

Contribution from the Department of Chemistry,
West Virginia University, Morgantown, West Virginia 26506

Preparation, Infrared Spectra, Visible Reflectance Spectra, and Magnetic Moments of Copper(II) Complexes of *N,N'*-Di(2-hydroxyethyl)ethylenediamine, *N*-(2-Hydroxyethyl)ethylenediamine, and *N*-(2-Hydroxypropyl)ethylenediamine^{1,2}

DONALD N. ZIMMERMAN and JAMES L. HALL*

Received January 16, 1973

Mononuclear compounds of the type $\text{Cu(L)}_2\text{X}_2$ have been prepared, where L is *N,N'*-di(2-hydroxyethyl)ethylenediamine (2hn), *N*-(2-hydroxyethyl)ethylenediamine (hn), or *N*-(2-hydroxypropyl)ethylenediamine (hpn) and X^- is ClO_4^- , $1/2\text{SO}_4^{2-}$, Cl^- , or NO_3^- . A Schiff base complex was formed from $\text{Cu}(\text{NO}_3)_2$, hpn, and acetone. Each complex was characterized by elemental analysis, infrared spectrum, electronic reflectance spectrum, and magnetic moment. For each a distorted octahedral pattern of coordination about the copper(II) ion is probable. Four coordination positions in an approximate plane are occupied by four nitrogen atoms at nearly equal distances. For all of the complexes of 2hn and for the perchlorate and sulfate complexes of hn and hpn, the axial positions of the distorted octahedron are occupied by coordinated hydroxyl oxygen atoms of the amino alcohol molecules. These axial positions are occupied by chloride ions in the hn and hpn chlorides. For the nitrate complex of hn and the Schiff base complex it appears that one axial position is occupied by a hydroxyl oxygen atom and the other has coordinated a nitrate ion.

Introduction

This study was designed to determine the pattern of coordination about the copper(II) ion for a number of crystalline complexes in which the ligand is a mono- or di-*N*-(2-hydroxyethyl)- or *N*-(2-hydroxypropyl)-substituted ethylenediamine molecule. In particular we wished to determine whether or not the oxygen atoms of the alcoholic groups participated in the coordination and, if so, whether or not the hydroxyl proton was lost upon coordination. For the three ethanolamines and for a number of *N*- and *C*-alkyl-substituted ethanolamines, polarographic studies,³ in aqueous solution at high pH, have shown that complexes of the type $\text{Cu}(\text{AOH})_p(\text{AO})_q^{2-q}$ may be formed where AOH represents the amino alcohol molecule, AO^- represents the ion formed by loss of a hydroxyl proton; *p* may be 0-3, and *q* may be 0-2. The ranges of *p* and *q* differ greatly for different ligands. Similar species may be formed in alkaline solutions by the copper(II) ion and alkanol-substituted ethylenediamine molecules.^{4,5} For each complex which loses an alcoholic proton a five-membered chelate ring is formed by coordination of a nitrogen and an alkoxy oxygen atom to the metallic ion. Studies of crystalline compounds of the ethanolamines and of substituted ethanolamines^{6,7} have shown, also, that complexes of the same general formula, above, may be formed. Four-, five-, and six-coordinate structures have been proposed to account for the properties of these compounds in crystalline form or in solution. Only a few studies have been reported on properties of crystalline copper(II) complexes of alkanol-substituted ethylenediamine molecules⁸⁻¹⁴

and in no case has a species been reported in which a hydroxyl proton has been lost. Very extensive studies have been made of crystalline copper(II) complexes of ethylenediamine and of *N*-alkyl-substituted ethylenediamines¹⁵ and these studies are of value for comparison with the results of the present work.

With the aid of two complete structural determinations^{14,16} we are able to postulate structures of all of the compounds described here.

Experimental Section

Physical Measurements. Infrared spectra were recorded from 4000 to 600 $\text{K} (\text{K} = \text{cm}^{-1})$ by use of a Beckman IR-8 spectrophotometer. Spectra of the crystalline dihydrochloride salts, of crystalline 2hn, and of the coordination compounds were obtained from Nujol and perfluorocarbon mulls. The diffuse reflectance spectra of the copper(II) complexes were measured with a Beckman Model DU spectrophotometer. The reflectance attachment provided by the manufacturer was modified to permit work at liquid nitrogen temperature.¹⁷ Absorbances were recorded over the range 24-9 kK. The reflectance spectra were analyzed into gaussian components by use of a Du Pont curve analyzer and by a method of calculation suggested by Jorgensen.¹⁸ Magnetic susceptibilities were measured at 20° with a Gouy balance, following usual techniques for calibration and calculation.¹⁹

Analyses. Neutral equivalents (NE) of the copper(II) complexes were found by titration of a weighed sample with 0.1 *N* nitric acid. End points were determined by plotting pH as a function of acid added. The copper analyses were made by a conductometric titration with a standard solution of the disodium salt of ethylenediaminetetraacetic acid.²⁰ Carbon, nitrogen, hydrogen, sulfur, and chlorine analyses were made by Galbraith Laboratories, Inc. The analyses of all compounds are shown in Table I.

Reagents. 2-(2-Aminoethylamino)ethanol [*N*-(2-hydroxyethyl)ethylenediamine, $\text{H}_2\text{NC}_2\text{H}_4\text{NHC}_2\text{H}_4\text{OH}$, hn] was obtained from the

(1) Presented in part at the 2nd Central Regional Meeting, American Chemical Society, Columbus, Ohio, June 1970.

(2) Taken in part from the Ph.D. dissertation of D. N. Z., West Virginia University, 1969.

(3) J. L. Hall, R. B. Simmons, E. Morita, E. Joseph, and J. F. Gavlas, *Anal. Chem.*, **43**, 634 (1971), and references therein.

(4) J. L. Hall, W. E. Dean, and E. A. Pacofsky, *J. Amer. Chem. Soc.*, **82**, 3303 (1960), and references therein.

(5) J. L. Hall, E. Joseph, and M. B. Gum, *J. Electroanal. Chem. Interfacial Electrochem.*, **34**, 529 (1972).

(6) D. G. Brannon, R. H. Morrison, J. L. Hall, G. L. Humphrey, and D. N. Zimmerman, *J. Inorg. Nucl. Chem.*, **33**, 981 (1971), and references therein.

(7) I. A. Cody, S. I. Woodburn, M. W. Blackmore, and R. J. Magee, *J. Inorg. Nucl. Chem.*, **32**, 3263 (1970).

(8) J. G. Breckenridge, *Can. J. Res., Sect. B*, **26**, 11 (1948).

(9) V. C. Patel and N. F. Curtis, *J. Chem. Soc. A*, 1607 (1969).

(10) R. Nasanen, L. Lemmetti, K. Anttila, K. Jokisalo, and K. Loytane, *Suom. Kemistilehti B*, **42**, 124 (1969).

(11) R. Nasanen, L. Lemmetti, K. Anttila, L. Lehtinen, and M. Maunula, *Suom. Kemistilehti B*, **42**, 357 (1969).

(12) R. Nasanen, L. Lemmetti, and P. Ilvonen, *Suom. Kemistilehti B*, **41**, 111 (1968).

(13) A. Pajunen and M. Lehtonen, *Suom. Kemistilehti B*, **41**, 343 (1968).

(14) A. Pajunen and M. Nasakkala, *Suom. Kemistilehti B*, **45**, 47 (1972).

(15) A. B. P. Lever and E. Mantovaini, *Inorg. Chem.*, **10**, 817 (1971), and references therein.

(16) R. V. Chastain, Jr., and T. L. Dominick, *Inorg. Chem.*, **12**, 2621 (1973).

(17) D. G. Brannon and J. L. Hall, *Proc. W. Va. Acad. Sci.*, **39**, 359 (1967).

(18) C. K. Jorgensen, *Acta Chim. Scand.*, **8**, 1495 (1954).

(19) N. F. Curtis, *J. Chem. Soc.*, 3147 (1961).

(20) J. L. Hall, J. A. Gibson, Jr., P. R. Wilkinson, and H. O. Phillips, *Anal. Chem.*, **26**, 1484 (1954).

Table I. Analytical Data^a

No		NE	% Cu	% C	% N	% H	% Cl	% S
I	Cu(2hn) ₂ (ClO ₄) ₂	139.7	11.37	25.79	10.03	5.78	12.69	
	Cu ₁₂ H ₃₂ N ₄ O ₄ (ClO ₄) ₂	140.0	11.55	25.89	10.00	5.82	12.90	
II	Cu(2hn) ₂ SO ₄	114.0	13.93	31.60	12.29	7.07		
	Cu ₁₂ H ₃₂ N ₄ O ₄ SO ₄	112.6	14.09	31.29	12.06	6.95		
III	Cu(2hn) ₂ Cl ₂	107.7	14.74	33.44	13.00	7.50	16.45	
	Cu ₁₂ H ₃₂ N ₄ O ₄ Cl ₂	108.6	14.56	32.35	12.40	7.23	16.88	
IV	Cu(2hn) ₂ (NO ₃) ₂	121.0	13.13	29.78	17.37	6.67		
	Cu ₁₂ H ₃₂ N ₄ O ₄ (NO ₃) ₂	118.0	13.05	29.72	17.58	6.75		
V	Cu(hn) ₂ (ClO ₄) ₂	117.7	13.50	20.41	11.90	5.15	15.06	
	Cu ₈ H ₂₄ N ₄ O ₂ (ClO ₄) ₂	116.8	13.76	20.73	11.71	5.31	15.46	
VI	Cu(hn) ₂ SO ₄	92.0	17.27	26.11	15.23	6.59		8.71
	Cu ₈ H ₂₄ N ₄ O ₂ SO ₄	91.0	17.84	25.47	14.81	6.27		8.48
VII	Cu(hn) ₂ Cl ₂	85.7	18.54	28.03	16.35	7.07	20.68	
	Cu ₈ H ₂₄ N ₄ O ₂ Cl ₂	84.0	19.04	28.09	16.18	7.12	20.84	
VIII	Cu(hn) ₂ (NO ₃) ₂	99.0	16.05	24.27	21.23	6.12		
	Cu ₈ H ₂₄ N ₄ O ₂ (NO ₃) ₂	97.4	16.62	24.41	21.59	6.16		
IX	Cu(hpn) ₂ (ClO ₄) ₂	124.7	12.74	24.07	11.23	5.67	14.21	
	Cu ₁₀ H ₂₈ N ₄ O ₂ (ClO ₄) ₂	123.7	12.96	23.99	11.09	5.60	14.36	
X	Cu(hpn) ₂ SO ₄	99.0	16.04	30.33	14.15	7.14		8.10
	Cu ₁₀ H ₂₈ N ₄ O ₂ SO ₄	97.4	16.55	29.46	13.39	7.42		7.96
XI	Cu(hpn) ₂ Cl ₂	92.7	17.13	32.38	15.11	7.63	19.12	
	Cu ₁₀ H ₂₈ N ₄ O ₂ Cl ₂	90.8	17.36	32.32	15.19	7.60	19.44	
XII	Cu(HSB)(NO ₃) ₂	126.0	12.60	38.12	16.67	7.21		
	Cu ₁₆ H ₃₆ N ₄ O ₂ (NO ₃) ₂	125.9	12.78	38.00	16.54	6.95		

^a The first row of numbers for a compound gives the calculated values, while the second row gives the found values.

Union Carbide Corp., Chemicals and Plastics. 1-(2-Aminoethyl-amino)-2-propanol [*N*-(2-hydroxypropyl)ethylenediamine, H₂NC₂H₄NHCH₂CH(OH)CH₃, hpn] was obtained from the Wyandotte Chemical Corp. For preparation of crystalline compounds these were used as received or after redistillation. *N,N'*-Di(2-hydroxyethyl)ethylenediamine (HOC₂H₄NHC₂H₄NHC₂H₄OH, 2hn) was obtained as a crystalline solid from the Ames Laboratories, Inc., and was used as received.

Preparations. The dihydrochloride salts of hn and hpn were formed by passing hydrogen chloride gas into an ethanol solution of the diamine. They were washed with ethanol and diethyl ether.

Crystalline copper(II) complexes were prepared by mixing and subsequent processing of solutions of the copper(II) salt and ligand. All products were washed until a colorless filtrate was obtained and the final washing was with dry diethyl ether. The solutions and samples were protected from atmospheric moisture during preparation and were stored in a sealed container over a drying agent. The chloride, perchlorate, and nitrate complexes of hn have been obtained by methods alternate to those given below.^{8,10}

Preparation of Bis[*N,N'*-di(2-hydroxyethyl)ethylenediamine]copper(II) Perchlorate, Cu(2hn)₂(ClO₄)₂ (I), Bis[*N*-(2-hydroxyethyl)ethylenediamine]copper(II) Perchlorate, Cu(hn)₂(ClO₄)₂ (V), and Bis[*N*-(2-hydroxypropyl)ethylenediamine]copper(II) Perchlorate, Cu(hpn)₂(ClO₄)₂ (IX). These compounds were prepared by a method similar to that previously described for (2-aminoethoxido)(2-aminoethanol)copper(II) perchlorate.⁵ For these diamine complexes, copper(II) perchlorate hexahydrate (0.05 mol) dissolved in 50 ml of methanol was dehydrated by stirring with 60 ml of 2,2-dimethoxypropane. Sixty milliliters of 1-propanol was added and the acetone and methanol were removed by evaporation. Ligand (0.15 mol) was added and stirring was continued until crystallization was complete. For these preparations extreme precautions were taken for handling mixtures of perchlorate salts and organic compounds. No difficulties were experienced. The solid compounds "sparkle" or flash when ignited but we have had no explosions.

Preparation of Bis[*N,N'*-di(2-hydroxyethyl)ethylenediamine]copper(II) Sulfate, Cu(2hn)₂SO₄ (II), Bis[*N*-(2-hydroxyethyl)ethylenediamine]copper(II) Sulfate, Cu(hn)₂SO₄ (VI), and Bis[*N*-(2-hydroxypropyl)ethylenediamine]copper(II) Sulfate, Cu(hpn)₂SO₄ (X). Compound II was formed by addition of 150 ml of 1-propanol to a solution which had been formed by mixing the ligand (0.04 mol) into a solution of copper(II) sulfate pentahydrate (0.02 mol) in 150 ml of methanol. For VI and X, anhydrous copper(II) sulfate (0.05 mol) was suspended in 100 ml of anhydrous methanol. Ligand (0.10 mol) was added. A dark solution was produced with evolution of heat. After 1 hr of stirring and cooling, the precipitate separated. These two compounds are particularly sensitive to decomposition by moisture while being washed (with methanol or diethyl ether) but after being dried they absorb moisture only very slowly.

Preparation of Bis[*N,N'*-di(2-hydroxyethyl)ethylenediamine]copper(II) Chloride, Cu(2hn)₂Cl₂ (III), Bis[*N*-(2-hydroxyethyl)

ethylenediamine]copper(II) Chloride, Cu(hn)₂Cl₂ (VII), and Bis[*N*-(2-hydroxypropyl)ethylenediamine]copper(II) Chloride, Cu(hpn)₂Cl₂ (XI). For each of these, ligand (0.05 mol) was added to copper(II) chloride dihydrate (0.02 mol) dissolved in 200 ml of 1-propanol. Upon mixing, heat was evolved and a deep blue solution formed. After about 2 hr of stirring, the crystalline product separated.

Preparation of Bis[*N,N'*-di(2-hydroxyethyl)ethylenediamine]copper(II) Nitrate, Cu(2hn)₂(NO₃)₂ (IV), Bis[*N*-(2-hydroxyethyl)ethylenediamine]copper(II) Nitrate, Cu(hn)₂(NO₃)₂ (VIII), and 1,15-Dihydroxy-1,7,7,9,15-pentamethyl-3,6,10,13-tetraazon-10-enecopper(II) Nitrate, Cu(HSB)(NO₃)₂ (XII). For IV copper(II) nitrate dihydrate (0.02 mol) in 25 ml of methanol was slowly mixed with the ligand (0.05 mol) in 50 ml of methanol. The product was separated after stirring for 1 hr. The same procedure was followed for VIII except that the compound was obtained by pouring the stirred mixture into 300 ml of acetone and allowing the solution to stand for 3 days. Similar procedures failed to produce a precipitate using hpn as ligand. Subsequently, 100 ml of 1-propanol was added to a fresh mixture of the methanol solution, the volume was reduced to 100 ml by use of a rotary evaporator, and the mixture was then poured into 300 ml of acetone. The Schiff base compound, XII, formed as fine crystals over a period of 2 weeks. The conditions used here were less drastic than had been used for a similar complex from hn.⁹

Results and Discussion

The crystal structures of two of the complexes of the present work are known. Cu(hn)₂Cl₂ has four nitrogen atoms coordinated in an approximate square in the radial positions of a distorted octahedral structure.¹⁴ The primary amine nitrogen atoms are trans to one another. The two chloride ions are coordinated in the axial positions at somewhat greater distances. Greater distortion of the octahedron is found¹⁶ for Cu(hn)₂(ClO₄)₂. For this complex the four nitrogen atoms are in the radial positions but the primary nitrogen atoms are cis to one another. The two alcoholic oxygen atoms are coordinated to the axial positions and the O-Cu-O angle is reduced to about 155°. More limited X-ray data for Cu(hn)₂(NO₃)₂¹⁰ indicate a distorted octahedral structure, also. The magnetic moments and reflectance spectra support the proposal that all of the complexes of this report have similar octahedral structures. The infrared spectra give a good indication as to whether the anions or alcoholic oxygen atoms are coordinated in the axial positions.

Magnetic Moments. The magnetic moments of the complexes, included in Table II, fall within a very limited range.

Table II. Magnetic Moments and Resolved Components of Low-Temperature Reflectance Spectra^a

No.		μ_{eff} , BM	$\bar{\nu}_1$	$\bar{\nu}_2$	$\bar{\nu}_3$	$10Dq$, kK
I	Cu(2hn) ₂ (ClO ₄) ₂	1.87	13.2 (0.28)	16.2 (0.24)	17.9 (0.39)	10.5
II	Cu(2hn) ₂ SO ₄	1.86	13.2 (0.56)	16.1 (0.27)	18.0 (0.49)	10.5
III	Cu(2hn) ₂ Cl ₂	1.89	13.5 (0.35)	15.7 (0.22)	18.2 (0.34)	10.2
IV	Cu(2hn) ₂ (NO ₃) ₂	1.86	13.4 (0.19)	15.4 (0.37)	18.0 (0.41)	10.0
V	Cu(hn) ₂ (ClO ₄) ₂	1.89	13.0 (0.24)	15.7 (0.21)	18.6 (0.25)	11.0
VI	Cu(hn) ₂ SO ₄	1.85	13.6 (0.27)	17.6 (0.13)	18.8 (0.41)	11.4
VII	Cu(hn) ₂ Cl ₂	1.94	14.0 (0.15)	17.2 (0.14)	19.2 (0.20)	11.2
VIII	Cu(hn) ₂ (NO ₃) ₂	1.85	12.6 (0.41)	16.3 (0.24)	18.4 (0.27)	11.1
IX	Cu(hpn) ₂ (ClO ₄) ₂	1.88	13.1 (0.45)	15.9 (0.22)	18.3 (0.38)	10.6
X	Cu(hpn) ₂ SO ₄	1.88	13.0 (0.48)	16.2 (0.25)	18.3 (0.47)	10.8
XI	Cu(hpn) ₂ Cl ₂	1.86	14.0 (0.21)	17.1 (0.12)	18.8 (0.36)	11.0
XII	Cu(HSB)(NO ₃) ₂	1.85	13.3 (0.17)	15.5 (0.21)	18.3 (0.28)	10.3

^a Wave numbers are in kK. Relative intensities are given in parentheses.

This range, from 1.85 to 1.94 BM, indicates that all of the complexes are mononuclear. These values permit assignment of a distorted octahedral structure about the copper(II) ion. There is no discernible trend for the moments as the anion or ligand is changed.

Electronic Spectra. The diffuse reflectance spectra all show a broad band in the approximate range 21–11 kK. As is shown in Figure 1, all give indication of more than one component within this band and the relative intensities of the high- and low-frequency components vary greatly from compound to compound. The resolution of these spectra, shown in Table II, is subject to some error, particularly in the position and intensity of the middle band.²¹ The resolution is least satisfactory for the three sulfate complexes for which two bands give nearly as good a fit to the experimental curves as the three shown. Some trends may be observed in the frequencies. Within each ligand, the chloride complex gives the highest frequencies. The variation between the perchlorate, nitrate, and sulfate complexes is relatively small. The highest frequencies are shown by the complexes of hn. Those of hpn are nearly the same and the frequencies for the 2hn complexes are significantly lower. These differences correlate closely with the basic strengths of the ligand molecules. For hn, hpn, and 2hn, the values of the base constants, determined at amine concentrations near 0.01 M and at ionic strength 0.50 and expressed as $\text{p}K_{\text{AH}}$ are respectively 9.83 and 6.72, 9.77 and 6.93, and 9.32 and 6.52.²²

The three-band spectrum in the range 22–10 kK is typical of tetragonally distorted copper(II) ions. In the present case, the low-frequency band seems to be consistently more prominent than usual and the components which make up the envelope are more obvious. These spectra resemble somewhat the spectra for copper(II)-ethylenediamine complexes reported by Proctor, Hathaway, and Nichols²³ and some of them are similar to some of the spectra shown for tetragonal copper(II)-tetraamine complexes by Tomlinson, Hathaway, Billing, and Nichols.²⁴ The frequencies for the resolved components of the en complexes²³ are generally greater than for those of the present work and this possibly reflects the greater basic strength of ethylenediamine (as $\text{p}K_{\text{AH}}$ the constants for en are 10.13 and 7.47²²). It is surprising to us that the different groups coordinated in the axial positions make almost negligible difference in the spectra obtained.

In spite of the distortion of the tetragonal structure in our complexes an approximate treatment assuming validity of

(21) C. K. Jorgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, Oxford, 1962, p 100.

(22) J. L. Hall, *Proc. W. Va. Acad. Sci.*, **35**, 104 (1963).

(23) I. M. Proctor, B. J. Hathaway, and P. Nichols, *J. Chem. Soc. A*, 1678 (1968).

(24) A. A. G. Tomlinson, B. J. Hathaway, D. E. Billing, and P. Nichols, *J. Chem. Soc. A*, 65 (1969).

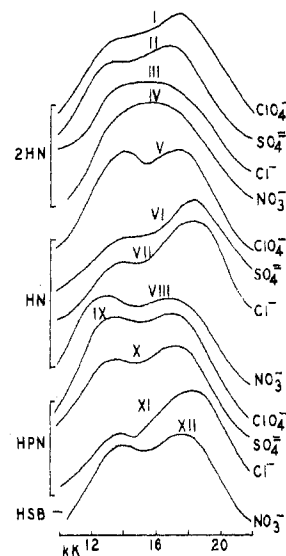


Figure 1. Diffuse reflectance spectra, at liquid nitrogen temperature, of the copper(II) perchlorate, sulfate, chloride, and nitrate complexes of 2hn, hn, and hpn.

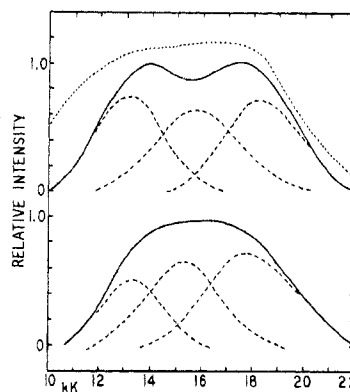


Figure 2. Diffuse reflectance spectra and resolved components for Cu(hn)₂(ClO₄)₂ (top) and Cu(2hn)₂Cl₂ (bottom). All data are at liquid nitrogen temperature except the dotted line which is for room temperature.

D_{4h} symmetry appears to be valid as for somewhat similar complexes of ammonia^{24,25} and of ethylenediamine.²³ In agreement with these previous studies we assume that the low-, middle-, and high-frequency bands shown in Table II are due to transitions from the ${}^2B_{1g}$ level to the ${}^2A_{1g}$, ${}^2B_{2g}$, and 2E_g levels, respectively. The first transition is designated Δ_1 , and the difference between the last two is designated Δ_2 . An approximate value for $10Dq$ is obtained by assuming that

(25) H. Elliott and B. J. Hathaway, *Inorg. Chem.*, **5**, 885 (1966).

the baricenter is maintained for the splitting of the ²E_g and ²T_{2g} terms in going to D_{4h} symmetry and using the formula²⁵

$$10Dq = \left(\bar{\nu}_3 - \frac{\Delta_2}{2} \right) - \frac{\Delta_1}{2}$$

It is noted from Table II that the values of 10Dq are nearly the same for all of the complexes of a given ligand and that the values are in the same order as the values of pK_{AH}: hn > hpn > 2hn. This is as expected and is further evidence for the distorted octahedral structure of the complexes.

Infrared Spectra. The infrared spectra of the anions and coordinated ligands indicate the groups coordinated at the axial positions of the distorted octahedral structure. In no complex are the perchlorate or sulfate ions coordinated. Chloride ions are coordinated at both axial positions of the hn and hpn complexes. For the nitrate complexes of hn and HSB one position is occupied by a monodentate nitrate ion. For all of the 2hn complexes, for the perchlorate and sulfate complexes of hn and hpn, and for the remaining positions on the nitrate complexes of hn and HSB, the axial positions have coordinated hydroxyl oxygen atoms of the ligands.

Spectra Due to Anions. Each of the perchlorate complexes gives a very strong and broad band in the range 1160-1040 K ($\bar{\nu}_3$) with a weak band near 926 K ($\bar{\nu}_1$) and a strong, sharp band in the range 623-617 K ($\bar{\nu}_4$). This pattern is typical of uncoordinated perchlorate ion.²⁶ Each sulfate complex gives a very strong and broad band in the range 1160-1040 K ($\bar{\nu}_3$) with a weak, sharp spike near 967 K ($\bar{\nu}_1$) and a strong sharp band in the range 618-605 K ($\bar{\nu}_4$). These features are characteristic for uncoordinated sulfate ion.²⁷ Due to the superposition of strong ligand frequencies on the $\bar{\nu}_3$ sulfate band of Cu(hpn)₂SO₄ and to modifications due to hydrogen bonding, splitting of this band corresponding to bidentate coordination of the sulfate ion cannot be absolutely excluded.²⁸ However, the strong, sharp band near 610 K and the presence of the band at 967 K favor uncoordinated sulfate.

For Cu(2hn)₂(NO₃)₂, the nitrate ion produces a very strong single absorption at 1364 K ($\bar{\nu}_3$), a medium, sharp band at 823 K ($\bar{\nu}_2$), and a band at 714 K ($\bar{\nu}_4$). This pattern is typical for uncoordinated nitrate ion.²⁹ For Cu(hn)₂(NO₃)₂ and Cu(HSB)(NO₃)₂ the spectra show the frequencies expected for both uncoordinated and monodentate nitrate ions.²⁹ For Cu(hn)₂(NO₃)₂, $\bar{\nu}_3$ appears as two very strong bands at 1395 and 1328 K (monodentate ion) and as a strong, sharp band at 1367 K (uncoordinated ion). For the Schiff base complex these bands are at 1384, 1324, and 1345 K, respectively. For each complex the band from 720 to 710 K which includes a contribution from the mulling agents is broad enough to include splitting of the $\bar{\nu}_4$ band. For the nitrate complexes of hn and HSB there is a remote possibility that the symmetry of the nitrate ion is sufficiently lowered by hydrogen bonding to produce the observed splitting.

Hydroxyl Stretching Frequencies. The OH stretching frequencies of gaseous alcohols are usually well above 3500 K.³⁰ In liquid and solid compounds they may be lowered to 3200 K or less due to hydrogen bonding or to coordination

Table III. Infrared Spectra: Hydroxyl Stretching Frequencies, 3555-3180 K; Ligand Frequencies, 1200-700 K

2hn	I	II	IIIe	IV	V	VI	VII	VIII	hpn-2HCl	IX	X	XI	XII ^a
3280 s	3500 s 3440 s	3310 s 3230 s	3275 s 3180 s	3350 m 3262 s	3300 vs 3555 vs	3330 sh 3320 vs	3320 vs 3340 s 3307 s	3345 vs 3340 s	3500 s	3250 sh	3350 m	3575 m 3480 m	
1181 s	1200 m	1200 w	1200 m	1200 sh	1193 m	1177 m	1195 s	1172 m	1190 m	1150 s ^b	1195 m	1180 w	
1122 s	1134 s ^b	1138 m	1135 m	1160 m	1148 sh ^b	1137 s ^b	1145 s	1135 vs	1138 sh	1129 sh ^b	1137 s	1122 s	
	1113 s ^b	1105 sh ^b	1107 s	1108 sh	1109 s ^b	1105 vs ^b	1103 s		1108 s ^b		1108 w		
	1095 s ^b	1095 sh ^b	1093 sh	1095 sh	1091 m							1093 sh	
1074 vs	1079 s ^b	1080 vs ^b	1082 s	1087 vs	1085 s ^b	1098 s ^b	1082 vs	1098 vs	1085 s ^b	1100 vs ^b	1093 s	1076 s	
1060 vs	1057 sh ^b	1060 s ^b	1050 vs	1058 vs	1070 sh	1070 vs ^b	1060 vs	1077 m	1056 s ^b	1056 s ^b	1072 vs	1065 sh	
	1043 m ^b	1042 s ^b	1047 m	1047 m							1055 m		
	1023 vs	1027 sh ^b	1022 s	1024 s ^b	1033 vs	1038 s ^b	1019 s	1033 vs	1028 vs	1040 sh ^b	1031 m	1022 vs ^b	
	990 s	1007 s	992 m	1008 m	998 s	996 s	1005 w	998 sh	992 s	1000 s	996 m	993 m	
950 vs	968 vs	977 m	980 vs	987 vs	980 s	996 s	977 vs	988 vs	974 vs	978 s	974 vs	974 s	
									913 s		922 m	926 m	
									917 s		910 w	910 m	
											884 w		
											875 w		
											850 w	840 m	
861 s	855 s	861 s	855 m	856 s							853 w		
845 vs	848 sh										841 w		
											822 s		
805 m	811 m	827 m	830 m	822 s							813 m		
		818 m	815 w								820 m		
											784 vs		
											714 s		
													758 m

^a A few weak frequencies are omitted. ^b Modified or partially obscured by strong band due to anion.

(26) M. E. Farago, J. M. James, and V. C. Trew, *J. Chem. Soc. A*, 820 (1967).

(27) K. Nakamoto, F. Fujita, S. Tanaka, and M. Kobayashi, *J. Amer. Chem. Soc.*, 79, 4904 (1957).

(28) A. Hezel and S. D. Ross, *Spectrochim. Acta, Part A* 24, 985 (1968).

(29) N. F. Curtis and Y. M. Curtis, *Inorg. Chem.*, 4, 804 (1965).

(30) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen, London, 1958, p 96.

of the oxygen atom. The assignment of the OH frequencies of the complexes (Table III) is based on the separation and appearance of the bands and upon the known structures of the two crystalline compounds. For crystalline 2hn the OH stretching frequency appears as a very strong, very sharp band at 3280 K. In each of the 2hn complexes this band is split. We assume that the higher frequency is associated with an uncoordinated oxygen atom and that the lower frequency results from coordination of the oxygen atom.

For $hn \cdot 2HCl$, the OH band at 3300 K is very sharp and strong. For $Cu(hn)_2Cl_2$ the OH band (uncoordinated oxygen atom) is strong and sharp at 3320 K. For $Cu(hn)_2(ClO_4)_2$ the single, strong band (coordinated oxygen atom) is at 3555 K. It is evident that the effect of hydrogen bonding in lowering the frequency in the hn salt and chloride complex is much greater than is the effect of coordination of the oxygen atom in the perchlorate complex. For the nitrate complex of hn and of the Schiff base the pairs of hydroxyl frequencies indicate one coordinated and one uncoordinated hydroxyl group for each copper(II) ion.

Intermediate Infrared Region. Except for the complex containing the Schiff base, complexes formed from hn and hpn all show a strong band near 1600 K which is characteristic for the NH_2 group. The Schiff base complex gives a band at 1670 K due to the $C=N$ group. Except for bands due to anions (above), other frequencies between those of the hydroxide groups and 1200 K are not reported.

1200-700 K Region. Table III shows the frequencies due to 2hn, to the salts of hn and hpn, and to the ligands in the complexes, from 1200 to 700 K. For all of these ligands as for en,³¹ it is evident that the various vibrational modes are strongly coupled and it is very difficult to make a direct assignment of each frequency to a vibration between a particular pair of atoms. No attempt will be made here to assign or discuss in detail the frequencies which do not give direct information about the arrangement of ligands about the copper(II) ion. We have, however, made detailed comparisons of our spectra with some published spectra of en, its salts, and its complexes.³¹⁻³⁸ It is possible to identify, among the many bands of our spectra, the bands due to corresponding complexes of en. The spectra show an increased number of bands as the ligand is changed from en to 2hn to hn to hpn. The complexes all show more bands than do the uncomplexed ligands.

Especially attention is called to one frequency region which has been the subject of speculation for complexes of en. All of the complexes and the two salts of the present work show a strong, characteristic absorption in the range 1040-1019 K which is absent from the free ligands. For $Cu(en)_2Cl_2$ a corresponding band occurs at 1047 K³³ and this band is found in complexes of en generally. It has been variously attributed to a CN stretch,³⁵ to a ring skeletal³⁶ or ring "breathing"³⁷ type of motion, or to an NH_2 twisting motion.³⁸ Since this

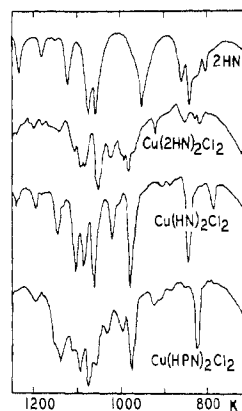


Figure 3. Infrared spectra, 1200-700 K, for 2hn and for the copper(II) chloride complexes of 2hn, hn, and hpn.

frequency is absent from the spectrum of 2hn but is present in $hn \cdot 2HCl$ and $hpn \cdot 2HCl$ and since the complexes of 2hn have no NH_2 group, some of these assignments cannot be made for our work. While more than one vibrational mode may possibly contribute to this absorption in the complexes and ligand salts of the present work, we are inclined to believe that it and a somewhat weaker band near 915 K contain contributions due to N-H motions which are strengthened and modified by coordination or protonation of the nitrogen atoms. A similar interpretation may be made for a band in the range 995-960 K which, in each case, is accompanied by a less prominent band 60-70 K lower in frequency.

The range 860-810 K offers the greatest correlation with and evidence for the assumptions concerning coordination and noncoordination of the hydroxyl oxygen atoms. In each of the complexes of 2hn there is a medium to strong band near 856 K which is evidently associated with an uncoordinated OH group. Each complex (except for the nitrate where it is obscured by an anion frequency) has also a pair of bands spaced at 10-15 K in the range 829-811 K. These appear to be associated with coordinated OH. For $Cu(hn)_2Cl_2$ a very strong band at 842 K is attributed to the presence of the uncoordinated OH group. For the perchlorate and sulfate complexes of hn, medium to weak bands at 822 and 812 K, respectively, indicate coordinated OH groups. For the nitrate complex of hn, interpretation is somewhat confused by the presence of the anion band, but the very strong band at 824 K is characteristic for the uncoordinated group while the shoulder at 815 K is at the correct frequency for complexes having the coordinated ligand oxygen atom. For hpn and its complexes, we are accepting the characteristic, very strong bands near 822 K, for $Cu(hpn)_2Cl_2$ and $Cu(HSB)(NO_3)_2$, as evidence for uncoordinated hydroxyl groups and accept the absence of such bands for the perchlorate and sulfate complexes as evidence for coordinated hydroxyl groups in these complexes.

Acknowledgments. D. N. Z. is grateful for support in the form of an NDEA fellowship for the 1966-1969 academic years. We are grateful to Professor B. E. Douglas and the University of Pittsburgh for the use of the Du Pont 310 curve resolver.

Registry No. $Cu(2hn)_2(ClO_4)_2$, 41574-63-4; $Cu(2hn)_2SO_4$, 41574-64-5; $Cu(2hn)_2Cl_2$, 41574-65-6; $Cu(2hn)_2(NO_3)_2$, 41697-43-2; $Cu(hn)_2(ClO_4)_2$, 36539-67-0; $Cu(hn)_2SO_4$, 41574-66-7; $Cu(hn)_2Cl_2$, 36445-04-2; $Cu(hn)_2(NO_3)_2$, 41574-67-8; $Cu(hpn)_2(ClO_4)_2$, 41574-68-9; $Cu(hpn)_2SO_4$, 41697-46-5; $Cu(hpn)_2Cl_2$, 41574-69-0; $Cu(HSB)(NO_3)_2$, 39386-75-9.

(31) N. Tanaka, N. Sato, and J. Fujita, *Spectrochim. Acta*, **22**, 577 (1966).

(32) A. Sabatini and S. Califano, *Spectrochim. Acta*, **16**, 677 (1960).

(33) W. R. McWhinnie, *J. Inorg. Nucl. Chem.*, **26**, 21 (1964).

(34) J. Bellanato, *Spectrochim. Acta*, **16**, 1344 (1960).

(35) G. W. Watt and D. S. Klett, *Inorg. Chem.*, **5**, 1278 (1966).

(36) D. B. Powell and N. Sheppard, *Spectrochim. Acta*, **17**, 68 (1961).

(37) R. J. Mureinik and W. Robb, *Spectrochim. Acta, Part A*, **24**, 837 (1968).

(38) A. D. Allen and C. V. Senoff, *Can. J. Chem.*, **43**, 888 (1965).