H peaks in hydrates must be interpreted with caution. As a general rule, it appears that if water of hydration absorbs in the 3500 cm.$^{-1}$ region, the N–H stretching vibration is but little affected; if the water absorbs at appreciably lower frequencies the N–H vibration may be affected considerably by hydration. The relation between hydration and the O–H stretching vibration has been studied by Kaye and Thompson.[7]

Table I

Analysis of Compounds

Compound[a]	Component analyzed	% Calcd.	% Found	Ref.
$[Co(NH_3)_6]Cl_3$	NH_3	38.20	37.94	*b*
$[Co(NH_3)_6]Cl_2$	NH_3	44.04	43.71	*c*
$[Ag(NH_3)_2]_2SO_4$	NH_3	17.93	17.58	*c*
$[Cu(NH_3)_4]SO_4 \cdot H_2O$	NH_3	27.72	27.34	*c*
$[Cu(NH_3)_4]SO_4 \cdot H_2O$	Cu	25.86	25.19	
$[Ni(NH_3)_6]Cl_2$	NH_3	44.08	43.83	*c*
$[Cr(NH_3)_6]Cl_3$	NH_3	39.22	38.77	*c*
$[Co(NH_3)_6]_2(C_2O_4)_3 \cdot 4H_2O$	NH_3	31.04	30.82	*d*
$[Co(NH_3)_6]_2(C_2O_4)_3 \cdot 4H_2O$	H_2O	10.95	11.15	
$[Co(NH_3)_5Cl]Cl_2$	NH_3	34.00	33.61	*e*
$[Co(NH_3)_5Br]Br_2$	NH_3	22.18	22.06	*f*
$[Cr(NH_3)_5Cl]Cl_2$	NH_3	34.96	34.58	*c*
$[Co(NH_3)_5NO_2]Cl_2$	NH_3	32.62	32.38	*g*
$[Co(NH_3)_5NO_3]Cl_2$	NH_3	30.74	30.64	*h*
$[Co(NH_3)_5H_2O]Cl_3$	NH_3	31.71	31.58	*c*
$[Co(NH_3)_4(H_2O)_2]Cl_3$	NH_3	25.28	24.99	*i*
cis-$[Co(NH_3)_4(NO_2)_2]Cl$	NH_3	26.76	27.15	*c*
$[Co(NH_3)_3(NO_2)_3]$	NH_3	20.60	20.57	*c*
$K[Co(NH_3)_2(NO_2)_4]$	NH_3	10.77	11.19	*c*
$Cu(sal)_2$	Cu	20.92	21.07	*j*
$Ni(sal)_2$	Ni	19.63	19.58	*k*
$Cu(acet)_2$	Cu	19.16	19.29	
$Ni(acet)_2$	Ni	17.95	17.97	*l*
$Zn(sal)_2 \cdot H_2O$	H_2O	5.57	5.67	*l*
$Zn(sal)_2 \cdot H_2O$	Zn	20.20	20.16	
$Fe(sal)_3$	Fe	13.42	13.56	*m*
$Cu(sar)_2 \cdot 2H_2O$	H_2O	13.00	13.00	*n*
$Cu(sar)_2 \cdot 2H_2O$	Cu	23.05	22.79	
$Zn(sar)_2 \cdot 2H_2O$	Zn	23.55	23.45	
$Zn(sar)_2 \cdot 2H_2O$	H_2O	12.98	12.55	
$[Cu(dn)_2]Cl_2 \cdot H_2O$	H_2O	5.02	5.32	*n*
$[Cu(dn)_2]Cl_2 \cdot H_2O$	m.p.	210	210	
$[Ni(dn)_2]Cl_2 \cdot H_2O$	m.p.	232	232.5	*n*
$Cu(ant)_2$	Cu	18.82	18.82	*o*

[a] Abbreviations: Hsal = salicylaldimine; Hacet = *o*-hydroxyacetophenoneimine; Hsar = sarcosine; dn = diethylenetriamine; Hant = anthranilic acid. [b] J. Bjerrum and J. P. McReynolds, *Inorg. Syn.*, **2**, 216 (1946). [c] H. Biltz and W. Biltz, "Laboratory Methods of Inorganic Chemistry," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1928. [d] J. Bjerrum and J. P. McReynolds, *Inorg. Syn.*, **2**, 219 (1946). [e] W. A. Hynes, L. K. Yanowski and M. Shiller, This Journal, **60**, 3053 (1938). [f] H. Diehl, H. Clark and H. H. Willard, *Inorg. Syn.*, **1**, 186 (1939). [g] H. F. Walton, "Inorganic Preparations," Prentice-Hall, Inc., New York, N. Y., 1948, p. 92. [h] S. M. Jorgensen, *J. prakt. Chem.*, **23**, 237 (1881). [i] H. Hecht, "Preparative Anorganische Chemie," Springer Verlag, Berlin, 1951, p. 173. [j] L. Hunter and J. A. Marriott, *J. Chem. Soc.*, 2002 (1937). [k] P. Pfeiffer, E. Buchholz and O. Bauer, *J. prakt. Chem.*, **129**, 169 (1931). [l] W. Klemm and K. H. Raddatz, *Z. anorg. allgem. Chem.*, **250**, 220 (1942). [m] E. Abderhalden and E. Schnitzler, *Z. Physiol. Chem.*, **163**, 94 (1927). [n] J. G. Breckenridge, *Can. J. Research*, **26B**, 15 (1948). [o] H. Funk and M. Ditt, *Z. Anal. Chem.*, **93**, 245 (1933).

C. Hydrogen Bonding.—As hydrogen bonding also results in a decrease in the frequencies of the N–H stretching vibration, and as the extent of this bonding differs from compound to compound, it was necessary to determine the relative importance of hydrogen bonding and of N–M bond formation on the shifts of the NH absorption peaks. The four compounds listed in Table IIC were selected for this comparison. Gaseous ammonia absorbs at 3337 and 3450 cm.$^{-1}$. Ammonium bromide and ammonium fluoride show broad absorption bands in potassium bromide disks, with maxima at 3110 and 3130 cm.$^{-1}$, respectively. The fluoride ion is known to form much stronger hydrogen bonds than the bromide ion, and the crystal structure of ammonium fluoride (wurtzite lattice) is much more favorable for hydrogen bonding than that of ammonium bromide (cesium chloride lattice). The larger shift in absorption maximum (from NH_3 to NH_4^+) observed for the ammonium bromide spectrum indicates that the formation of the fourth N–H bond is much more effective than hydrogen bond-

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(7) W. Kaye and A. Thompson, "Symposium on Molecular Structure," The Ohio State University, June, 1953.

TABLE II

INFRARED ABSORPTION IN THE 3 μ REGION OF COÖRDINATION COMPOUNDS IN KBR DISKS

	Compound	Concn., wt. %	ν, cm.$^{-1}$	%T	ν, cm.$^{-1}$	%T	ν, cm.$^{-1}$	%T	ν, cm.$^{-1}$	%T
A.	Intensity of absorption									
1	Ethylenediamine (liquid film)		3340	50	3280	52	2920	40	2840	45
2	$Pt(en)Br_2$	0.34	3270	4	3210	12	2950	59	2890	63
B.	Hydration									
3	$[Co(NH_3)_5H_2O]Cl_3$	0.17	3230	47	3150	45				
4	$[Co(NH_3)_4(H_2O)_2]Cl_3$	.17	3250	55	3150	55				
5	$Zn(sar)_2 \cdot 2H_2O$	.26	3236	35						
6	$Cu(sar)_2 \cdot 2H_2O$	.26	3311	57	3118	46				
7	$Zn(sal)_2 \cdot H_2O$	.34	3322	65						
8	$[Cu(NH_3)_4]SO_4 \cdot H_2O$	.17	3290	23	3230	30	3140	33		
9	$[Co(NH_3)_6]_2[C_2O_4]_3 \cdot 4H_2O$	.34	3290	15	3160	18	3110	19		
10	$[Co(NH_3)_6]_2[C_2O_4]_3$	.34	3280	26	3160	30	3110	34		
11	$[Cu(dn)_2]Cl_2 \cdot H_2O$	.34	3460	33	3330	30	3250	24	3130	8
12	$[Cu(dn)_2]Cl_2$	.26	3460	90	3330	79	3250	70	3130	55
13	$[Ni(dn)_2]Cl_2 \cdot H_2O$	.26	3450	34	3330	33	3270	17	3170	12
C.	Hydrogen bonding									
14	NH_4Br	0.34	3120	70						
15	NH_4F	.34	3130	72						
16	Na Anthranilate	.34	3410	53	3310	51				
17	$Cu(ant)_2$	.68	3280	0.5	3126	3	3125	0.5		
D.	Configuration									
18	$Ni(sal)_2$	0.34	3303	22						
19	$Cu(sal)_2$	.34	3313	35						
20	$Zn(sal)_2$	.34	unresolved		3213	17				
21	$Fe(sal)_2$	.34	3297	58	3167	37	3076	56	3055	56
22	$Ni(acet)_2$	.34	3324	48	3219	38	3183	41		
23	$Cu(acet)_2$	.34	3326	60	3191	52	3164	54		
24	$Cu(sar)_2$	.34	3181	47						
25	$Zn(sar)_2$	.34	3220	50						
E.	Charge and covalent character									
1.	Cobalt complexes									
26	$K[Co(NH_3)_2(NO_2)_4]$	0.17	3340	25	3250	38				
27	$[Co(NH_3)_3(NO_2)_2]$	.17	3330	31	3260	40				
28	*cis*-$[Co(NH_3)_4(NO_2)_2]Cl$	.17	3300	19	3160	21				
29	$[Co(NH_3)_5NO_2]Cl_2$	.17	3280	22	3160	23				
30	$[Co(NH_3)_5NO_3]Cl_2$	.34	3260	34	3120	32				
31	$[Co(NH_3)_5Cl]Cl_2$	.34	3290	5	3190	7				
32	$[Co(NH_3)_5Br]Br_2$	.34	3270	7	3170	9				
33	$[Co(NH_3)_6]Cl_2$	.17	3330	54	3250	55	3140	53	3040	61
34	$[Co(NH_3)_6]Cl_3$	.34	3240	49	3170	47				
2.	Ammine complexes									
35	$[Cr(NH_3)_6]Cl_3$	0.34	3260	36	3205	33	3140	37		
36	$[Cr(NH_3)_5Cl]Cl_2$	.34	3280	20	3190	17	3140	21		
37	$[Ag(NH_3)_2]_2SO_4$	.17	3330	52	3250	64	3140	72		
38	$[Ni(NH_3)_6]Cl_2$	.17	3320	8	3180	20				
39	$[Co(en)_3]Cl_3$	.34	3210	18	3160	22	3100	25		
40	*trans*-$[Co(en)_2Cl_2]Cl$	.34	3280	27	3240	14	3130	38	3100	54
41	$[Pt(en)_2]Cl_2$	.17	3180	47	3130	40	3060	15		
3.	Glycine complexes									
42	K Glycinate	0.17	3380	55	3360	60				
43	$Cu(gly)_2 \cdot H_2O$	.34	3330	37	3260	21	3150	48		
44	$Ni(gly)_2 \cdot 2(H_2O)$	.34	3330	10	3280	17	3190	12		
45	*trans*-$Pt(gly)_2$	.34	3240	45	3100	36				
46	$Co(gly)_3 \cdot H_2O$	.34	3260	15	3230	10	3130	12		
47	$Co(gly)_3 \cdot 2H_2O$	.34	3230	18	3130	17				
48	Glycine (zwitterion)	.42	3160	35						

ing in decreasing the frequency of the N–H stretching vibration.

In sodium anthranilate an intramolecular hydrogen bridge is undoubtedly formed between the ni-

TABLE III

INFRARED ABSORPTION SPECTRA OF SOLUTIONS

Compound	ν, cm.$^{-1}$	% T	Compound	ν, cm.$^{-1}$	% T
1. Chloroform			2. Pyridine		
Ni(sal)$_2$	3336	77	Ni(sal)$_2$	3341	68
Cu(sal)$_2$	3346	10	Ni(acet)$_2$	3307	69
Zn(sal)$_2$	3350	10			
Fe(sal)$_3$	3327	46			
Ni(acet)$_2$	3320	10			
Cu(acet)$_2$	3330	25			

trogen and the carboxylate ion. This bridge is broken when the anthranilate group forms a copper complex and any intermolecular hydrogen bonds formed in the crystalline complex are expected to be weaker than the N–H---O bridge in sodium anthranilate. From Table IIC it is evident that the high frequency peak in the spectrum of bis-(anthranilato)-copper(II) is at a longer wave length than the low frequency peak in the spectrum of the sodium salt. The formation of the N–Cu bond is thus much more effective than hydrogen bonding in slowing down the N–H stretching vibration. In compounds containing exposed negative groups, however, a portion of the shifts in absorption maxima may result from the formation of intermolecular hydrogen bridges.

D. Configuration.—In the event that strong N–M bonds are formed in coördination compounds, coupling may occur between N–H vibrations in the two or more ligand molecules chelated with the metal ion: H–N–M–N–H. If there is no rotation about the N–M bonds, the absorption pattern in the 3300 cm.$^{-1}$ region should depend on the configuration of the complex. The effect of this coupling on the spectra of *cis* and *trans* isomers will be reported in a later article. The present study is confined to a comparison of the spectra of coplanar, tetrahedral and octahedral complexes.

X-Ray analysis of bis-(salicylaldimino)-copper-(II)[8] has revealed a *trans* planar square configuration for this compound. A coupling of the two *trans* N–H vibrations would yield symmetric and antisymmetric vibrations, only the latter being infrared active. The spectra of the copper and nickel complexes with salicylaldimine show a single, sharp peak in the 3300 cm.$^{-1}$ region, illustrated in Fig. 2A, indicating that if coupling occurs the nickel complex must also have a *trans* configuration. Bis-(salicylaldimino)-zinc(II) is expected to have a tetrahedral configuration. Both the symmetric and antisymmetric N–H vibrations in this compound result in a change in dipole moment and so are infrared active. The spectrum of this compound is illustrated in Fig. 2B, showing an unresolved shoulder at 3300 cm.$^{-1}$ and a broad peak with a maximum at 3205 cm.$^{-1}$. The spectrum of octahedral tris-(salicylaldimino)-iron(III) is similar to that of the zinc complex, as expected, with a sharp peak at 3297 cm.$^{-1}$ and a broad peak at 3169 cm.$^{-1}$, plus two small peaks at lower frequencies.

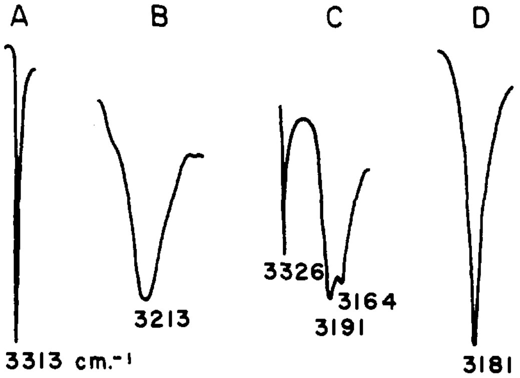

Fig. 2.—Absorption spectra in KBr disks: A, bis-(salicylaldimino)-copper(II); B, bis-(salicylaldimino)-zinc(II); C, bis-(*o*-hydroxyacetophenoneimino)-copper(II); D, bis-(sarcosino)-copper(II).

The spectra of the acetophenone–imine chelates of copper and nickel, illustrated in Fig. 2C, show a doublet in the 3200 cm.$^{-1}$ region, indicating either a *cis* configuration (improbable), a twisting of the N–H bonds out of the plane due to the steric effects of the methyl groups, or a coupling between vibrations of NH groups in separate molecules in the crystal.[9]

Earlier work in this Laboratory[10] has indicated that in chelate compounds having bidentate ligands with COO$^-$ groups as one of the coördinating centers, the COO$^-$---M bonds are essentially electrostatic. This suggests that in aminoacid complexes of zinc the bond orbitals used by the zinc are sp, resulting in *trans* coplanar configurations for these complexes. X-Ray diffraction studies on bis-(glycino)-zinc(II) monohydrate reveal a *trans* planar arrangement of the glycine molecules about the metal ion.[11] In an attempt to obtain spectroscopic evidence for coplanar complexes of zinc the spectra of bis-(sarcosino)-copper(II) and bis-(sarcosino)-zinc(II) were obtained. A single peak in the 3200 cm.$^{-1}$ region was observed in the spectrum of each compound, illustrated in Fig. 2D. This similarity suggests a planar configuration for the zinc complex, but further evidence is needed to substantiate this interpretation. In square sarcosine complexes having linear N–M–N bonds the two N–H bonds may be *cis* or *trans* to each other, further complicating the problem. Complexes with other ligands having single N–H bonds are being investigated in this Laboratory.

E. Covalent Character of the N–M Bond.—The covalent character of nitrogen-to-metal bonds in coördination compounds depends on the charge on the metal ion, the type of available bond orbitals and the tendency of the metal to form covalent bonds. The effect of the magnitude of the positive charge on cobalt atoms in complexes on the frequency of the N–H stretching vibration is illustrated in Table II-E 1. In compounds 26, 27, 28, 30 and 34 the formal charge on the complex increases regularly from −1 to +3 and it is seen that the frequencies of the short wave length maxima decrease regularly from 3340 to 3240 cm.$^{-1}$. The effects of charge, orbital type and tendency to

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(8) M. v. Stackenberg, *Z. anorg. allgem. Chem.*, **253**, 136 (1947).

(9) This third possibility was suggested by Dr. G. B. B. M. Sutherland.

(10) D. N. Sen, S. Mizushima, C. Curran and J. V. Quagliano, THIS JOURNAL, **77**, 211 (1955).

(11) B. W. Low, private communication.

form covalent bonds are evident in the order of decreasing N–H frequencies in other amines listed in Table II-E 1: $[Ag(NH_3)_2]^+ > [Ni(NH_3)_6]^{++} = [Co(NH_3)_6]^{++} > [Cu(NH_3)_4]^{++} > [Cr(NH_3)_6]^{+++} > [Co(NH_3)_6]^{+++} > [Pt(NH_3)_4]^{++}$. The spectra of some ammine complexes do not have well-defined absorption bands in the 3200 cm.$^{-1}$ region and the high frequency peaks in particular are not clearly resolved. In the ethylenediamine–metal chelates the effect of the charge on the complex on the H–N stretching frequency is seen in compounds 40 and 39 and 2 and 41: $[Co(en)_2Cl_2]^+ > [Co(en)_3]^{+++}$ and $[Pt(en)Br_2] > [Pt(en)_2]^{++}$. Again, $[Co(en)_3]^{+++} > [Pt(en)_2]^{++}$ indicating that the strong tendency of platinum(II) to form covalent bonds is more effective than the greater charge on the cobalt in determining the H–N frequency shift.

The N–H stretching vibration in the glycinate ligand (Table II-E2) decreases in frequency from the glycinate ion (potassium salt) to the copper(II), cobalt(III) and platinum(II) complexes, respectively. Glycine itself ($^+H_3NCH_2COO^-$) absorbs at the lowest frequency, indicating that the addition of a proton to the glycinate ion to form a third strong N–H bond is more effective than N–M bond formation in decreasing the N–H stretching vibration frequency.

The spectra of the salicylaldimine complexes reveal the following order for the N–H stretching frequencies: $Zn(sal)_2 > Be(sal)_2 > Cu(sal)_2 > Ni(sal)_2 > Fe(sal)_2$. Irving and Williams[12] have pointed out that the stability of Cu(II) complexes is greater than that of the corresponding Ni(II) complexes irrespective of the nature of the coördinating group. The small difference between the N–H frequencies in the spectra of the salicylaldimines indicates that N–Ni bond is stronger than the N–Cu bond in these complexes. This is substantiated by the relative positions of the sharp absorption peak in the 1600 cm.$^{-1}$ region, attributed to the C=N stretching vibration, in the spectra of the nickel and copper salicylaldimines. The copper complex absorbs at 1620 cm.$^{-1}$ and the nickel complex at 1616 cm.$^{-1}$. Bellamy and Branch[13] have shown that the frequency of the CO stretching vibration in salicylaldehyde complexes with metals decreases with increasing strength of the O–M bond, and work in this Laboratory has revealed a similar correlation of C=N frequencies with N–M bond strengths in the spectra of salicylaldimine and N-methylsalicylaldimine complexes. The spectra of the salicylaldimine complexes of nickel and copper in the cesium bromide region offer additional evidence for the greater strength of the nitrogen-to-nickel bond. Peaks attributed to nitrogen-to-metal stretching vibrations occur at 450 and 470 cm.$^{-1}$ in the spectra of the copper and nickel complexes, respectively. An additional peak in the spectrum of the copper complex at 365 cm.$^{-1}$ (attributed to the O–Cu stretching vibration) has no counterpart in the spectrum of the nickel complex.

F. Spectra of Solutions.—The spectra of chloroform solutions of the complexes listed in Table III all show single, sharp peaks in the 3300 cm.$^{-1}$ region. The absence of the 3200 cm.$^{-1}$ peak in the spectra of the tetrahedral and octahedral complexes indicates a lack of coupling between the H–N vibrations in these complexes in solution. This suggests a weakening of the N–M bonds by the solvent. Willis and Mellor[14] have shown by magnetic measurements that N–M bonds in some complexes of this type which are covalent in the solid state become electrostatic (or weak, outer orbital type bonds) in chloroform solution.

The N–H stretching frequencies are higher in solution than in the solid state, compatible with weaker N–M bonding, but the same order of decreasing frequencies is observed for the salicylaldimine complexes in chloroform solutions. The maxima in pyridine are broad, owing to hydrogen bonding with the solvent, and are at higher frequencies than in chloroform, indicating that pyridine has a greater effect than chloroform in weakening the N–M bonds. This interpretation of the uncoupling of N–H vibrations in solution by the action of the solvent in weakening the N–M bonds is not supported by the observation that the peaks at 870 and 920 cm.$^{-1}$ in the spectrum of bis-(N-methylsalicylaldimino)-beryllium, attributed to the O–Be and N–Be stretching vibrations, occur at the same frequencies in the solid state as in chloroform solution.

The investigation of the spectra of these coördination compounds is being extended in this Laboratory to the region of the N–H rocking frequencies[15] and to the region of the O–M and N–M stretching vibrations.

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