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Syntheses and Magnetic Properties of N-[2-(2-Hydroxyethylthio)phenyl]arenesulfonamidatocopper(II) Chelates

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Various N-[2-(2-hydroxyethylthio)phenyl]arenesulfonamidatocopper(II) chelates and the addition compounds thereof with methanol or ethanol were synthesized, and several typical ones were subjected to magnetic determination at temperatures between about 80 and 300°K. The temperature dependence of the observed magnetic susceptibility indicates that the copper(II) chelate-bisalcohols form dimeric aggregates while the alcohol-free copper(II) complexes are trimeric when they are prepared by precipitation from chloroform solutions and heating in *n*-hexane rather than by heating the copper(II) chelate-bisethanol or -bismethanol under reduced pressure. The molecular weights of the alcohol-free complexes also are indicative of the existence of trimeric molecules in chloroform solutions.

Introduction

Sulfonamido groups, $-NHSO_2R$, are as strongly acidic as phenolic hydroxyl groups and act as proton donors. However, only a few papers¹⁻⁵ have ever been published on chelates having $-NSO_2R$ groups. In these chelates, nitrogen and oxygen occupy the coordination sites; in no examples is sulfur involved in coordination. Mizukami and Kono prepared compounds having a sulfur atom in addition to a sulfonamido group in an attempt to synthesize a new type of chelates possibly having applications in analytical chemistry. It was found⁶ that N-(2-mercaptophenyl)sulfonamides, $o-HSC_6H_4NH-SO_2R$, form water-soluble chelates with Co^{2+} , Ni^{2+} , and Cu^{2+} and that they can be used as analytical reagents for these metal ions. The present investigation has been undertaken in order to examine the reactions of N-[2-(2-hydroxyethylthio)phenyl]arenesulfonamides, $o-HOCH_2CH_2SC_6H_4NH-SO_2R$, with metal ions. Cu^{2+} , Pd^{2+} , Pt^{2+} , and Hg^{2+} have been found to form metal chelates. In particular, the copper(II) chelates show interesting magnetic properties.

Experimental Section

Syntheses of Ligands and Copper(II) Chelates. **2-(2-Hydroxyethylthio)aniline Hydrochloride.**—2-Aminobenzenethiol ($o-NH_2-C_6H_4SH$, 12.5 g) was added to a solution of sodium ethoxide prepared from metallic sodium (2.3 g) and dehydrated ethanol (40 ml). The mixture was cooled with ice and stirred, while 2-bromoethanol (12.5 g) was added to it in small quantities. Reaction took place with an intense heat evolution. Reflux was continued for 30 min. The system was cooled and ethanol was distilled off under reduced pressure. On adding water to the residue, a yellow oil ($o-NH_2C_6H_4SCH_2OH$) separated. It was extracted with diethyl ether. The extract was washed with dilute sodium hydroxide solution and water in succession and dried over anhydrous sodium sulfate. When the extract was saturated with dry hydrogen chloride, a white precipitate ($o-HOCH_2CH_2SC_6H_4NH_2 \cdot HCl$) separated. It was filtered off and dissolved in 90% methanol. On adding diethyl ether to the solution,

pale yellow needle crystals (12 g) precipitated, mp 137–138°. *Anal.* Calcd for $C_8H_{12}ONSCl$: C, 46.71; H, 5.88; N, 6.81; S, 15.59; Cl, 17.24. Found: C, 46.66; H, 6.01; N, 7.02; S, 15.54; Cl, 17.48.

N-[2-(2-Hydroxyethylthio)phenyl]arenesulfonamide.—2-(2-Hydroxyethylthio)aniline hydrochloride (0.05 mol) was dissolved in dehydrated pyridine (100 ml). The solution was cooled with ice and stirred, while arenesulfonyl chloride (RSO_2Cl , 0.05 mol) was added to it in small quantities. After standing at room temperature for 1 day, the system was heated over a water bath for 3 min. It was cooled and poured into water (300 ml). Separated oil was extracted with diethyl ether. The extract was washed with dilute hydrochloric acid. It was reextracted with dilute sodium hydroxide solution. On acidifying the extract with acetic acid, an oil layer ($o-RSO_2NHC_6H_4SCH_2CH_2OH$) separated. It solidified on cooling with ice ($R = p$ -bromophenyl, p -iodophenyl, or β -naphthyl). Phenyl, p -tolyl, and p -chlorophenyl derivatives, which did not solidify on cooling, were dissolved again in diethyl ether. The solution was extracted with 10% potassium hydroxide solution. On cooling the solution with ice, the potassium salt separated. Compounds thus synthesized are described in Table I.

N-[2-(2-Hydroxyethylthio)phenyl]arenesulfonamidatocopper(II)-Bismethanol.—N-[2-(2-Hydroxyethylthio)phenyl]arenesulfonamide (0.01 mol) was dissolved in methanol (50 ml). A 1% solution of copper(II) acetate in methanol (182 ml) was added to it. On allowing the mixture to stand at room temperature, the green crystals of $(o-RSO_2NC_6H_4SCH_2CH_2O)Cu \cdot 2CH_3OH$ separated. They were filtered off and dissolved in chloroform. The addition of methanol followed by standing yielded green crystals (yield, 95–97%). They lost methanol of crystallization gradually at room temperature and rapidly on heating. Compounds thus obtained are described in Table II.

N-[2-(2-Hydroxyethylthio)phenyl]arenesulfonamidatocopper(II).—When the copper(II) chelate-bismethanol was maintained at 100° under 2–3 mm, methanol escaped leaving the greenish brown powder of $(o-RSO_2NC_6H_4SCH_2CH_2O)Cu$. Compounds thus synthesized are described in Table III. Infrared spectra indicated the absence of NH and OH stretching vibrations. The molecular weight was determined by measuring the vapor pressure depression of chloroform solution using a Model 301-A vapor pressure osmometer from Mechrolab Co. The observed molecular weights agree with values calculated for trimers. When N-[2-(2-hydroxyethylthio)phenyl]-4-toluenesulfonamidatocopper(II) was examined in the mixtures of chloroform and ethanol, the degree of polymerization was found to decrease progressively with increasing volume fraction of ethanol in the solvent from about 3 in chloroform to 2.17 for chloroform:ethanol = 3:1. This indicates the partial transformation of the trimeric ethanol-free complex to a dimeric form. The copper(II)

(1) G. Schetty and H. Ackermann, *Angew. Chem.*, **70**, 222 (1958).

(2) G. Schetty, *Helv. Chim. Acta*, **45**, 1095 (1962); **48**, 1042 (1965); **49**, 461 (1966).

(3) J. H. Billman, N. S. Janetos, and R. Chernin, *Anal. Chem.*, **32**, 1342 (1960).

(4) J. H. Billman and R. Chernin, *ibid.*, **34**, 408 (1962); **36**, 552 (1964).

(5) T. R. Williams and F. G. Burton, *Anal. Chim. Acta*, **27**, 351 (1962).

(6) S. Mizukami and M. Kono, *Chem. Pharm. Bull. (Tokyo)*, **13**, 33 (1965).

TABLE I
 ANALYSIS OF σ -HOCH₂CH₂SC₆H₄NXSO₂R^a

R	% C		% H		% N		% S		% K	
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
C ₆ H ₅	48.39	48.49	4.06	4.31	4.03	4.15	11.25	11.21
<i>p</i> -CH ₃ C ₆ H ₄	49.83	49.71	4.46	4.47	3.87	3.94	10.82	10.84
<i>p</i> -ClC ₆ H ₄	44.02	44.01	3.43	3.55	3.67	3.75	10.23	10.24
<i>p</i> -BrC ₆ H ₄	43.30	43.19	3.63	3.70	3.61	3.77	16.52	16.21
<i>p</i> -IC ₆ H ₄	38.63	38.43	3.24	3.33	3.22	3.23	14.73	14.49
β -C ₁₀ H ₇	60.14	59.85	4.77	4.58	3.90	3.89	17.84	17.81

^a X is potassium for the first three compounds, while it is hydrogen for others. The first two and the last compounds form colorless needles, while the other three form colorless prisms. They melt at 197–198, 218, 166–168, 72–73, 69, and 120–121°, respectively.

 TABLE II
 ANALYSIS OF (σ -RSO₂NC₆H₄SCH₂CH₂O)Cu · 2CH₃OH^a

R	% C		% H		% N		% Cu		% CH ₃ O	
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
C ₆ H ₅	44.18	44.29	4.89	5.08	3.22	3.14	14.61	14.56	14.26	14.21
<i>p</i> -CH ₃ C ₆ H ₄	45.47	45.37	5.16	5.28	3.12	3.13	14.15	14.21	13.83	13.66
<i>p</i> -ClC ₆ H ₄	40.93	40.87	4.29	4.27	2.98	3.11	13.53	13.75	13.22	13.10
<i>p</i> -BrC ₆ H ₄	37.40	36.99	3.92	3.79	2.73	2.98	12.36	12.13	12.08	12.18
<i>p</i> -IC ₆ H ₄	34.26	34.13	3.59	3.74	2.50	2.26	11.33	11.31	11.06	11.30
β -C ₁₀ H ₇	49.52	49.34	4.78	4.84	2.89	2.82	13.10	12.89	12.80	12.80

^a These compounds form green prisms except for the *p*-iodophenyl compound, which forms green needles. They decompose on melting at 204–205, 184–185, 217–219, 198, >300, and 192–194°, respectively.

 TABLE III
 ANALYSIS OF (σ -RSO₂NC₆H₄SCH₂CH₂O)Cu^a

R	% C		% H		% N		% Cu	
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
C ₆ H ₅	45.33	45.36	3.53	3.92	3.77	3.73	17.13	17.41
<i>p</i> -CH ₃ C ₆ H ₄	46.80	46.67	3.93	4.11	3.64	3.71	16.51	16.35
<i>p</i> -ClC ₆ H ₄	41.48	41.34	2.98	3.24	3.46	3.40	15.67	15.68
<i>p</i> -BrC ₆ H ₄	37.38	37.19	2.69	2.87	3.11	3.03	14.12	14.04
<i>p</i> -IC ₆ H ₄	33.84	33.62	2.43	2.70	2.82	2.84	12.79	12.89
β -C ₁₀ H ₇	51.35	50.98	3.59	3.78	3.32	3.16	15.09	15.04

^a These compounds form greenish brown powders, which decompose on melting at 203–205, 183–185, 216–217, 196–197, >300, and 191–193°, respectively. The observed molecular weights are 1105, 1173, 1183, 1375, 1552, and 1272 in good agreement with 1110, 1155, 1216, 1347, 1488, and 1263 calculated as trimers, respectively.

chelate-bisethanol was sparingly soluble in ethanol-rich mixed solvents, in which molecular weight determination was unfeasible.

N-[2-(2-Hydroxyethylthio)phenyl]arenesulfonamidatocopper(II)-Bisethanol.—The foregoing compound was dissolved in a small quantity of chloroform and filtered. Ethanol (3–5 parts) was added to the filtrate. On standing, the green crystals of (σ -RSO₂NC₆H₄SCH₂CH₂O)Cu · 2C₂H₅OH separated. These compounds are described in Table IV.

The following compounds were subjected to magnetic measurements: N-[2-(2-hydroxyethylthio)phenyl]-4-toluenesulfonamidatocopper(II)-bisethanol, N-[2-(2-hydroxyethylthio)phenyl]-4-toluenesulfonamidatocopper(II) (sample A), N-[2-(2-hydroxyethylthio)phenyl]-2-naphthalenesulfonamidatocopper(II)-bis-methanol, and N-[2-(2-hydroxyethylthio)phenyl]-2-naphthalenesulfonamidatocopper(II) (sample A) described above. Because samples A were powders formed by removing methanol or ethanol of crystallization at 75–100° under reduced pressure, an attempt was made to let crystals grow in the following way. Sample A was dissolved in chloroform. On adding *n*-hexane (3–5 parts) to the solution, a precipitate was formed. After being heated for several hours in *n*-hexane, it was taken out and dried in a desiccator at 60°. Pale greenish brown, crystalline powders were obtained (samples B). *Anal.* Calcd for C₁₅H₁₅O₃NS₂Cu: see Table III. Found: C, 46.73; H, 4.14; N, 3.82; Cu, 16.30. Calcd for C₁₈H₁₈O₂NS₂Cu: see Table III. Found: C, 50.07; H, 3.83; N, 3.06; Cu, 15.19.

Results

Table V shows magnetic susceptibilities observed at room temperature. The molar susceptibilities were corrected for diamagnetic contributions using molar susceptibilities (in cgs emu mol⁻¹) of N-[2-(2-hydroxyethylthio)phenyl]-4-toluenesulfonamide (-194×10^{-6}),

 TABLE IV
 ANALYSIS OF (σ -RSO₂NC₆H₄SCH₂CH₂O)Cu · 2C₂H₅OH^a

R	% C		% H		% N		% Cu		% C ₂ H ₅ O	
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
C ₆ H ₅	46.69	46.73	5.44	5.52	3.02	2.83	13.72	13.95	19.46	19.17
<i>p</i> -CH ₃ C ₆ H ₄	47.83	47.69	5.70	5.51	2.93	2.81	13.32	13.41	18.89	19.01
<i>p</i> -ClC ₆ H ₄	43.45	43.10	5.38	5.49	2.82	2.96	12.77	13.00	18.11	18.29
<i>p</i> -BrC ₆ H ₄	39.89	39.71	4.46	4.48	2.58	2.71	11.72	11.93	16.63	16.38
<i>p</i> -IC ₆ H ₄	36.71	36.51	4.11	4.06	2.38	2.28	10.78	11.04	15.30	15.56
β -C ₁₀ H ₇	51.50	51.25	5.30	5.11	2.72	2.66	12.38	12.49	17.56	17.20

^a These compounds form green prisms, except for the fourth and the last compounds, which form green plates and green needles, respectively. They decompose on melting at 212–213, 185–186, 217–218, 197–198, >300, and 196–197°, respectively.

Magnetic Measurements.—The magnetic susceptibility was determined from liquid nitrogen temperature to about 300°K by the Gouy method using an Ainsworth recording semimicrobalance, the magnetic field strength amounting to about 10,000 Oe.⁷ The temperature was automatically controlled and determined by means of a copper-constantan thermocouple.

N-[2-(2-hydroxyethylthio)phenyl]-2-naphthalenesulfonamide (-220×10^{-6}), methanol (-23×10^{-6}), and ethanol (-35×10^{-6}). The first two data are based on the observed magnetic susceptibility (-207×10^{-6} cgs emu mol⁻¹) of the potassium salt of N-[2-(2-hydroxyethylthio)phenyl]-4-toluenesulfonamide.

TABLE V
MOLAR MAGNETIC SUSCEPTIBILITY χ_A CORRECTED FOR
DIAMAGNETIC CONTRIBUTIONS AND EFFECTIVE MAGNETIC
MOMENTS μ_{eff}

Compound	Temp, °C	$10^3\chi_A$, emu/mol	μ_{eff} , BM
N-[2-(2-Hydroxyethylthio)phenyl]-4-toluenesulfonamidatocopper(II)-bisethanol	25	0.664	1.26
N-[2-(2-Hydroxyethylthio)phenyl]-4-toluenesulfonamidatocopper(II)	18	0.858	1.42
N-[2-(2-Hydroxyethylthio)phenyl]-2-naphthalenesulfonamidatocopper(II)-bismethanol	22	0.694	1.28
N-[2-(2-Hydroxyethylthio)phenyl]-2-naphthalenesulfonamidatocopper(II)	18	0.864	1.42

Experimental data are available in the literature⁸ for the alcohols. From the corrected molar susceptibility, χ_A , the effective magnetic moments, μ_{eff} , were evaluated per copper atom using

$$\mu_{eff} = 2.83[(\chi_A - N\alpha)T]^{1/2} \quad (1)$$

where $N\alpha$ stands for the temperature-independent paramagnetism assumed to be equal to 60×10^{-6} cgs emu for Cu(II).⁹ The magnetic moments are considerably smaller than 1.8–2.0 BM commonly observed for copper(II) compounds having magnetically isolated copper(II) ions, indicating the presence of spin interaction between copper atoms. Figures 1 and 2 illustrate the temperature dependence of magnetic susceptibilities of four compounds listed in Table V.

Discussion

The magnetic susceptibility of N-[2-(2-hydroxyethylthio)phenyl]-4-toluenesulfonamidatocopper(II)-bisethanol decreases with decreasing temperature. Bleaney and Bowers¹⁰ have proposed a theoretical equation for the susceptibility of isolated dimeric aggregates as a function of temperature on the basis of exchange coupling in a pair of electron spins

$$\chi = \frac{Ng^2\beta^2}{3kT} \left[1 + \frac{1}{3} \exp \frac{E}{kT} \right]^{-1} \quad (2)$$

Here, apart from obvious notations, g stands for the g factor, β is the Bohr magneton, and E is the energy separation between the singlet and triplet states and is equal to twice the absolute value of the exchange integral. As shown in Figure 1, the observed data of $\chi = \chi_A - N\alpha$ can be fitted excellently to the theoretical curve with $E/k = 544^\circ\text{K}$ and $g = 2.10$. This fact, along with the similarity of this compound to acetylacetonemono(*o*-hydroxyanil)copper(II) regarding chemical structure, suggests that binuclear complex molecules exist in crystals and that, in each molecule, copper atoms are bridged by two oxygen atoms as verified by X-ray analysis for the latter compound.¹¹ A con-

(8) G. Foëx, "Constantes Sélectionnées, Diamagnétisme et Paramagnétisme," Mason & Cie., Editeurs, Paris, 1957.

(9) B. N. Figgis and R. L. Martin, *J. Chem. Soc.*, 3837 (1956).

(10) B. Bleaney and K. D. Bowers, *Proc. Roy. Soc. (London)*, **A214**, 451 (1952).

(11) G. A. Barclay, C. M. Harris, B. F. Hoskins, and E. Kokot, *Proc. Chem. Soc.*, 264 (1961).

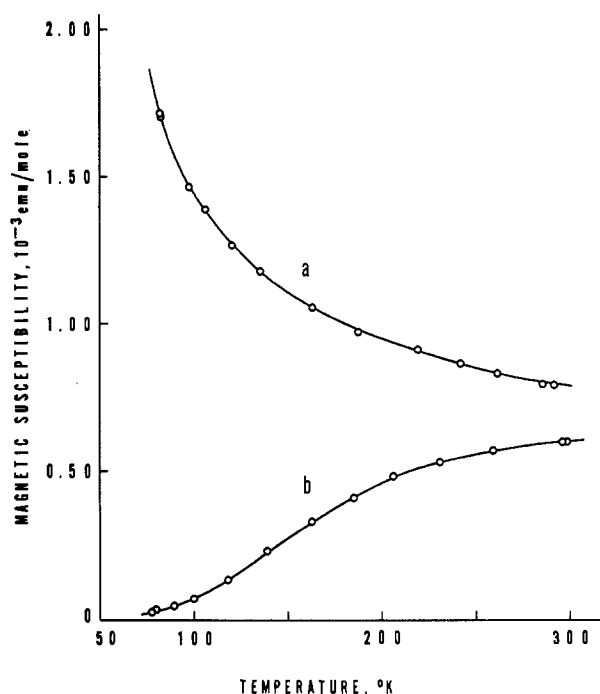


Figure 1.—Magnetic susceptibilities corrected for the temperature-independent paramagnetism of N-[2-(2-hydroxyethylthio)phenyl]-4-toluenesulfonamidatocopper(II) (a) and the bisethanol compound thereof (b) as functions of temperature. Curve b can be fitted to the Bleaney-Bowers equation.

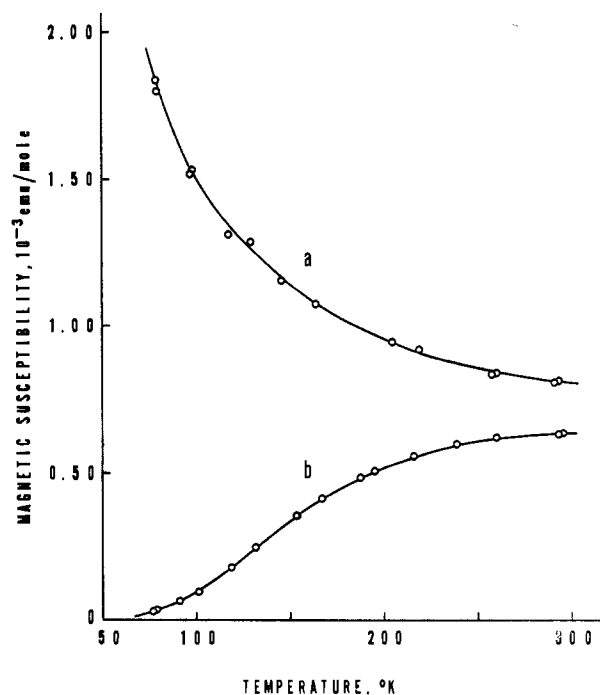


Figure 2.—Magnetic susceptibilities corrected for the temperature-independent paramagnetism of N-[2-(2-hydroxyethylthio)phenyl]-2-naphthalenesulfonamidatocopper(II) (a) and the bismethanol compound thereof (b) as functions of temperature. Curve b can be fitted to the Bleaney-Bowers equation.

ceivable dimeric molecule is shown in Figure 3, which illustrates only a probable skeletal structure involving copper atoms, the steric configuration of side chains being quite arbitrary. The role of ethanol in crystal formation is open to speculation.

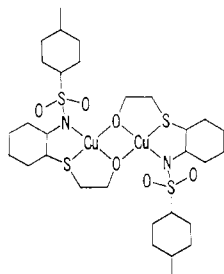


Figure 3.—Dimeric structure proposed for N-[2-(2-hydroxyethylthio)phenyl]-4-toluenesulfonamidatocopper(II)-bisethanol. Ethanol molecules are not shown.

The temperature dependence of the magnetic susceptibilities of ethanol-free preparations is quite different from that of the bisethanol compound: the susceptibility increases with decreasing temperature. As shown in Figure 4, the Curie-Weiss law is not obeyed. The magnetic susceptibility χ of isolated polymeric aggregates of spins has been discussed theoretically by Kambe and others.¹²⁻¹⁴ It can be shown (see Appendix) that the magnetic susceptibility of isolated trimeric aggregates of equivalent electron spins is given by

$$\chi = \frac{Ng^2\beta^2}{12kT} \left[\frac{1 + 5e^{-E/kT}}{1 + e^{-E/kT}} \right] \quad (3)$$

where E is the energy separation between the doublet and quartet states and is equal to three times the absolute value of the exchange integral. As shown in Figure 4, the theoretical equation can be fitted to the experimental data of sample B with $E/k = 495^\circ\text{K}$ and $g = 2.15$. The agreement of the observed susceptibility with the theoretical curve based on trimeric aggregates of equivalent spins, as well as the molecular weight observed in chloroform, indicates the formation of trimeric molecules possibly having a structure shown in Figure 5. The proposed structure is plausible as confirmed by constructing a molecular model.

Although the curve of magnetic susceptibility observed for sample A resembles that of sample B, it cannot be fitted exactly to the theoretical equation for the trimer. In addition, the value fluctuated among different preparations, the fluctuation being considerably greater than experimental errors in magnetic measurements. It is conceivable that when ethanol is removed from the bisethanol compound having a dimeric structure, monomeric molecules and various types of polymeric structures are formed in addition to the trimer giving rise to the observed behavior.

The results obtained for N-[2-(2-hydroxyethylthio)phenyl]-2-naphthalenesulfonamidatocopper(II) chelates were quite analogous to those obtained for the corresponding N-[2-(2-hydroxyethylthio)phenyl]-4-toluenesulfonamidatocopper(II) complexes as shown in Figures 2 and 4, in which $E/k = 504^\circ\text{K}$ and $g = 2.07$ were taken for the bismethanol complex and $E/k = 495^\circ\text{K}$

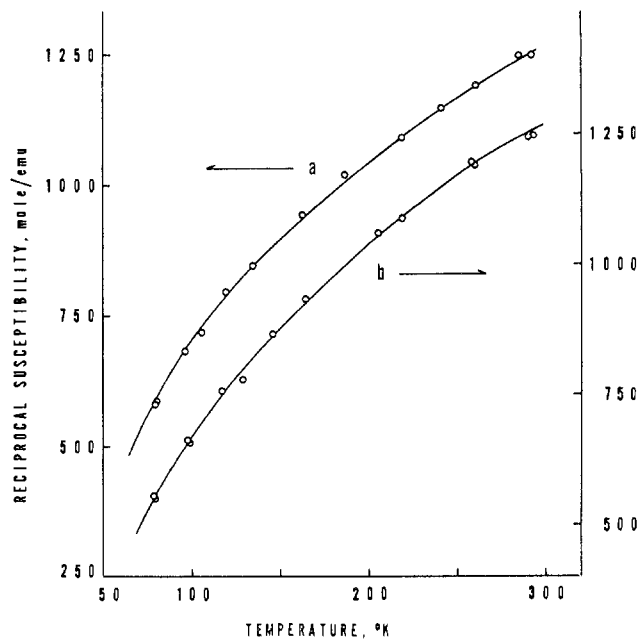


Figure 4.—Temperature dependence of the reciprocal magnetic susceptibility corrected for the temperature-independent paramagnetism of N-[2-(2-hydroxyethylthio)phenyl]-4-toluenesulfonamidatocopper(II) (a) and N-[2-(2-hydroxyethylthio)phenyl]-2-naphthalenesulfonamidatocopper(II) (b). The curves are drawn for trimeric aggregates.

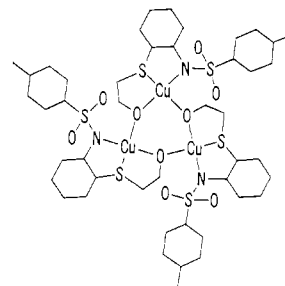


Figure 5.—Trimeric structure proposed for N-[2-(2-hydroxyethylthio)phenyl]-4-toluenesulfonamidatocopper(II).

and $g = 2.10$ were taken for the methanol-free complex (sample B).

Appendix

The magnetic susceptibility of isolated n -meric aggregates of equivalent electron spins is given by

$$\chi = \frac{(N/n)g^2\beta^2}{3kT} \left[\frac{\sum S_i(S_i + 1)w_i(2S_i + 1)e^{-E_i/kT}}{\sum w_i(2S_i + 1)e^{-E_i/kT}} \right] \quad (4)$$

where S is the total spin of an aggregate and w is the statistical weight for spin functions with given S and can be evaluated by group theory.¹⁵ For a dimeric aggregate, one has $w_0 = w_1 = 1$, yielding the Bleaney-Bowers expression, eq 2. For a trimeric aggregate, the number of spin functions is $2^3 = 8$. Four of them correspond to $S = 3/2$ ($m_S = \pm 3/2, \pm 1/2$) and the remaining four functions can be divided into two sets each corresponding to $S = 1/2$ ($m_S = \pm 1/2$). Accordingly, one has $w_0 = 2$ ($S = 1/2$) and $w_1 = 1$ ($S = 3/2$), leading to eq 3.

(15) P. L. Corio, *Chem. Rev.*, **60**, 363 (1960).

(12) K. Kambe, *J. Phys. Soc. Japan*, **5**, 48 (1950).

(13) J. Wucher and H. M. Gijssman, *Physica*, **20**, 361 (1954).

(14) N. Uryū and S. A. Friedberg, *Phys. Rev.*, **140**, A1803 (1965).