

The relative yield of hypochlorous acid formed from chlorine given by the concurrent reactions (eq 5-7) is

$$[\text{HOCl}]/[\text{Cl}_2] = \frac{k_5[\text{OH}^-]}{k_5[\text{OH}^-] + k_6[\text{HO}_2^-] + k_7[\text{RNH}_2]}$$

In amine buffered solutions $[\text{OH}^-] \approx 10^{-4}$ M, whereas the other reactants are present in molar concentrations. With estimates of k_6 and k_7 provided by the data on the corresponding reactions with HOCl, it is apparent that HOCl formation can account for only a few percent of the loss of Cl_2 under the reactor conditions and, therefore, that HOCl cannot be an intermediate along the major pathways for singlet oxygen production. Furthermore, because chloramines formed from simple alkylamines do not react rapidly with HO_2^- ion (Table II) they also cannot serve as intermediates in the singlet oxygen forming reactions. The absence of appreciable loss of oxygen yields in the amine-containing solutions must therefore be due to preferential direct reaction between Cl_2 and the HO_2^- ion.²¹

In summary, the reactivities of several compounds containing monovalent chlorine toward hydrogen peroxide can be understood in terms of the electrophilic nature of their constituent chlorine atoms. The mechanism proposed for these reactions is probably quite general, with hydroperoxide ion representing one example of nucleophilic centers susceptible to oxidative attack by these reagents.

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Registry No. H_2O_2 , 7722-84-1; *t*-BuOCl, 507-40-4; NCS, 128-09-6; $\text{HO}(\text{CH}_2)_2\text{NHCl}$, 52316-60-6.

- (21) The oxygen yields from reactors containing propylamine have been found to decrease with increasing concentration levels of the amine; a rate constant ratio of $k_5/k_6 \approx 4$ can be estimated from the data.²²
 (22) Richardson, R. J.; Ageno, H. Y.; Carr, P. A.; Hovis, F. E.; Hurst, J. K., manuscript in preparation.

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Synthesis, Characterization, and Reactivity of Copper(I) and Copper(II) Complexes of *N,N'*-Bis(3-(2-thenylideneimino)propyl)piperazine (tipp) and *N,N'*-Bis(3-(2-thenylamino)propyl)piperazine (tapp). Crystal Structure of $[\text{Cu}(\text{tapp})][\text{ClO}_4]_2$

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Copper(I) and copper(II) complexes of the new ligands *N,N'*-bis(3-(2-thenylideneimino)propyl)piperazine (tipp) and *N,N'*-bis(3-(2-thenylamino)propyl)piperazine (tapp) have been synthesized. Complexes of the type $[\text{Cu}(\text{ligand})][\text{ClO}_4]$, ligand = tipp or tapp, have been prepared by the reaction of tipp or tapp with $[\text{Cu}(\text{MeCN})_4][\text{ClO}_4]$. Complexes of the type $[\text{Cu}(\text{ligand})\text{X}_2]$ ($\text{X} = \text{ClO}_4^-$, NO_3^- , $\text{OSO}_2\text{CF}_3^-$) have been prepared by the reaction of tipp or tapp with $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, or $\text{Cu}(\text{OSO}_2\text{CF}_3)_2$, respectively. The complexes have been characterized by conductivity measurements and by infrared, electronic, and EPR spectroscopy. In addition the structure of $[\text{Cu}(\text{tapp})][\text{ClO}_4]_2$ has been determined by diffraction methods. The $[\text{Cu}(\text{ligand})][\text{ClO}_4]_2$ complexes display CuN_4 coordination in solution and in the solid state. The nitrate complexes are properly described as $[\text{Cu}(\text{ligand})(\text{ONO}_2)][\text{NO}_3]$ in both solution and the solid state, with CuN_4O coordination. While the $\text{Cu}^{\text{II}}\text{OSO}_2\text{CF}_3$ salts show CuN_4O coordination in the solid state, they display CuN_4 coordination in solution. For the Cu(I) complexes the $\text{Cu}(\text{tapp})^+$ ion is rapidly oxidized in solution while the $\text{Cu}(\text{tipp})^+$ ion is more stable and probably displays CuN_2S_2 or CuN_4S_2 coordination. For both the Cu(I) and Cu(II) complexes the tipp derivatives undergo the expected hydrolysis of the imine linkages in solution. In the solid state the $\text{Cu}(\text{tapp})^{2+}$ ion of $[\text{Cu}(\text{tapp})][\text{ClO}_4]_2$ displays a CuN_4 coordination that is severely distorted from square planar with N-Cu-N angles as small as $74.2(2)^\circ$ and deviations from the CuN_4 plane as large as $0.397(4)$ Å. The disposition of the thiophene S atoms about the Cu ion is suggestive of an incipient CuN_4S_2 coordination. The material crystallizes with 4 formula units in space group C_{2h}^2-C2ca of the orthorhombic system in a cell of dimensions $a = 11.302(5)$, $b = 16.239(7)$, and $c = 13.948(6)$ Å. A crystallographic twofold axis is imposed on the cation. The structure has been refined to a final R index on F^2 of 0.079, on the basis of 167 variables and 2331 observations collected at -150°C .

Introduction

Much current interest in the coordination chemistry of sulfur-containing ligands centers on the search for synthetic models for the metal sites of biological macromolecules and especially on attempts to understand the unusual physical properties of a variety of copper-containing proteins.² The

X-ray structural determination of copper(II) poplar plastocyanin at $2.7\text{-}\text{\AA}$ resolution³ has provided valuable information about the structure of one "blue" copper center $\text{Cu}(\text{his})_2(\text{cys})(\text{met})$, CuN_2SS^* . Yet important differences exist in the amino acid contents and hence the nature of the "blue" sites within the various proteins. An improved understanding of the structure/function relationships in these and related copper proteins must arise from complementary biological and model studies. Despite recent activity the chemistry and reactivity of copper(II) and especially copper(I) ions in nonclassical N_xS_y coordination environments remains largely undeveloped. There are a number of recent reports of low molecular weight complexes whose properties may be related to those of the Cu(II)

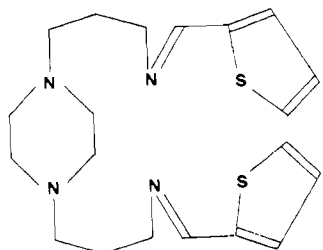
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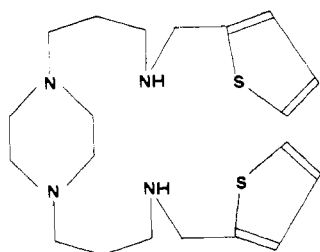
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type 1 core,⁴⁻⁹ but data on the corresponding Cu(I) complexes are scarce.¹⁰⁻¹³

Our interest here focuses on the coordination chemistry of copper(I) and copper(II) ions with polyfunctional ligands having nitrogen and sulfur donor atoms. We wish to provide some understanding of the stereochemical preferences of the two ions in an environment which can potentially provide a variety of different arrangements. To this end we have synthesized the new ligands *N,N'*-bis(3-(2-thienylidenimino)propyl)piperazine (tipp) and *N,N'*-bis(3-(2-thienylamino)propyl)piperazine (tapp), which can adopt a range of different conformations and contain four nitrogen atoms and two thiophene sulfur atoms as potential donor sites. The two molecules differ mainly in the rigidity that the conjugation of the Schiff base azomethine group to the thiophene ring confers to that portion of the molecule in tipp compared with



tipp



tapp

propyl)piperazine (tapp), which can adopt a range of different conformations and contain four nitrogen atoms and two thiophene sulfur atoms as potential donor sites. The two molecules differ mainly in the rigidity that the conjugation of the Schiff base azomethine group to the thiophene ring confers to that portion of the molecule in tipp compared with

the more flexible thenylamino group in tapp and in the concomitant donating vs. accepting abilities of the functional groups involved. We report here the synthesis and the spectral and chemical properties of copper(I) and copper(II) complexes of these ligands and the X-ray structural investigation of a member of this series of compounds, [Cu(tapp)](ClO₄)₂.

Experimental Section

All chemicals were reagent grade and used as received. The solvents were dried over molecular sieves (4 Å). Elemental analyses were performed by the Analytical Services Laboratory, Chemistry Department, Northwestern University, and the Microanalytical Laboratory, University of Milano. Infrared spectra were obtained with a Perkin-Elmer 283 infrared spectrophotometer. Electronic spectra were recorded on a Beckman DK-2A spectrophotometer equipped with a reflectance attachment. EPR spectra were obtained with a Varian E-109 spectrometer operating at X-band frequencies. ¹H NMR spectra were recorded on a Hitachi Perkin-Elmer R-20B instrument. Natural-abundance ¹³C NMR spectra were obtained on a JEOL FX-90Q spectrometer operating at 22.5 MHz in pulsed Fourier transform proton noise decoupled mode. Mass spectra were obtained on a HP 5985 GC/MS system with a quadrupole mass analyzer. Solution conductivities were measured on a ESI Model 293 impedance bridge, using a cell calibrated with a standard aqueous solution of potassium chloride.

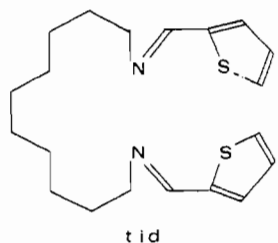
Preparation of tipp. A solution of 2-thiophenecarboxaldehyde (2.24 g, 20 mmol) and *N,N'*-bis(3-aminopropyl)piperazine (2.00 g, 10 mmol) in methanol (100 mL) was refluxed for 3 h. The solution was then evaporated to dryness under vacuum to give a light yellow oil which solidified upon standing at room temperature. The crude Schiff base was crystallized from boiling hexane (100 mL). The light yellow crystals which separated upon cooling were collected by filtration and dried under vacuum (3.45 g, 89%). Anal. Calcd for C₂₀H₂₈N₄S₂: C, 61.82; H, 7.26; N, 14.42. Found: C, 61.73; H, 7.35; N, 14.53. IR (KBr): $\nu(\text{C}=\text{N})$ 1630 (s); $\nu(\text{thiophene ring})$ 720 (s) cm⁻¹. UV (acetonitrile): λ_{max} 276 (23 840), 259 nm (25 180 L/(mol cm)). ¹H NMR (CDCl₃/Me₄Si): δ 1.85 (m, 4 H, CH₂CH₂CH₂), 2.38 (t, 4 H, NCH₂CH₂CH₂), 2.42 (s, 8 H, NCH₂CH₂N), 3.56 (t, 4 H, CH₂N=), 6.9–7.4 (m, 6 H, thienyl=CH), 8.32 (s, 2 H, CH=N), ¹³C NMR (CDCl₃/Me₄Si):¹⁴ δ 27.9 (t, CH₂CH₂CH₂), 53.1 (t, NCH₂CH₂N), 56.1 (t, NCH₂CH₂CH₂), 59.2 (t, CH₂N=), 127.2, 128.5, 130.0 (d, thienyl=CH), 142.5 (s, thienyl=C=), 154.1 (d, CH=N). Mass spectrum, *m/e* (%): 388 (80, M⁺), 264 (19), 207 (13), 181 (100), 152 (34), 151 (29), 139 (36), 138 (29), 125 (94), 124 (77), 97 (61).

Preparation of tapp. To a methanolic solution (100 mL) of tipp (3.88 g, 10 mmol) was added excess solid NaBH₄ (2.0 g) in small portions while the solution was cooled in a water bath. When evolution of H₂ had ceased, the mixture was warmed slowly and refluxed for 0.5 h. After evaporation of the solution under vacuum, the residue was partitioned between chloroform (100 mL) and water (50 mL). The organic phase was washed with an aqueous NaHCO₃ solution almost saturated with NaCl, dried (MgSO₄), and evaporated to dryness under vacuum. The residue was a yellow oil (~3 g, 75%). Anal. Calcd for C₂₀H₃₂N₄S₂·0.1CHCl₃: C, 59.69; H, 8.00; N, 13.86. Found: C, 59.55; H, 8.05; N, 14.07. IR (liquid film): $\nu(\text{NH})$ 3280 (w); $\nu(\text{thiophene ring})$ 700 (s) cm⁻¹. UV (acetonitrile): λ_{max} 233 nm (18 100 L/(mol cm)). ¹H NMR (CDCl₃/Me₄Si): δ 1.5–2.1 (m, 6 H, NH, CH₂CH₂CH₂), 2.38 (t, 4 H, NCH₂CH₂CH₂), 2.42 (s, 8 H, NCH₂CH₂N), 2.67 (t, 4 H, CH₂NH), 3.93 (s, 4 H, thenyl CH₂), 6.8–7.3 (m, 6 H, thienyl=CH). ¹³C NMR (CDCl₃/Me₄Si): δ 26.8 (CH₂CH₂CH₂), 47.9 (NHCH₂CH₂CH₂), 48.4 (NCH₂CH₂CH₂), 53.3 (NCH₂CH₂N), 56.9 (thenyl CH₂), 124.1, 124.7, 126.5 (thienyl=CH), 144.3 (thienyl=C=). Mass spectrum *m/e* (%): 392 (2, M⁺), 295 (3), 352 (8), 222 (10), 211 (20), 197 (14), 183 (71), 127 (50), 126 (39), 97 (100).

Preparation of *N,N'*-Bis(2-thienylidenimino)-1,10-decene (tid). A mixture of 1,10-decanediamine (1.72 g, 10 mmol) and 2-thiophenecarboxaldehyde (2.24 g, 20 mmol) in methanol (100 mL) was refluxed for 4 h and then cooled. The small amount of undissolved solid was filtered off, and the filtrate was evaporated to dryness under vacuum. The residue was an oil which solidified upon standing. This crude

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- (14) Signal multiplicity was established by appropriate decoupling experiments.



Schiff base was crystallized from boiling hexane (50 mL). The white crystals which separated upon cooling were filtered and dried under vacuum (2.9 g, 80%). Anal. Calcd for $C_{20}H_{28}N_2S_2$: C, 66.62; H, 7.83; N, 7.77. Found: C, 66.37; H, 8.03; N, 7.69. IR (KBr): $\nu(C=N)$ 1630 (s); ν (thiophene ring) 730, 710 (s) cm^{-1} . 1H NMR ($CDCl_3/Me_4Si$): δ 1.1–1.9 (m, 16 H, CH_2), 3.51 (t, 4 H, $CH_2N=$), 6.9–7.4 (m, 6 H, thienyl $=CH$), 8.30 (s, 2 H, $CH=N$). Mass spectrum, m/e (%): 360 (4, M^+), 262 (4), 251 (10), 236 (5), 180 (12), 166 (17), 151 (16), 138 (20), 111 (46), 57 (100).

Preparation of Copper(I) Complexes. The copper(I) complexes were prepared under nitrogen by addition of solid $[Cu(MeCN)_4][ClO_4]$ (1 mmol) to a stirred solution of the ligand (1 mmol) in dichloromethane (30 mL). The resulting solution soon deposited a yellow precipitate which was collected by filtration, washed with dichloromethane, and dried under vacuum.

$[Cu(tipp)][ClO_4]$. Anal. Calcd for $C_{20}H_{28}ClCuN_4O_4S_2$: C, 43.55; H, 5.12; N, 10.16. Found: C, 43.20; H, 5.11; N, 10.01. IR:¹⁶ $\nu(C=N)$ 1612 (s); $\nu(ClO_4)$ 1100 (vs, br), 620 (m); ν (thiophene ring) 720 (s) cm^{-1} . UV (acetonitrile): λ_{max} 390 sh (400), 276 (22 780), 259 nm (24 430 L/(mol cm)). 1H NMR ($MeCN-d_3/Me_4Si$): δ 2.0 (m, $CH_2CH_2CH_2$, obscured by solvent), 2.65 (s, 8 H, NCH_2CH_2N), 2.73 (t, 4 H, $NCH_2CH_2CH_2$), 3.85 (t, 4 H, $CH_2N=$), 7.1–7.8 (m, δ H, thienyl $=CH$), 8.52 (s, 2 H, $CH=N$). ^{13}C NMR ($MeCN-d_3/Me_4Si$): δ 28.5 ($CH_2CH_2CH_2$), 54.3 (NCH_2CH_2N), 58.5 ($NCH_2CH_2CH_2$), 61.8 ($CH_2N=$), 129.0, 131.2, 133.9 (thienyl $=CH$), 141.7 (thienyl C), 157.3 ($CH=N$).

$[Cu(tapp)][ClO_4]$. Anal. Calcd for $C_{20}H_{32}ClCuN_4O_4S_2$: C, 43.23; H, 5.81; N, 10.09. Found: C, 41.72; H, 5.00; N, 9.79. IR: $\nu(NH)$ 3220 (m); $\nu(ClO_4)$ 1100 (vs, br), 620 (m); ν (thiophene ring) 740 (s) cm^{-1} .

$[Cu(tid)][ClO_4]$. Anal. Calcd for $C_{20}H_{28}ClCuN_4O_4S_2$: C, 45.88; H, 5.39; N, 5.35. Found: C, 44.56; H, 5.34; N, 5.01. IR: $\nu(C=N)$ 1615 (s); $\nu(ClO_4)$ 1100 (vs, br), 620 (m); ν (thiophene ring) 730 (s) cm^{-1} .

Preparation of Copper(II) Complexes. The copper(II) complexes with perchlorate or nitrate anions were prepared by mixing equimolar methanolic solutions (20 mL) of the ligand (1 mmol) and $Cu(ClO_4)_2 \cdot 6H_2O$ or $Cu(NO_3)_2 \cdot 3H_2O$. The blue precipitates which formed were collected by filtration, washed with methanol, and dried under vacuum. The copper(II) complexes with trifluoromethanesulfonate anion were prepared by adding a methanolic solution (10 mL) of $Cu(OSO_2CF_3)_2$ ¹⁷ (1 mmol) to a dichloromethane solution (20 mL) of the ligand. After evaporation of the solvent under vacuum, the solid residue was stirred in diethyl ether (40 mL), filtered, washed with diethyl ether, and dried under vacuum. The complex $[Cu(tipp)(OSO_2CF_3)](OSO_2CF_3)$ is very hygroscopic.

$[Cu(tipp)][ClO_4]_2$. Anal. Calcd for $C_{20}H_{28}Cl_2CuN_4O_8S_2$: C, 36.90; H, 4.34; N, 8.61. Found: C, 36.79; H, 4.34; N, 8.51. IR: $\nu(C=N)$ 1615, 1600 (s); $\nu(ClO_4)$ 1060–1110 (vs, br), 620 (m); ν (thiophene ring) 760, 730 (s) cm^{-1} .

$[Cu(tapp)][ClO_4]_2$. Anal. Calcd for $C_{20}H_{32}Cl_2CuN_4O_8S_2$: C, 36.67; H, 4.92; N, 8.55. Found: C, 36.25; H, 4.95; N, 8.31. IR: $\nu(NH)$ 3220 (m); $\nu(ClO_4)$ 1060–1120 (vs, br), 620 (m); ν (thiophene ring) 730 (s) cm^{-1} .

$[Cu(tipp)(OSO_2CF_3)](OSO_2CF_3)$. Anal. Calcd for $C_{22}H_{28}CuF_6N_4O_6S_4$: C, 35.22; H, 3.76; N, 7.47. Found: C, 34.08;

Table I. Crystallographic Details for $[Cu(tapp)][ClO_4]_2$

formula	$C_{20}H_{32}Cl_2CuN_4O_8S_2$
fw	655.08
a, Å	11.302 (5)
b, Å	16.239 (7)
c, Å	13.948 (6)
Z	4
ρ_o , g/cm ³	1.63 (20 °C)
ρ_c , g/cm ³	1.699 (–150 °C)
space group	$C_{2h}^{12}-C2ca$
temp, °C	–150 ^a
radiation	Mo K α from graphite monochromator ($\lambda(Mo K\alpha_1) = 0.7093$ Å)
boundary faces of the wedge-shaped cryst	{001}, {010}, ($\bar{1}\bar{1}\bar{1}$), ($\bar{1}\bar{1}1$), (100)
cryst vol, mm ³	0.0076
μ , cm ^{–1}	12.73
transmission factors	0.726–0.912
receiving aperture	5 mm high by 6 mm wide, 32 cm from cryst
takeoff angle, deg	3.3
scan speed, deg in 2θ /min	2
scan range, deg	1.0 below $K\alpha_1$ to 0.9 above $K\alpha_2$
bkgd counts, s	10 ($2\theta < 50^\circ$), 20 ($2\theta > 50^\circ$) with rescans option ^b
2θ limits, deg	$4 \leq 2\theta \leq 64$
data collected	+h, +k, +l; also –h, –k, –l ($2\theta \leq 35^\circ$)
final no. of variables	167
final no. of observns	2331
R (on F^2)	0.079
R_w (on F^2)	0.099
error in observn of unit weight, e ²	1.13
R (on F for $F_o^2 > 3\sigma(F_o^2)$)	0.048
R_w (on F for $F_o^2 > 3\sigma(F_o^2)$)	0.045

^a The low-temperature system is based on a design by J. C. Huffman, Ph.D. Thesis, Indiana University, 1974. ^b The diffractometer was run under the Vanderbilt disk-oriented system: Lenhart, P. G. *J. Appl. Crystallogr.* 1978, 8, 568–571.

H, 3.71; N, 7.52. IR: $\nu(C=N)$ 1605 (s); $\nu(OSO_2CF_3)$ 1305, 1280, 1270, 1245, 1225 (s), 1150 (s, br), 1030 (s, doublet), 640 (m); ν (thiophene ring) 760 (s) cm^{-1} .

$[Cu(tapp)(OSO_2CF_3)](OSO_2CF_3)$. Anal. Calcd for $C_{22}H_{32}CuF_6N_4O_6S_4$: C, 35.03; H, 4.28; N, 7.43. Found: C, 34.40; H, 4.14; N, 7.34. IR: $\nu(NH)$ 3230, 3200 (m); $\nu(OSO_2CF_3)$ 1305, 1290, 1275, 1260, 1240, 1225 (s), 1150 (s, br), 1030 (s, doublet), 640 (s); ν (thiophene ring) 725 (m) cm^{-1} .

$[Cu(tipp)(ONO_2)](NO_3)$. Anal. Calcd for $C_{20}H_{28}CuN_6O_6S_2$: C, 41.70; H, 4.90; N, 14.59. Found: C, 41.20; H, 4.95; N, 14.40. IR: $\nu(C=N)$ 1605 (s); $\nu(NO_3)$ 1750 (w, br), 1470, 1420, 1350, 1330, 1290 (s), 1030 (m), 830 (m), 700–750 (s, br, containing also thiophene ring absorptions) cm^{-1} .

$[Cu(tapp)(ONO_2)](NO_3)$. Anal. Calcd for $C_{20}H_{32}CuN_6O_6S_2$: C, 41.41; H, 5.56; N, 14.49. Found: C, 41.65; H, 5.63; N, 14.67. IR: $\nu(NH)$ 3240, 3180 (m); $\nu(NO_3)$ 1740 (w, br), 1470, 1420, 1365, 1340, 1320 (s), 1040 (m), 820 (w), 700–740 (m–w, several bands containing also thiophene ring absorptions) cm^{-1} .

X-ray Study of $[Cu(tapp)][ClO_4]_2$. Crystals suitable for X-ray study were obtained by carrying out the synthesis of $[Cu(tapp)][ClO_4]_2$ from dilute methanolic solutions of tapp and $Cu(ClO_4)_2 \cdot 6H_2O$. On the basis of a series of Weissenberg and precession photographs, the material crystallizes in the orthorhombic system in space group $D_{2h}^{12}-Cmca$ or $C_{2h}^{12}-C2ca$, a nonstandard aspect of $C_{2h}^{12}-Aba2$. The cell dimensions and measured density are consistent with 4 formula units per cell. This would require the cation to possess $2/m$ symmetry in $Cmca$. This unlikely possibility, coupled with the obvious acentric habit of the crystals, suggested to us that the correct space group is $C2ca$ and that the cation has a crystallographically imposed C_2 axis.

Data collection proceeded on a Picker automatic diffractometer by methods standard in this laboratory.¹⁸ Various details are given in Table I. The structure was solved in space group $C2ca$ ¹⁹ by direct

(15) Hemmerich, P.; Sigwart, C. *Experientia* 1963, 19, 488–489.

(16) Infrared data for Cu(I) and Cu(II) complexes are from samples prepared as Nujol mulls.

(17) Anhydrous $Cu(SO_2CF_3)_2$ was obtained by the reaction of freshly prepared cupric hydroxide and trifluoromethanesulfonic acid in methanol. After evaporation of the solvent under vacuum, benzene was added to the residue, which was then filtered and dried under high vacuum at 80–85 °C. Titration for copper with EDTA gave a molecular weight of 364 (calcd 361.7 for the anhydrous salt).

(18) See, for example: Waters, J. M.; Ibers, J. A. *Inorg. Chem.* 1977, 16, 3273–3277.

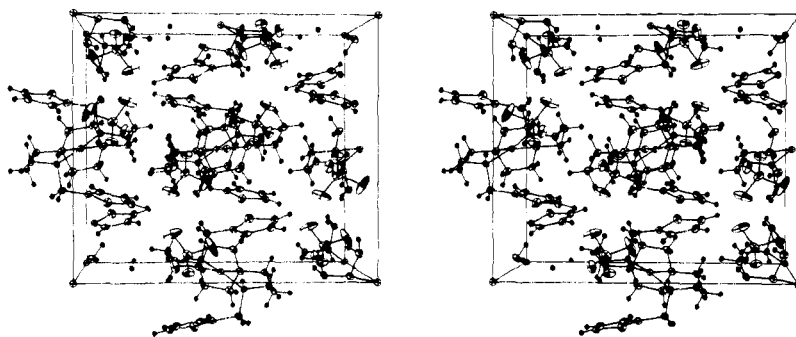


Figure 1. Stereoview of the unit cell of $[\text{Cu}(\text{tapp})][\text{ClO}_4]_2$. Thermal ellipsoids are drawn at the 50% probability level except for hydrogen atoms, which are drawn artificially small. The view is approximately down a , with b from right to left.

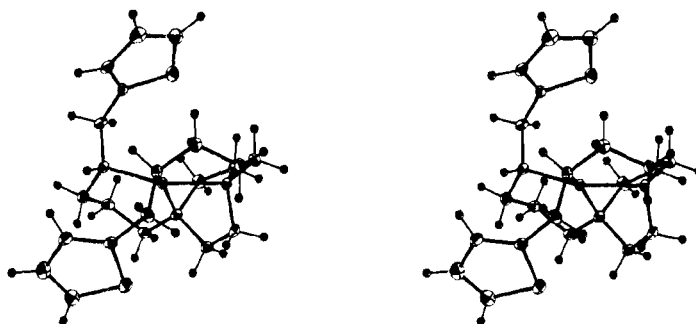


Figure 2. Stereoview of the $[\text{Cu}(\text{tapp})]^{2+}$ cation. The 50% probability ellipsoids are shown for the nonhydrogen atoms. Hydrogen atoms are drawn artificially small.

methods and was refined by standard procedures.¹⁸ After a suitable trial structure had been obtained and an absorption correction applied, both possible enantiomers in the polar space group $C2ca$ were examined to establish the correct enantiomer for the particular crystal chosen for study. Refinement of enantiomer A, in which all atoms were assigned isotropic thermal parameters, converged to values of R and R_w on F_o of 0.088 and 0.095 for the 2103 observations (including Friedel pairs) and 74 variables. A similar refinement of enantiomer B, in which all atomic coordinates had been reversed in sign, converged to values of 0.082 and 0.087. Of the 413 Friedel pairs collected, the 74 pairs showing the largest differences were selected and of these 73 showed the correct trends for enantiomer B. There is no doubt from these calculations that enantiomer B is correct and in ensuing calculations it was selected. The final refinement was carried out on F_o^2 , with the use of only those reflections for which h , k , and l are nonnegative. In this refinement the nonhydrogen atoms were refined anisotropically. The hydrogen atoms were not refined but were placed at their calculated positions ($\text{C-H} = \text{N-H} = 0.95 \text{ \AA}$), and each was assigned a fixed isotropic thermal parameter 1 \AA^2 greater than the equivalent isotropic thermal parameter of the atom to which it is attached. This refinement of 167 variables converged to values of R and R_w (of F_o^2) of 0.079 and 0.099 and to an observation of unit weight of 1.13 electrons² for the 2331 observations. The corresponding conventional R indices on F_o for those 1682 reflections having $F_o^2 > 3\sigma(F_o^2)$ and hkl positive are 0.048 and 0.045, respectively.

Table II lists the final values of the atomic parameters. Table III²⁰ lists the values of $10|F_o|$ and $10|F_c|$. A negative entry implies that F_o^2 was observed to be negative.

Results and Discussion

Synthesis of the Complexes. The synthesis of 1:1 complexes of copper(II) or copper(I) with tipp or tapp is straightforward. On mixing the ligands and $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ or $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in methanol or dichloromethane, blue precipitates of the Cu(II) complexes readily form. The Cu(I) complexes are obtained by adding $[\text{Cu}(\text{MeCN})_4][\text{ClO}_4]$ to the ligands in

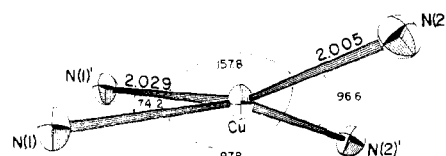
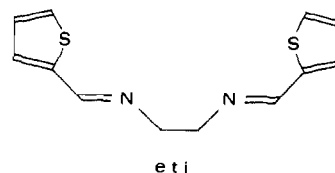


Figure 3. Inner coordination of $[\text{Cu}(\text{tapp})]^{2+}$ showing bond distances and angles. Note that the cation has crystallographically imposed C_2 symmetry.

dichloromethane under an inert atmosphere. The ligands tipp and tapp cannot accommodate two cations at the same time. On mixing the ligand and Cu(I) or Cu(II) ions in 1:2 ratio, we obtained as unique products the 1:1 complexes.

As we will discuss later in more detail, the complexes with tipp undergo hydrolysis of the imine linkage in solution when water is present, but the almost immediate precipitation of the complexes and their stability in the solid state allow their isolation. Such a hydrolysis reaction is known to occur on complex formation of the parent N,N' -ethylenebis(2-thenylideneimine) (eti).²¹



For comparison purpose we have synthesized the ligand N,N' -bis(2-thenylideneimine)-1,10-decane (tid), which has a size comparable with that of tipp and tapp and by similarity with the parent ligand eti is not expected to bind the copper(II)

(19) The general equivalent positions of $C2ca$ are $(0, 0, 0; 1/2, 1/2, 1/2) + x, y, z; x, y, z; x, 1/2 + y, 1/2 - z; x, 1/2 - y, 1/2 - z$.

(20) Supplementary material.

(21) (a) Eichhorn, G. L.; Bailar, J. C., Jr. *J. Am. Chem. Soc.* **1953**, *75*, 2905-2907. (b) Eichhorn, G. L.; Trachtenberg, I. M. *Ibid.* **1954**, *76*, 5183-5185. (c) Ho, R. K. Y.; Livingstone, S. E. *Aust. J. Chem.* **1965**, *18*, 659-671. (d) Coakley, M. P.; Young, L. H.; Gallagher, R. A. *J. Inorg. Nucl. Chem.* **1969**, *31*, 1449-1458.

Table II. Positional and Thermal Parameters for the Atoms of $[\text{Cu}(\text{tapp})][\text{ClO}_4]_2$

ATOM	X ^a	Y	Z	B ₁₁ ^b	B ₂₂	B ₃₃	B ₁₂	B ₁₃	B ₂₃
CU	0	0	0	11.95(46)	11.56(25)	13.26(31)	0	0	-0.29(29)
CL	-0.04193(15)	-0.371185(85)	-0.101344(93)	25.25(83)	22.59(49)	23.39(58)	-8.61(60)	9.38(63)	-7.55(45)
S	0.04767(15)	0.097736(82)	0.217720(94)	21.11(84)	18.23(47)	26.17(61)	0.87(60)	5.19(68)	-1.91(46)
O(1)	0.06232(38)	-0.33107(24)	-0.06539(29)	27.1(31)	18.8(15)	44.9(25)	-3.8(19)	4.4(25)	-6.5(16)
O(2)	-0.01049(55)	-0.45084(27)	-0.13535(39)	78.7(58)	31.0(20)	99.6(40)	-31.7(32)	58.9(44)	-37.9(24)
O(3)	-0.12831(35)	-0.37802(27)	-0.02636(25)	19.1(28)	37.2(20)	20.4(19)	2.7(21)	8.3(18)	2.2(15)
O(4)	-0.08912(50)	-0.32225(38)	-0.17762(34)	60.2(47)	83.6(35)	31.0(26)	-25.2(36)	-11.9(29)	28.4(26)
N(1)	-0.14317(35)	-0.07497(25)	0.00908(30)	13.0(27)	15.1(14)	15.9(19)	-2.5(17)	1.5(20)	-2.5(14)
N(2)	0.11797(38)	-0.07585(23)	0.06100(27)	21.0(29)	9.5(13)	12.7(18)	-0.9(17)	-1.8(20)	2.4(13)
C(1)	-0.20021(49)	-0.03915(32)	0.09536(37)	19.6(36)	16.8(19)	21.0(25)	-3.4(23)	8.7(25)	-1.4(18)
C(2)	-0.21866(45)	0.05229(33)	0.07516(35)	15.3(34)	18.9(20)	17.8(23)	2.0(21)	1.9(23)	-4.3(17)
C(3)	-0.12766(50)	-0.16573(31)	0.01547(34)	28.4(37)	13.0(17)	17.5(24)	-4.4(21)	0.0(24)	-3.9(16)
C(4)	-0.02786(47)	-0.19144(28)	0.08273(33)	30.4(43)	10.0(15)	15.9(21)	-4.4(20)	-0.2(22)	0.2(15)
C(5)	0.09398(47)	-0.16656(31)	0.05075(34)	24.3(38)	10.9(16)	18.0(23)	0.6(21)	-1.6(24)	0.9(16)
C(6)	0.14036(48)	-0.05581(31)	0.16512(36)	25.4(38)	14.5(17)	15.1(22)	-1.8(22)	-5.8(24)	-0.7(16)
C(7)	0.16107(46)	0.03578(31)	0.17982(33)	19.3(35)	13.9(17)	13.9(22)	3.9(21)	-0.9(23)	-1.8(16)
C(8)	0.26325(46)	0.07860(32)	0.16877(33)	20.5(35)	20.2(19)	11.9(20)	0.1(22)	-1.7(23)	-0.7(17)
C(9)	0.24915(53)	0.16345(34)	0.19168(36)	37.9(45)	17.1(19)	20.9(24)	-4.7(25)	-4.1(28)	5.2(18)
C(10)	0.13629(54)	0.18292(31)	0.21792(36)	42.5(46)	12.5(17)	21.1(24)	0.1(24)	-2.3(29)	2.5(17)
H1N(2)	0.188	-0.068	0.023	1.9					
H1C(1)	-0.274	-0.067	0.110	2.4					
H2C(1)	-0.150	-0.048	0.152	2.4					
H1C(2)	-0.195	0.086	0.129	2.3					
H2C(2)	-0.300	0.064	0.062	2.3					
H1C(3)	-0.199	-0.191	0.038	2.3					
H2C(3)	-0.110	-0.188	-0.046	2.3					
H1C(4)	-0.042	-0.166	0.144	2.2					
H2C(4)	-0.029	-0.250	0.091	2.2					
H1C(5)	0.152	-0.197	0.087	2.3					
H2C(5)	0.104	-0.182	-0.015	2.3					
H1C(6)	0.074	-0.073	0.202	2.2					
H2C(6)	0.209	-0.086	0.186	2.2					
H1C(8)	0.336	0.054	0.145	2.3					
H1C(9)	0.312	0.203	0.189	2.7					
H1C(10)	0.110	0.238	0.237	2.5					

^a Estimated standard deviations in the least significant figure(s) are given in parentheses. ^b The form of the anisotropic thermal ellipsoid is $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$. The quantities given in the table are the thermal coefficients $\times 10^4$.

ion through the thiophene groups. We could isolate the Cu(I) complex of *tid*, but any attempt to isolate the corresponding complexes of Cu(II) in reasonable purity was unsuccessful owing to their extreme instability toward hydrolysis even in the solid state.

Description of the Structure. The crystal structure of $[\text{Cu}(\text{tapp})][\text{ClO}_4]_2$ consists of the packing of four $[\text{Cu}(\text{tapp})]^{2+}$ cations and eight ClO_4^- anions in the unit cell (Figure 1). The ions are well separated, there being no unusually short intermolecular interactions. Figure 2 displays the $[\text{Cu}(\text{tapp})]^{2+}$ cation, which possesses crystallographically imposed C_2 symmetry. Figure 3 displays the CuN_4 coordination geometry. Bond distances and angles are tabulated in Table IV.

The ClO_4^- anion in the present structure has nearly perfect T_d symmetry, despite the fact that two of the O atoms show anisotropy of thermal motion which seems large for a structure determined at -150°C (root mean square amplitudes of vibration for O(1) through O(4) are 0.127 (8), 0.153 (7), 0.218 (6); 0.121 (10), 0.169 (9), 0.384 (7); 0.093 (9), 0.153 (6), 0.224 (6); and 0.138 (8), 0.079 (8), 0.361 (7) Å).

The CuN_4 coordination sphere (Figure 3) is severely distorted from square planar. The deviations of atoms N(1), N(1)', N(2), and N(2)' from the best-weighted, least-squares plane through the CuN_4 group are 0.397 (4), -0.397 (4), -0.254 (4), and 0.254 (4) Å. While this distortion is toward tetrahedral, the dihedral angle between the $\text{Cu}-\text{N}(1)-\text{N}(2)$ and $\text{Cu}-\text{N}(1')-\text{N}(2)'$ planes being 25.4° , the $\text{N}(1)-\text{Cu}-\text{N}(1)'$ angle of $74.2(2)^\circ$ represents a rhombic distortion. The $\text{Cu}-\text{N}(\text{aminopropyl})$ and $\text{Cu}-\text{N}(\text{piperazine})$ distances are essentially equal and are typical for $\text{Cu}^{\text{II}}-\text{N}_4$ distances.

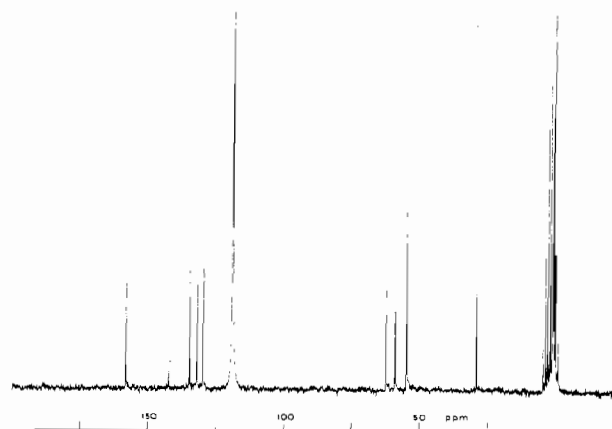


Figure 4. ^{13}C NMR spectrum at 22.5 MHz of $[\text{Cu}(\text{tipp})][\text{ClO}_4]$ in $\text{MeCN}-d_3/\text{Me}_4\text{Si}$. The intense signal at 118.2 ppm is due to the CN group of the solvent.

Although the Cu(II) ion in the present structure is bonded to the four available nitrogen atoms, Figure 2 displays a very interesting aspect of the structure, namely, the rotation of the thiophene groups so that the S atoms complete a reasonably symmetric octahedral environment about the Cu(II) ion. The $\text{Cu}-\text{S}$ interaction of $3.469(2)$ Å is well beyond a bonding distance. Yet there is no obvious packing interaction that appears to be responsible for this rotation, and it is tempting to describe the Cu(II) ion in $[\text{Cu}(\text{tapp})]^{2+}$ as possessing an incipient CuN_4S_2 coordination.

Table IV. Bond Distances (Å) and Angles (Deg) for [Cu(tapp)] [ClO₄]₂

atoms	dist	atoms	dist
Cu-N(1)	2.029 (4)	C(6)-C(7)	1.520 (7)
Cu-N(2)	2.005 (4)	C(7)-C(8)	1.357 (7)
Cu...S	3.469 (2)	C(8)-C(9)	1.423 (7)
N(1)-C(1)	1.484 (6)	C(9)-C(10)	1.364 (8)
N(1)-C(2)' ^a	1.498 (6)	C(10)-S	1.708 (6)
N(1)-C(3)	1.487 (6)	S-C(7)	1.713 (5)
C(1)-C(2)	1.526 (7)	Cl-O(1)	1.437 (4)
C(3)-C(4)	1.526 (7)	Cl-O(2)	1.423 (4)
C(4)-C(5)	1.503 (7)	Cl-O(3)	1.435 (4)
C(5)-N(2)	1.505 (6)	Cl-O(4)	1.431 (5)
N(2)-C(6)	1.510 (6)		

atoms	angle	atoms	angle
N(1)-Cu-N(1)'	74.2 (2)	C(4)-C(5)-N(2)	113.6 (4)
N(1)-Cu-N(2)	97.8 (2)	C(5)-N(2)-C(6)	109.4 (4)
N(1)-Cu-N(2)'	157.8 (2)	N(2)-C(6)-C(7)	111.5 (4)
N(2)-Cu-N(2)'	96.6 (2)	C(7)-C(8)-C(9)	112.0 (5)
N(1)-Cu-S	110.1 (1)	C(8)-C(9)-C(10)	112.9 (5)
N(1)-Cu-S'	84.5 (1)	C(9)-C(10)-S	111.1 (4)
N(2)-Cu-S	78.8 (1)	C(10)-S-C(7)	92.1 (3)
N(2)-Cu-S'	89.3 (1)	S-C(7)-C(8)	111.8 (4)
S-Cu-S'	162.1 (1)	C(6)-C(7)-S	120.0 (4)
N(1)-C(1)-C(2)	106.9 (4)	C(6)-C(7)-C(8)	128.1 (5)
C(1)-N(1)-C(2)'	107.0 (4)	O(1)-Cl-O(2)	108.9 (3)
C(1)-C(2)-N(1)'	107.8 (4)	O(1)-Cl-O(3)	109.8 (2)
C(1)-N(1)-C(3)	113.0 (4)	O(1)-Cl-O(4)	108.3 (3)
C(2)'-N(1)-C(3)	111.0 (4)	O(2)-Cl-O(3)	110.0 (3)
N(1)-C(3)-C(4)	113.3 (4)	O(2)-Cl-O(4)	110.5 (4)
C(3)-C(4)-C(5)	114.9 (4)	O(3)-Cl-O(4)	109.3 (3)

^a The primed atoms are related to the corresponding unprimed atoms by the twofold symmetry operation.

Other distances and angles within the cation are remarkably consistent and normal, probably as a result of the efficacy of low-temperature crystallography and the lack of severe strain in the multidentate ligand.

Conductivity Data. Conductivity data in various solvents for the copper complexes of tipp and tapp stable in solution are reported in Table V. Since the rather low values of the molar conductivity at 10⁻³ M concentration obtained for some copper(II) complexes could be indicative of anion coordination, the equivalent conductance was measured over a concentration range to establish the ion type in solution. From Onsager plots ($\Lambda_0 - \Lambda_c$ vs. $c^{1/2}$) the slope A was obtained for the complexes; theoretical A values could be calculated from the limiting law expression²² with use of the constants appropriate to each solvent.²³ For all solvents the magnitude of the A slopes clearly establishes the electrolyte type as 1:1 for [Cu(tipp)][ClO₄] and as 1:2 for all copper(II) complexes except for those containing the nitrate anion.²⁴ Even though the copper(II) complexes containing the trifluoromethanesulfonate anion have Λ_M values in nitromethane and acetone which lie between the ranges expected for 1:1 and 1:2 electrolytes,²⁵ the magnitude of the slopes A establishes that these are 1:2

Table V. Conductivity Data for Copper Complexes in Solution at 25 °C

complex	solvent ^a	Λ_M^b	A^c
[Cu(tipp)][ClO ₄]	AN	166	450 (363) ^d
	NM	98	248 (202) ^d
	AC	163	940 (685) ^d
[Cu(tipp)][ClO ₄] ₂	AN	314	880 (1049) ^e
	NM	170	570 (577) ^e
	AC	156	1500 (1582) ^e
[Cu(tapp)][ClO ₄] ₂	AN	300	950 (1044) ^e
	NM	160	575 (563) ^e
	AC	145	1440 (1545) ^e
[Cu(tipp)(ONO ₂)] [NO ₃]	AN	178	
[Cu(tapp)(ONO ₂)] [NO ₃]	AN	146	
[Cu(tipp)][OSO ₂ CF ₃] ₂	AN	276 ^f	
	NM	126	560 (539) ^e
	AC	122	1310 (1485) ^e
[Cu(tapp)][OSO ₂ CF ₃] ₂	AN	248 ^g	
	NM	128	570 (534) ^e
	AC	126	1340 (1473) ^e

^a AN = acetonitrile, NM = nitromethane, AC = acetone. ^b Values interpolated at 10⁻³ M. ^c In parentheses are A values calculated from the limiting law expression,²² with use of constants appropriate to each solvent. ^d 1:1 electrolyte. ^e 1:2 electrolyte. ^f 1.7 × 10⁻³ M. ^g 1.9 × 10⁻³ M.

electrolytes. Good agreement is also generally found between calculated and experimental A parameters. The Λ_M values for the copper(II) complexes containing the nitrate ions fall in the range for 1:1 electrolytes, and Onsager plots resulted in unreliable extrapolation to high dilution. In these complexes one of the two nitrate ions appears to be coordinated and the other to function as a noncoordinating counterion. At high dilution partial displacement of the coordinated ion by the solvent apparently occurs. Therefore, we formulate these complexes as [Cu(tapp)(ONO₂)] [NO₃] and [Cu(tipp)(ONO₂)] [NO₃], respectively. Molecular association in solution can be excluded for all the complexes. This would give rise to ion types higher than 1:1 or 1:2 and could be easily recognized by larger magnitudes of the A slopes.^{24,25}

Copper(II) Complexes. IR Spectra. Consistent with X-ray structural data, the solid-state IR spectrum of [Cu(tapp)] [ClO₄]₂ exhibits two pronounced features: a single sharp band at 3220 cm⁻¹, associated with the N-H stretching mode of symmetrically coordinated tapp ligand, and two bands in the region 1070–1100 cm⁻¹ and at 620 cm⁻¹, typical for noncoordinated perchlorate.²⁶ Similar bands for noncoordinated perchlorate are present also in the IR spectrum of [Cu(tipp)][ClO₄]₂. We thus conclude that in the solid state Cu(tipp)²⁺ also possesses a CuN₄ center. The symmetry of coordination of the tapp ligand in [Cu(tapp)][ClO₄]₂ is apparently broken in the related nitrate and trifluoromethanesulfonate derivatives. In the IR spectra of these compounds two sharp bands occur in the 3150–3250-cm⁻¹ region of the infrared spectrum, at 3230 and 3200 cm⁻¹ for [Cu(tapp)] [OSO₂CF₃]₂, and at 3240 and 3180 cm⁻¹ for [Cu(tapp)(ONO₂)] [NO₃]. The relatively large separation between the two ν (N-H) peaks, especially in the latter case, is a strong indication of nonequivalence of the two N-H groups within the molecule. Yet both N-H groups must be coordinated, as judged from the reduced frequency (compared with that in free tapp) and sharpness of their absorption peaks.

Conductivity data have shown for [Cu(tapp)(ONO₂)] [NO₃] the presence of a coordinated nitrate ion in solution. In the solid-state IR spectrum of this compound several bands in the 1300–1500- and 700–750-cm⁻¹ region as well as bands at 1740, 1040, and 820 cm⁻¹ can be assigned to nitrate absorptions.^{26–28}

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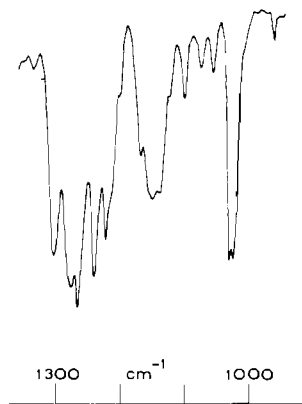


Figure 5. Infrared spectrum of $[\text{Cu}(\text{tipp})(\text{OSO}_2\text{CF}_3)]_2[\text{OSO}_2\text{CF}_3]$ (Nujol mull) in the $1000\text{--}1300\text{-cm}^{-1}$ region, showing the absorptions of coordinate trifluoromethanesulfonate. Ionic trifluoromethanesulfonate has strong and unsplit bands at 1270 , 1160 , and 1030 cm^{-1} .

The bands at 1365 and 820 cm^{-1} are at approximately the positions expected for ionic nitrate.²⁷ The 1470- , 1420- , and the apparently split 1330-cm^{-1} band are assigned to coordinated nitrate.^{26,27} The other bands are less helpful for structural diagnosis or fall in the region of other absorptions (e.g., the thiophene nuclei). However, IR data are apparently consistent with the formulation as $[\text{Cu}(\text{tapp})(\text{ONO}_2)]_2[\text{NO}_3]$ for this compound also in the solid state. Infrared spectroscopy is of only limited value in determining the mode of nitrate coordination.²⁷ But we prefer the monodentate coordination (and hence CuN_4O) because for a chelating bidentate nitrate the highest energy vibration mode ($\nu(\text{N}=\text{O})$) usually occurs at frequencies higher ($1480\text{--}1650\text{ cm}^{-1}$)²⁶ than those observed here. A similar pattern for the bands of nitrate anions is exhibited by $[\text{Cu}(\text{tipp})(\text{ONO}_2)]_2[\text{NO}_3]$, which therefore we believe has CuN_4O coordination in the solid state and in solution.

The IR spectra of complexes containing the trifluoromethanesulfonate anions, when obtained as Nujol mulls, display strong bands attributable to trifluoromethanesulfonate in the region $1220\text{--}1310\text{ cm}^{-1}$ and at 1150 , 1030 , and 640 cm^{-1} . The absorptions in the $1220\text{--}1310\text{-cm}^{-1}$ region comprise several strong, sharp, and well-resolved bands, while those at 1150 and 1030 cm^{-1} appear as resolved doublets, broad and sharp, respectively (Figure 5). Interestingly, when the IR spectra are obtained from KBr pellets only a rather broad band at 1270 cm^{-1} and unsplit bands at 1225 , 1160 , 1030 , and 640 cm^{-1} appear. Since these bands belong to ionic trifluoromethanesulfonate, we ascribe the loss of extensive splitting to a large extent of substitution of coordinated trifluoromethanesulfonate by bromide ions in the KBr fusion mixture. For $[\text{Cu}(\text{tapp})(\text{ONO}_2)]_2[\text{NO}_3]$ and $[\text{Cu}(\text{tipp})(\text{ONO}_2)]_2[\text{NO}_3]$ almost identical spectra are obtained in Nujol mulls and KBr pellets, indicating that here substitution of coordinated nitrate by bromide ion does not occur to a noticeable extent.

Coordination of trifluoromethanesulfonate anion occurs only in the solid state, and conductivity data of $[\text{Cu}(\text{tapp})][\text{OSO}_2\text{CF}_3]_2$ and $[\text{Cu}(\text{tipp})][\text{OSO}_2\text{CF}_3]$ show that in solution the anions are noncoordinated. Therefore the coordinating ability of trifluoromethanesulfonate appears to be intermediate between that of nitrate and that of the perchlorate anion. On the basis of this and of the presence of bands in the positions expected for ionic trifluoromethanesulfonate under the envelope of the IR bands assigned to this anion, we believe that the copper(II) complexes of tapp and tipp contain one coordinated and one noncoordinated trifluoromethanesulfonate

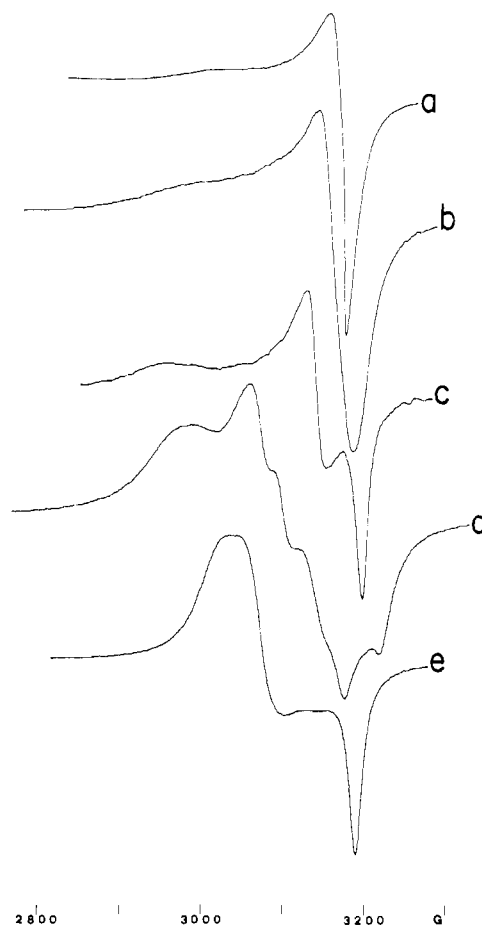


Figure 6. EPR spectra of undiluted powder sample of copper(II) complexes recorded at room temperature: (a) $[\text{Cu}(\text{tapp})][\text{ClO}_4]_2$ ($\nu = 9.073\text{ GHz}$), (b) $[\text{Cu}(\text{tipp})][\text{ClO}_4]_2$ ($\nu = 9.073\text{ GHz}$), (c) $[\text{Cu}(\text{tapp})(\text{ONO}_2)]_2[\text{NO}_3]$ ($\nu = 9.073\text{ GHz}$), (d) $[\text{Cu}(\text{tipp})(\text{ONO}_2)]_2[\text{NO}_3]$ ($\nu = 9.074\text{ GHz}$), (e) $[\text{Cu}(\text{tapp})(\text{OSO}_2\text{CF}_3)]_2[\text{OSO}_2\text{CF}_3]$ ($\nu = 9.073\text{ GHz}$).

Table VI. Powder EPR Data of Copper(II) Complexes at Room Temperature

complex	g_{\perp} (av)	g_{\parallel}	
$[\text{Cu}(\text{tapp})][\text{ClO}_4]_2$	2.05	2.167	
$[\text{Cu}(\text{tipp})][\text{ClO}_4]_2$	2.05	2.172	
complex	g_1	g_2	g_3
$[\text{Cu}(\text{tapp})(\text{ONO}_2)]_2[\text{NO}_3]$	2.030	2.065	2.195
$[\text{Cu}(\text{tapp})(\text{OSO}_2\text{CF}_3)]_2[\text{OSO}_2\text{CF}_3]$	2.032	2.108	2.147
$[\text{Cu}(\text{tipp})(\text{ONO}_2)]_2[\text{NO}_3]$	2.013	2.090	2.171

group in the solid state. Therefore, the complexes should be correctly formulated as $[\text{Cu}(\text{tapp})(\text{OSO}_2\text{CF}_3)]_2[\text{OSO}_2\text{CF}_3]$ and $[\text{Cu}(\text{tipp})(\text{OSO}_2\text{CF}_3)]_2[\text{OSO}_2\text{CF}_3]$ when in the solid state and as $[\text{Cu}(\text{tapp})][\text{OSO}_2\text{CF}_3]_2$ and $[\text{Cu}(\text{tipp})][\text{OSO}_2\text{CF}_3]_2$ in solution. By analogy with the corresponding nitrate complex, we propose a monodentate mode of coordination for trifluoromethanesulfonate. Its size (larger) and donor properties (weaker than nitrate) are in favor of this suggestion.

The solid-state IR spectra of $[\text{Cu}(\text{tapp})][\text{ClO}_4]_2$, $[\text{Cu}(\text{tipp})(\text{ONO}_2)]_2[\text{NO}_3]$, and $[\text{Cu}(\text{tipp})(\text{OSO}_2\text{CF}_3)]_2[\text{OSO}_2\text{CF}_3]$ show a shift to lower frequencies of the bands associated with the $\text{C}=\text{N}$ linkage relative to the position in the free ligand, indicative of coordination. In $[\text{Cu}(\text{tipp})][\text{ClO}_4]_2$ the $\nu(\text{C}=\text{N})$ stretching band appears as a resolved doublet, at 1615 and 1600 cm^{-1} . Besides nonequivalence of the coordinated Schiff base groups, splitting of this entity may be accounted for also by coupling of the $\text{C}=\text{N}$ groups in the ligand. In fact, in acetonitrile solution a single band at 1605 cm^{-1} is observed.

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Table VII. EPR Spectral Data of Copper(II) Complexes in Frozen Solution at 77 K

complex	solvent ^a	g_{\parallel}	$10^4 A_{\parallel}$, cm ⁻¹
[Cu(tapp)][ClO ₄] ₂	AC	2.204	180
	NM	2.243	209
	TL/AN ^b	2.190	179
[Cu(tipp)][ClO ₄] ₂	AC	2.210	155
	NM	2.235	185
	TL/AN ^{b,c}	2.190	179
[Cu(tapp)(ONO ₂)] [NO ₃]	TL/AN ^b	2.212	165
[Cu(tipp)(ONO ₂)] [NO ₃]	TL/AN ^{b,c}	2.197	154
[Cu(tapp)][OSO ₂ CF ₃] ₂	DC	2.203	180
	TL/AN	2.197	174
	DC	2.197	190
[Cu(tipp)][OSO ₂ CF ₃] ₂	TL/AN	2.193	184

^a AC = acetone, NM = nitromethane, DC = dichloromethane, TL/AN = toluene/acetonitrile (1:1). ^b Spectra recorded at 143 K. ^c Tetraethylammonium perchlorate was added to the solution to enhance resolution of the hyperfine structure.

Electronic and EPR Spectra. The X-band EPR spectra of undiluted powder samples of copper(II) complexes of tapp and tipp are shown in Figure 6, and the derived g values are summarized in Table VI. Although the powder technique is of only limited value for determining the local copper environment,²⁹ the spectra display marked differences among the complexes as a function of the anions. The EPR spectra of perchlorate complexes show unresolved high-field components and appear roughly axial (with $g_{\parallel} > g_{\perp}$), those of nitrate complexes are rhombic and show completely resolved g anisotropy, and that of [Cu(tapp)(OSO₂CF₃)] [OSO₂CF₃] has "reversed" g values ($g_{\perp} > g_{\parallel}$) while the spectrum of [Cu(tipp)(OSO₂CF₃)] [OSO₂CF₃] falls into the uninformative "F" class in the Hathaway classification.²⁹ According to the IR results and the structure of [Cu(tapp)]²⁺, in all the copper(II) complexes the amino groups of tapp or the imino groups of tipp are both coordinated to the metal ion, and it seems reasonable to assume that these ligands provide a N₄-binding site. Therefore, we propose the following qualitative description for the copper(II) chromophores of these complexes in the solid state. In [Cu(tipp)][ClO₄]₂, with noncoordinated perchlorate, a distorted square-planar CuN₄ geometry is present (lowest $g > 2.04$, $d_{x^2-y^2}$ ground state),²⁹ similar to that of [Cu(tapp)][ClO₄]₂ and of other CuN₄ chromophores.²⁹⁻³¹ The nitrate complexes, with a monodentate bound nitrate, contain CuN₄O centers with stereochemistries intermediate between distorted square pyramidal and trigonal bipyramidal. (For [Cu(tapp)(ONO₂)] [NO₃] the value of $R = (g_2 - g_1)/(g_3 - g_2)$ of 0.27 suggests a predominantly $d_{x^2-y^2}$ ground state.^{32,33}) In [Cu(tapp)(OSO₂CF₃)] [OSO₂CF₃], on the assumption of a monodentate coordination of the trifluoromethanesulfonate ion and a CuN₄O core, the reversed g -value spectrum suggests a nearly trigonal-bipyramidal geometry,³⁴ with the value of $R = 1.95$ indicative of a predominantly d_{z^2} ground state.^{32,33}

The features of the intermediate field component in the EPR spectrum of [Cu(tipp)(ONO₂)] [NO₃] may arise from copper hyperfine structure.

The electronic reflectance spectra of the copper(II) complexes are less informative than EPR data. A broad asymmetric band roughly centered at ca. 600 nm is generally spread over the range 450–950 nm, with poorly resolved shoulders near 800 nm.

The EPR spectra of copper(II) complexes of tipp and tapp recorded in frozen solutions do not mirror the large dissimilarities observed in the powder spectra (Table VII). All the complexes exhibit spectra consistent with nearly tetragonal symmetry ($g_{\parallel} > g_{\perp}$), well-resolved parallel hyperfine structure, and large A_{\parallel} values. From these results we can exclude either trigonal-bipyramidal or severely distorted structures in solution.^{29,35} The A_{\parallel} values, more than the g_{\parallel} values, show solvent dependence, but in general both g_{\parallel} and A_{\parallel} values are typical of N- or O-bonded Cu in tetragonal stereochemistries.³⁰ The spectra of tipp complexes are somewhat more spread out in the high-field region than those of tapp complexes. This may reflect the higher degree of rhombic distortion of the in-plane component of the chromophore which is observed in the powder spectra, but larger A_{\perp} values would also give rise to the same effect. The quotient $g_{\parallel}/A_{\parallel}$, proposed as an empirical index of tetrahedral distortion,³⁰ ranges here from 107 to 143 and indicates that such a distortion is not important for Cu(II)-tapp and -tipp complexes in solution.

The optical spectra seem more sensitive than EPR spectra in revealing small differences in the coordination environment in solution (Table VIII). In the visible region the complexes of tapp exhibit a band near 600 nm, and those of tipp exhibit two partially overlapping bands near 600 and 700 nm. The spectra of the complexes containing perchlorate anions are identical with those containing trifluoromethanesulfonate anions, as expected from loss of coordination by the latter ions in solution. The same spectra as those of the nitrate complexes are obtained by adding nitrate ions to [Cu(tapp)]²⁺ or [Cu(tipp)]²⁺.

The addition of various salts to solutions of [Cu(tapp)]²⁺ or [Cu(tipp)]²⁺ results in significant and often large changes in the electronic and EPR spectra as a consequence of ready coordination by the added anion. The same changes occur if the nitrate complexes are used, indicating that the coordinated anion can be displaced by a stronger ligand. For example, the absorption maximum in the visible region shifts to longer wavelength upon addition of chloride or bromide ions to [Cu(tapp)]²⁺ (735 nm) or [Cu(tipp)]²⁺ (810 nm) complexes. An increase in the extinction coefficient in both cases (to above 400 for [Cu(tapp)]²⁺ and to 590 L/(mol cm) for [Cu(tipp)]²⁺ in acetonitrile, upon addition of bromide) is probably the result of a slight lowering of the symmetry of the metal complex to accommodate the larger anion. The change in EPR spectra can clearly be followed upon adding the anions to the trifluoromethanesulfonate complexes in dichloromethane, where a better resolution of hyperfine structure can be obtained. Consistent with symmetry lowering upon coordination of bulky anions,^{35,36} g_{\parallel} is found to increase slightly and A_{\parallel} to decrease markedly (to 165×10^{-4} cm⁻¹ for [Cu(tapp)]²⁺ with added

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Table VIII. Electronic Spectral Data of Copper(II) Complexes in Solution

complex	solvent ^a	λ_{max} , nm (ϵ , L/(mol cm)) ^b	
[Cu(tapp)][ClO ₄] ₂	AC	610 (390)	303 (7350)
	AN	616 (370)	
	NM	580 (460)	
[Cu(tapp)(ONO ₂)] [NO ₃]	AN	637 (330)	295 (7860)
	DC	617 (290)	
[Cu(tapp)][OSO ₂ CF ₃] ₂	AN	615 (380)	303 (7280)
	AC	680 (250)	295 (23 820)
AN	690 (275)		
NM	680 (190)		
[Cu(tipp)][ClO ₄] ₂	AN	710 (285)	637 (295)
	DC	700 (220)	
[Cu(tipp)] [NO ₃]	AN	690 (270)	612 (300)
	DC	690 (270)	612 (300)

^a AC = acetone, AN = acetonitrile, NM = nitromethane, DC = dichloromethane. ^b Poorly resolved shoulders of low intensity in the range 800–850 nm occur in the spectra of all the complexes.

bromide and to 133×10^{-4} for [Cu(tipp)]²⁺ with chloride). The EPR spectra obtained from [Cu(tipp)]²⁺ complexes, however, can hardly be considered of the axial type, because of a broad and badly resolved feature in the high-field region. Note that all these changes do not arise by displacement of the ligand by the added anions. For instance, the IR spectrum of a solution of [Cu(tipp)][ClO₄]₂ in acetonitrile containing excess bromide ions shows clearly the bands of the coordinated C=N bonds at 1605 and 1615 cm⁻¹. Therefore, coordination of bulky anions to [Cu(tapp)]²⁺ and [Cu(tipp)]²⁺, either in the solid state or in solution, produces structural distortions toward irregular stereochemistries. The effect is larger with tipp complexes, and it is possible that steric repulsion between the coordinating anions and the thiophene residues of the ligands is responsible for this progressive distortion of the chromophore with increasing size of the anion.

Somewhat surprisingly, the intensities of the visible bands of [Cu(tapp)]²⁺, near 600 and 300 nm, decrease slowly with time in donor solvents (acetonitrile, nitromethane) without appreciable change in their positions, but they remain constant in weaker donor solvents (dichloromethane, acetone). Slow changes in the optical spectra are also observed in solutions of [Cu(tipp)]²⁺ but occur mainly as a consequence of the hydrolysis reaction of the ligand, as discussed below. Coordination of [Cu(tapp)]²⁺ and [Cu(tipp)]²⁺ by solvent is likely to occur; it is evidenced by some solvent dependence of the electronic and EPR spectra and is consistent with the loss of coordination by trifluoromethanesulfonate in solution. The decrease in intensities of the visible absorptions in donor solvents may possibly be related to an increase of the overall symmetry of the complex as the solvent enters in the metal coordination sphere. The structural changes involved may be minor, as the EPR spectra in frozen solution do not show appreciable variation with time. No decrease in absorption occurs in solutions either of [Cu(tapp)(ONO₂)]⁺ or of [Cu(tapp)]²⁺ containing chloride or bromide ions.

Reactions of [Cu(tapp)]²⁺ and [Cu(tipp)]²⁺ with Thiolates. We have tried to exploit the apparent affinity of the Cu(II)-tapp and -tipp complexes for an additional anionic ligand to form complexes with the thiolate anion. A current problem in the chemistry of bioinorganic models is the difficulty of preparing stable copper(II) thiolate systems. On mixing solutions of [Cu(tapp)]²⁺ or [Cu(tipp)]²⁺ and of thiosalicylate dianion in methanol, the intense blue color which is diagnostic of copper(II) thiolate ligation³⁷ readily develops, but the systems are unstable at room temperature and the cupric ions are rapidly reduced. At low temperatures the reduction is slower, but attempts to isolate the complexes in reasonable purity have been unsuccessful. Recently a Cu^{II}N₄-thio-

salicylate complex (Cu(tet b)(*o*-SC₆H₄CO₂))^{8b} stable at room temperature has been synthesized and has been characterized by X-ray methods. The N₄ ligand is a macrocyclic tetramine containing four secondary nitrogen donor atoms and a cavity of the same size as that provided by tapp in [Cu(tapp)]²⁺. The analogy of both overall donor properties and size between tet b and tapp is therefore evident. The stability of the Cu(tet b)-thiolate system must therefore be related to the macrocyclic structure of the ligand. A rigid coordination environment around the Cu(II) ion is probably able to prevent the coupling of two thiolate residues to form the disulfide unit. This requisite is certainly more than satisfactorily fulfilled in the protein "blue" type 1 site. By contrast, a high degree of stereochemical flexibility seems to be connected with the type 2 site. In particular, it has been shown that the type 2 site has empty coordination positions readily available to the addition of even weak ligands.² These properties are clearly exhibited by the Cu(II)-tapp and Cu(II)-tipp complexes described here.

Copper(I) Complexes. The copper(I) complexes of tapp and tid, [Cu(tapp)][ClO₄] and [Cu(tid)][ClO₄], are moderately air stable in the solid state but in solution undergo a rapid aerobic oxidation as evidenced by the formation of paramagnetic blue products. The copper(I) complex of tipp, [Cu(tipp)][ClO₄], shows remarkable stability toward oxidation both in the solid state and in solution. It is not oxidized by dry oxygen, and it is only slowly decomposed in the presence of water, because the hydrolysis products are apparently less stable.

We have been unable to obtain suitable crystals of any of the Cu(I) complexes, and hence deductions of stereochemistry are based on spectroscopic data. In all the Cu(I) complexes the presence of noncoordinated perchlorate is inferred from infrared spectra. Bands related to ionic perchlorate are present in the region 1070–1105 cm⁻¹ and at 620 cm⁻¹, but the intense absorption band around 930 cm⁻¹, indicative of coordinated perchlorate,^{26,27} is absent. In [Cu(tipp)][ClO₄] and [Cu(tid)][ClO₄] the positions of the C=N stretching bands are shifted to lower frequencies compared with those of the free ligand (by 18 and 15 cm⁻¹, respectively), suggesting the coordination of the azomethine groups to the metal ion. The presence in each of a single band implies equivalence of the two coordinated C=N groups within the molecule. However, for [Cu(tipp)][ClO₄], a slight broadening of the imine band in acetonitrile solution perhaps indicates a partial displacement of this group by the solvent. In the IR spectrum of [Cu(tapp)][ClO₄] the sharp band at 3220 cm⁻¹ can be assigned to the N-H stretching mode associated with the secondary amine function of the ligand. The N-H stretching vibration is present as a weak band at 3280 cm⁻¹ in the free ligand tapp. The reduced frequency and sharpness of the band in [Cu(tapp)][ClO₄] suggest coordination of the secondary amine

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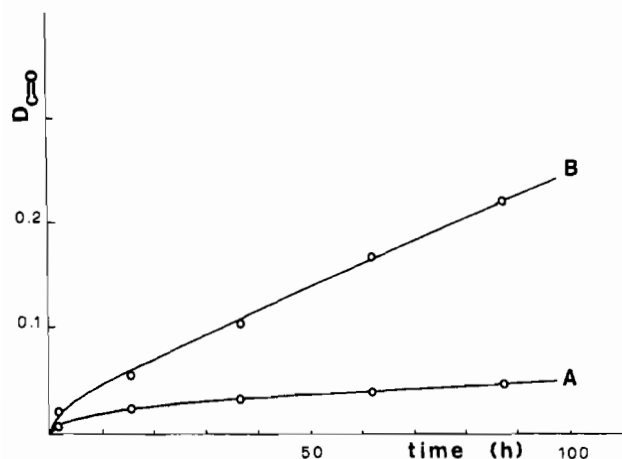
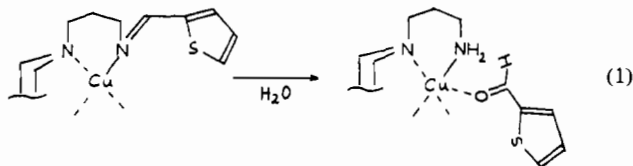


Figure 7. Increase in the rate of ligand hydrolysis in $[\text{Cu}(\text{tipp})][\text{ClO}_4]_2$ upon addition of a known amount of water. The concentration of $[\text{Cu}(\text{tipp})]^{2+}$ in both solutions is 1.54×10^{-2} M in undried acetonitrile at 25°C ; the cell path is 0.5 mm. A is the starting solution; B contains 5.55×10^{-2} M of added water.

nitrogen atoms by the Cu(I) ion. The occurrence of a single N–H stretching band must be related to the equivalence of the two secondary amine groups in the molecule.

The instability of $[\text{Cu}(\text{tapp})]^+$ and $[\text{Cu}(\text{tid})]^+$ precluded reliable studies in solution, but for $[\text{Cu}(\text{tipp})]^+$ additional information could be obtained from NMR spectra. In the ^1H NMR spectrum, the signals of the protons on the thiophene nuclei display a pattern which is different from that observed in the free ligand, as if the environment of both these groups has changed. The ^{13}C NMR spectrum of $[\text{Cu}(\text{tipp})][\text{ClO}_4]$ shows only signals attributable to one kind of thiophene nucleus and, in general, is consistent with symmetry between the two functional parts of the molecule, as is found in the free ligand (Figure 4). A symmetric environment around the Cu(I) ion can be provided by tipp with both thiophene groups either coordinated or noncoordinated to the metal ion. Since conductivity data show that the complex is monomeric in solution, we assume that the tipp ligand folds around the Cu(I) ion. From the stability of $[\text{Cu}(\text{tipp})]^+$ toward oxidation,^{3a,7,38} we conclude that here the Cu(I) ion is associated with the two thiophene groups in contrast to the copper(I) complexes with eti^{21c} and with simple *N*-(2-thenylidene)alkylamines.³⁹ Since the imine groups appear to be coordinated to the metal ion, we propose a CuN_2S_2 coordination set for $[\text{Cu}(\text{tipp})][\text{ClO}_4]$, although a CuN_4S_2 coordination, in which the Cu–S interaction is stronger than in $[\text{Cu}(\text{tapp})][\text{ClO}_4]_2$, is also possible.

Ligand Hydrolysis in Cu–tipp Complexes. The hydrolysis of imine linkages coordinated to metal ions is well-known,⁴⁰ and in particular the ligand hydrolysis in $[\text{Cu}(\text{eti})_2][\text{ClO}_4]_2$ has been recently studied in detail⁴¹ (see eq 1). The same



reaction occurs with copper–tipp complexes when they are

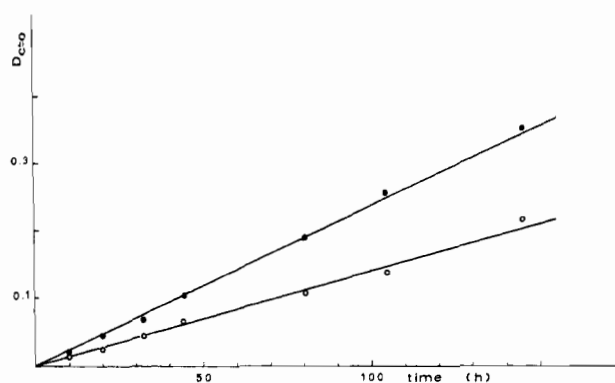


Figure 8. Comparison of the ligand hydrolysis rate between $[\text{Cu}(\text{tipp})][\text{ClO}_4]_2$ (●) and $[\text{Cu}(\text{tipp})][\text{ClO}_4]$ (○). Concentration of both solutions is 2.5×10^{-2} M in undried acetonitrile. Cell length = 0.5 mm. Temperature = 25°C .

dissolved in undried solvents. The hydrolysis can be followed by IR spectroscopy, through the appearance of the carbonyl band of 2-thiophenecarboxaldehyde at 1675 cm^{-1} and of the amine $\nu(\text{NH}_2)$ band at 3250 and 3300 cm^{-1} . We did not attempt to measure hydrolysis rates owing to the inaccuracy of measuring very small amounts of water. However, an indication of how fast the reaction occurs can be obtained from the plots in Figure 7. The difference between the upper (B) and lower (A) curve is related to the effect of the addition of a known amount of water ($[\text{H}_2\text{O}]:[\text{Cu}^{2+}] = 3.6$) on the rate of hydrolysis of $[\text{Cu}(\text{tipp})][\text{ClO}_4]_2$ in acetonitrile. A broadening of the coordinated $\text{C}=\text{N}$ band in the IR spectrum indicates that water molecules probably enter into the copper(II) coordination sphere.

By carrying out parallel experiments with the same solvent and at the same temperature, we have established that (i) the imine linkage undergoing the hydrolysis must be coordinated to the metal ion and (ii) the rate of hydrolysis of $[\text{Cu}(\text{tipp})]^{2+}$ is higher than that of $[\text{Cu}(\text{tipp})]^+$. Point i has been established with use of a ratio $[\text{tipp}]:[\text{Cu}^{2+}]$ of 2:1. Two bands of equal intensity are present at the beginning in the IR spectrum, at 1635 and 1605 cm^{-1} , the former related to noncoordinated and the latter to coordinated Schiff base groups, respectively. As the hydrolysis proceeds, only the 1605-cm^{-1} band decreases in intensity, while that at 1635 cm^{-1} remains unchanged. Thus the free Schiff base present in solution does not displace the hydrolysis products from coordination to copper(II). Point ii is readily explained. The charge of $[\text{Cu}(\text{tipp})]^{2+}$ is higher than that of $[\text{Cu}(\text{tipp})]^+$, and hence there is a higher degree of polarization of the coordinated $\text{C}=\text{N}$ bond and the carbon atom is more susceptible to nucleophilic attack. In Figure 8 a comparison of the rates of hydrolysis for $[\text{Cu}(\text{tipp})][\text{ClO}_4]$ and $[\text{Cu}(\text{tipp})][\text{ClO}_4]_2$ in undried acetonitrile is shown. The straight lines have been drawn only to aid in visualization of the effect and do not necessarily imply a linear relationship.

Conclusions

The copper(I) and copper(II) complexes with the new ligands tapp and tipp have been synthesized and characterized. These ligands provide a wide range of coordination arrangements to satisfy the stereochemical preferences of the metal ions and to accommodate within the metal coordination sphere even rather bulky anions which may act as competing ligands. In the Cu(II)–tipp and –tapp systems the ligands behave as N_4 tetradentates.⁴² The thiophene residues behave as bulky substituents to the copper(II) ion. The solid-state structure of $[\text{Cu}(\text{tapp})][\text{ClO}_4]_2$ shows an incipient CuN_4S_2 coordination. The nitrate and trifluoromethanesulfonate complexes contain

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one coordinated anion, and the metal ion is five-coordinate, with a CuN_4O core. Upon increasing the size of the coordinated anion, from nitrate to trifluoromethanesulfonate, a progressive structural distortion of the complex from nearly square pyramidal to nearly trigonal bipyramidal results. The trifluoromethanesulfonate anion must be considered a weak ligand, and its coordinating ability appears to be intermediate between that of the perchlorate and nitrate anions. In solution these Cu(II) complexes appear more regular because the bulky trifluoromethanesulfonate ions are displaced by solvent molecules. The EPR spectra from frozen solutions are typical for nearly tetragonal symmetry, in accordance with the finding that in solution the symmetry of the ligand field is higher than the ligand geometry.⁴³ The optical spectra, though in general not especially good indicators of geometry for copper(II) complexes, seem more sensitive to small differences in the coordination environment. Appreciable distortions from tet-

ragonal geometry, comparable with those occurring in the solid state, are evidenced by the EPR spectra from frozen solutions when chloride or bromide ions coordinate to the copper(II)-tapp and -tipp complexes. Rather drastic changes, in these cases, are also observed in the optical spectra.

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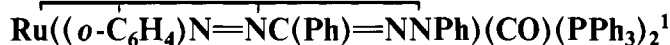
Registry No. tipp, 77136-33-5; tapp, 77136-34-6; tid, 77136-35-7; [Cu(tipp)][ClO₄], 77136-46-0; [Cu(tapp)][ClO₄], 77152-65-9; [Cu(tid)][ClO₄], 77136-48-2; [Cu(tipp)][ClO₄]₂, 77136-50-6; [Cu(tapp)][ClO₄]₂, 77136-52-8; [Cu(tipp)(OSO₂CF₃)] [OSO₂CF₃], 77136-54-0; [Cu(tipp)(ONO₂)] [NO₃], 77136-56-2; [Cu(tapp)(ONO₂)] [NO₃], 77136-58-4; [Cu(tapp)(OSO₂CF₃)] [OSO₂CF₃], 77152-67-1; [Cu(MeCN)₄][ClO₄], 14057-91-1; 2-thiophenecarboxaldehyde, 98-03-3; *N,N'*-bis(3-aminopropyl)piperazine, 7209-38-3; 1,10-decanediamine, 646-25-3.

Supplementary Material Available: A listing of structure amplitudes (Table III) (8 pages). Ordering information is given on any current masthead page.

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Cyclometalated Formazan Derivatives of Ruthenium and Osmium: Structure of



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1,5-Diphenylformazans, $\text{PhN}=\text{NC}(\text{R})=\text{NNHPh}$ ($\text{R} = \text{H, Me, or Ph}$), react with the complexes $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$, $\text{RuH}_2(\text{CO})(\text{AsPh}_3)_3$, $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$, $\text{Os}(\text{O}_2\text{CCF}_3)_2(\text{CO})(\text{PPh}_3)_2$, and $\text{OsH}(\text{O}_2\text{CCF}_3)(\text{CO})(\text{PPh}_3)_2$ in boiling 2-methoxyethanol or dimethylformamide over a period of 30 min to 4 h to afford cyclometalated formazan derivatives $\text{M}((o\text{-C}_6\text{H}_4)\text{N}=\text{NC}(\text{R})=\text{NNPh})(\text{CO})(\text{EPh}_3)_2$ ($\text{M} = \text{Ru, E} = \text{P, R} = \text{H, Me, or Ph}$; $\text{M} = \text{Ru, E} = \text{As, R} = \text{Ph}$; $\text{M} = \text{Os, E} = \text{P, R} = \text{H, Me, or Ph}$) as deep green, air-stable, crystalline solids. The initial products formed in these reactions appear to be N^1, N^5 -chelate formazan complexes which subsequently rearrange and undergo cyclometalation. Isomeric intermediates of the form $\text{Ru}(\text{PhN}=\text{NCH}=\text{NNPh})\text{H}(\text{CO})(\text{PPh}_3)_2$ have been isolated as pink (*cis*- PPh_3 ligands) or purple (*trans*- PPh_3 ligands) complexes from the reaction of $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$ with $\text{PhN}=\text{NCH}=\text{NNHPh}$ and have been shown to convert to the green cyclometalated complex $\text{Ru}((o\text{-C}_6\text{H}_4)\text{N}=\text{NCH}=\text{NNPh})(\text{CO})(\text{PPh}_3)_2$ on further heating. The structure of the green complex $\text{Ru}((o\text{-C}_6\text{H}_4)\text{N}=\text{NC}(\text{Ph})=\text{NNPh})(\text{CO})(\text{PPh}_3)_2$ has been established by an X-ray diffraction study. The complex crystallizes in space group $\text{C}_{2h}^2\text{-P2}_1/c$ ($a = 18.539$ (3) Å, $b = 25.381$ (6) Å, $c = 19.391$ (4) Å, $\beta = 97.36$ (1)° at 0 °C) with two pseudosymmetrically related molecules per asymmetric unit. The structure, described by 399 variable parameters, was refined with use of 8498 reflections having $F_o^2 > 3\sigma(F_o^2)$ to values for R and R_w of 0.081 and 0.107. The compound contains six-coordinated ruthenium(II) bound to a trans pair of triphenylphosphine ligands (average $\text{Ru-P} = 2.384$ (5) Å), a carbonyl group (average $\text{Ru-C} = 1.83$ (1) Å, $\text{C-O} = 1.17$ (1) Å), and a planar, tridentate, cyclometalated formazan ligand coordinated through nitrogen atoms N^1 ($\text{Ru-N} = 2.163$ (7) Å) and N^4 ($\text{Ru-N} = 2.02$ (1) Å) and the ortho carbon atom of the phenyl ring on the N^5 nitrogen atom ($\text{Ru-C} = 2.091$ (9) Å). The bond lengths found for the formazan skeleton are consistent with extensive electron delocalization throughout the chelate rings and the adjoining phenyl groups.

Introduction

Formazan, $\text{NH}^1=\text{N}^2\text{CH}^3=\text{N}^4\text{N}^5\text{H}_2$, is the hypothetical parent member of a series of 1,5- or 1,3,5-substituted formazans ($\text{ArN}=\text{NCR}=\text{NNHAr}$, where $\text{Ar} = \text{aryl and R} = \text{H, alkyl, or aryl}$), the first examples of which were synthesized in 1892 by Bamberger³ and von Pechmann.⁴ Subsequent

workers have introduced a wide variety of functional groups onto the 1-, 3-, and 5-substituents to generate a diverse range of formazans,^{5,6} which have found important applications as colorimetric agents,⁷ metal extractants,⁸ pigments,⁹⁻¹¹ and

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