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Synthesis and Spectroscopic Characterization of Copper(I) and Copper(II) Complexes with 1,6-Bis(2-benzimidazolyl)-2,5-dithiahexane (BBDH). X-ray Structure of Trigonal-Bipyramidal [Cu(BBDH)Cl]Cl·$2C_2H_5OH$

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Stable Cu^{I} and Cu^{II} complexes with the novel ligand 1,6-bis(2-benzimidazolyl)-2,5-dithiahexane [BBDH, $(C_7H_5N_2{-}CH_2{-}S{-}CH_2{-})_2$] have been prepared. The bulky nature of the ligand prevents planar four-coordination of Cu^{II}. The X-ray structure of [Cu(BBDH)Cl]Cl·$2C_2H_5OH$ shows that Cu^{II} is in a distorted trigonal-bipyramidal coordination geometry consisting of two axial benzimidazole N atoms and two thioether S atoms and a Cl$^-$ ion as equatorial ligands. The compound crystallizes in the monoclinic space group $P2_1/c$ with $a = 14.930$ (3) Å, $b = 17.109$ (4) Å, $c = 10.774$ (2) Å, $\beta = 97.23$ (2)°, $V = 2730$ Å^3, $d_{\text{measd}} = 1.43$ (1) g cm^{-3}, and $d_{\text{calcd}} = 1.414$ g cm^{-3} for $Z = 4$. The structure was solved by direct methods and refined with use of full-matrix least-squares techniques. The residual R value was 0.071 for 3023 independent reflections $\{I > 1.96[\sigma(I)]\}$ whose intensities were measured on an automatic diffractometer. The ESR and ligand field spectra of solid Cu^{II} BBDH compounds are consistent with a trigonal-bipyramidal coordination geometry. The spectroscopic data of solutions indicate a change in coordination geometry compared to that in the solid state. The NMR spectra of Cu^{I} BBDH compounds suggest binding of benzimidazole N atoms to the metal.

Introduction

The chemistry of Cu^{II} displays a variety of coordination numbers and geometries. Octahedral six-coordinated, square-pyramidal or trigonal-bipyramidal five-coordinated, and tetrahedral or square-planar four-coordinated Cu^{II} compounds are known.[2] Moreover compounds with Cu^{II} in many kinds of intermediate or distorted ligand geometries have been described.[2] The symmetry of the coordination polyhedron around Cu^{II} appears to be determined by subtle factors. Less than most other first-row transition-metal ions does the Cu^{II} ion require a particular ligand arrangement of high symmetry. The shape of the coordination polyhedron around Cu^{II} is determined to a much greater extent by ligand constraints, steric hindrance, or the donor properties of the ligand.[2–4] The ESR and visible spectroscopic properties of Cu^{II} compounds are strongly dependent on the kind, number, and symmetry of ligand atoms.[2] The redox properties of Cu^{II} compounds are determined by the same factors. Strong electron donors stabilize high oxidation states (e.g., Cu^{III} in complexes with deprotonated biuret[3]), whereas π-acceptor ligands may favor Cu^{I} (e.g., CN$^-$ and 1,10-phenanthroline).[4] Ligands that are so bulky that only low coordination numbers are possible are likely to stabilize Cu^{I} as well (e.g., 2,9-dimethyl-1,10-phenanthroline or neocuproine[4]).

Nature skillfully employs the fact that the redox potential of Cu can be tuned by the ligand system. In a wide scale of enzymes copper is found at the active site,[5] where it performs different tasks as a redox center catalyzing specific oxidations and/or reductions (e.g., in galactose oxidase), transferring electrons (e.g., in plastocyanin) or binding and transporting substrates (e.g., in hemocyanin).[5,6]

In order to gain a clearer insight into the influence of bulky chelating ligands on the coordination geometries and physical properties of Cu compounds, we are developing a series of such ligands with biologically relevant donor atoms.[7] This paper describes the reactivity of 1,6-bis(2-benzimidazolyl)-2,5-dithiahexane (BBDH; see Figure 1) toward Cu. This potentially tetradentate ligand contains two imidazole nitrogen donor atoms, sterically hindered by the fact that they are part of bulky benzimidazole groups. Imidazole groups are known to occur as ligands in Cu enzymes (e.g., in plastocyanin[8] and superoxide dismutase[9]). The other two donor atoms in BBDH are thioether sulfur atoms. A methionine thioether sulfur atom is weakly bonded to Cu^{II} in at least two Cu enzymes, plastocyanin[8a] and azurin.[8b]

A preliminary communication about the synthesis of the ligand and a few of its copper compounds has been published.[10]

Experimental Section

Preparations. 3,6-Dithiaoctanedioic acid was synthesized according to a published method.[11] All other reagents and solvents were of commercially available reagent grade quality.

1,6-Bis(2-benzimidazolyl)-2,5-dithiahexane, $(C_7H_5N_2{-}CH_2{-}S{-}CH_2{-})_2$ (BBDH). This ligand was prepared by means of a Phillips condensation reaction.[12] A 21.0-g (0.1-mol) quantity of 3,6-dithiaoctanedioic acid and 21.4 g of 1,2-diaminobenzene were refluxed in 500 mL of a 4 N aqueous HCl solution for 24 h. The solution was filtered, and after it cooled, white crystals of BBDH·2HCl precipitated (for NMR data see Table IV). BBDH·2HCl was dissolved in water, and the free base precipitated after addition of a concentrated aqueous NH_4OH solution. The crude product was purified by treatment with decolorizing charcoal in boiling ethanol solution and was precipitated by slow addition of water. The white precipitate was filtered off and dried in vacuo; yield 65% (NMR data in Table IV).

Cu(BBDH)Cl_2·$2C_2H_5OH$ and Cu(BBDH)Cl_2·H_2O. $CuCl_2$·$2H_2O$ (340 mg, 2 mmol) dissolved in 10 mL of absolute ethanol was added

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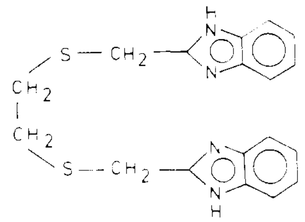

Figure 1. The 1,6-bis(2-benzimidazolyl)-2,5-dithiahexane ligand (BBDH).

to a boiling solution of 710 mg (2 mmol) of BBDH in 60 mL of the same solvent. The green solution was filtered at room temperature. Green crystals were obtained in the solution after cooling for several days at −20 °C. X-ray analysis proved that the composition of the crystals was $Cu(BBDH)Cl_2 \cdot 2C_2H_5OH$ (see below). The crystals rapidly deteriorated when isolated from the mother liquor due to loss of ethanol of crystallization. A powdered sample, which was dried at and stored at ambient laboratory conditions, was analyzed as $Cu(BBDH)Cl_2 \cdot H_2O$. Anal. Calcd for $CuC_{18}H_{20}N_4S_2OCl_2$: Cu, 12.53; C, 42.65; H, 3.98; N, 11.05; S, 12.65. Found: Cu, 12.5; C, 41.9; H, 4.1; N, 10.9; S, 12.4.

$Cu(BBDH)Br_2 \cdot H_2O$. A procedure analogous to the preparation of $Cu(BBDH)Cl_2 \cdot H_2O$ was used (see above). Anal. Calcd for $CuC_{18}H_{20}N_4S_2OBr_2$: Cu, 10.66; C, 36.28; H, 3.38; N, 9.40; S, 10.76. Found: Cu, 10.0; C, 36.7; H, 4.1; N, 9.2; S, 9.8.

$Cu(BBDH)(ClO_4)_2 \cdot H_2O$. This compound was prepared according to the same method as used for the preparation of the chloride (see above) starting with 2 mmol of $Cu(ClO_4)_2 \cdot 6H_2O$ and 2 mmol of BBDH in 60 mL of absolute ethanol. Anal. Calcd for $CuC_{18}H_{20}N_4S_2O_9Cl_2$: Cu, 10.01; C, 34.0; H, 3.17; N, 8.82; S, 10.10. Found: Cu, 9.7; C, 34.6; H, 3.4; N, 8.9; S, 10.0.

$Cu(BBDH)(BF_4)_2 \cdot H_2O$. The preparation of this compound is analogous to that of the perchlorate salt (see above). Anal. Calcd for $CuC_{18}H_{20}N_4S_2OB_2F_8$: Cu, 10.42; C, 35.46; H, 3.31; N, 9.19; S, 10.52. Found: Cu, 10.4; C, 35.4; H, 3.5; N, 9.2; S, 10.6.

$Cu^I(BBDH)ClO_4$. Method 1. A solution of 370 mg (1 mmol) of $Cu(ClO_4)_2 \cdot 6H_2O$ in 25 mL of acetonitrile was reduced with Cu powder under nitrogen until the solution was colorless. Excess Cu powder was removed by filtration. The filtrate was added to a solution of 710 mg of BBDH in 20 mL of $(CH_3)_2SO$. All manipulations were carried out under nitrogen. Dioxygen-free water was added until the white compound precipitated (about 150 mL). After 1 h the precipitate was filtered off and dried in vacuo. The dry compound is stable in air. Anal. Calcd for $CuC_{18}H_{18}S_2N_4ClO_4$: Cu, 12.3; C, 41.8; H, 3.51; N, 10.83; S, 12.4. Found: Cu, 11.6; C, 42.1; H, 3.7; N, 10.8; S, 12.9.

Method 2. $Cu(BBDH)ClO_4$ could also be prepared by the direct reaction of 750 mg of BBDH, 370 mg of $Cu(ClO_4)_2 \cdot 6H_2O$, and excess Cu powder in 100 mL of ethanol under stirring. The solution turned from green to colorless in about 10 min. The solution was filtered and cooled under nitrogen. The white precipitate was filtered off and washed with cold ethanol. It was identified by its infrared spectrum being identical with that of the compound prepared according to method 1.

$Cu(BBDH)BF_4$. This compound was prepared as described for $Cu(BBDH)ClO_4$ (method 1). Anal. Calcd for $CuC_{18}H_{18}S_2N_4BF_4$: C, 42.83; H, 3.59; N, 11.10; S, 12.70. Found: C, 42.7; H, 3.7; N, 11.4; S, 13.1.

$Cu(BBDH)NO_3$. This compound was prepared as described for $Cu(BBDH)ClO_4$ (method 2). Anal. Calcd for $CuC_{18}H_{18}S_2N_5O_3$: C, 45.04; H, 3.78; N, 14.60; S, 13.36. Found: C, 44.4; H, 3.9; N, 14.6; S, 13.2.

$Ag(BBDH)NO_3$. A solution of 170 mg (1 mmol) of $AgNO_3$ in 10 mL of water was added dropwise to a solution of 350 mg of BBDH in 15 mL of $(CH_3)_2SO$. Then water was added until the compound precipitated (about 10 mL). After 1 h the precipitate was filtered off and dried in vacuo. The compound was identified by its infrared spectrum being identical with that of the analogous Cu^I compound and further characterized by its NMR spectrum (see Table IV).

$Zn(BBDH)Cl_2 \cdot C_2H_5OH$. The preparation of this compound is analogous to the preparation of $Cu(BBDH)Cl_2 \cdot H_2O$. The product was characterized by its NMR spectrum (see Table IV).

Physical Measurements. Infrared spectra were measured on a Perkin-Elmer 580 spectrometer in KBr pellets and in Nujol mulls (4000–250 cm^{-1}). The visible spectra were recorded in solution on a Beckman DK-2A spectrophotometer or as solid powders on a similar instrument equipped with a diffuse reflectance unit. ESR spectra were measured with use of a Varian E3 X-band and a Varian V4500 Q-band spectrometer (the magnetic field was calibrated with use of an AEG proton NMR apparatus; the frequency was calibrated with use of DPPH as reference). NMR spectra were measured at 100 MHz on a JEOL PS100 spectrometer. For conductivity measurements a Philips PR9500 conductivity bridge and a Philips PR9510 cell were used. Metal analyses were carried out with use of standard EDTA titration techniques. Other elemental analyses were done by Dr. Pascher, Bonn, F.R.G.

X-ray Data Collection and Solution of the Structure. An irregularly shaped crystal of $Cu(BBDH)Cl_2 \cdot 2C_2H_5OH$ approximately 0.5 mm long in all directions was picked out of the solution and immediately sealed in a thin-walled glass capillary tube together with a small piece of filter paper soaked in the mother liquor. The systematic absences $l = 2n + 1$ for $h0l$ and $k = 2n + 1$ for $0k0$ on Weissenberg photographs indicated the space group $P2_1/c$. Intensity measurements were carried out on a Syntex $P2_1$ four-circle diffractometer using graphite-monochromated Mo Kα radiation [$\lambda(\alpha_1) = 0.70926$ Å, $\lambda(\alpha_2) = 0.71354$ Å] and a scintillation counter. The unit cell dimensions determined from the angular settings of 15 high-order reflections are $a = 14.930$ (3) Å, $b = 17.109$ (4) Å, $c = 10.774$ (2) Å, $\beta = 97.23$ (2)°, and $V = 2730$ Å^3. The measured density of 1.43 (1) g cm^{-3} (flotation in $C_2H_5OH/CHCl_3$) agreed with the calculated value of 1.414 g cm^{-3} for $Z = 4$. The intensities of 5990 reflections were measured ($\theta < 27°$; $(\sin \theta)/\lambda < 0.64$ Å^{-1}). The 3023 reflections with $I > 1.96[\sigma(I)]$ were considered as observed and used in all calculations. The reflections were scanned in the 2θ–θ mode. Variable scan speeds (4–30° min^{-1} in 2θ) were used, which depended on the intensities of the reflections. Stationary background measurements at both ends of the scans were done so that the total time spent measuring backgrounds equaled the scan time. An intensity control reflection was measured after every 100 reflections. There was 8% decomposition for which the data were corrected. Lorentz and polarization corrections were applied in the usual way. Due to its irregular shape the crystal was difficult to define and analytical absorption corrections were not very possible. The data were therefore corrected for the small absorption effects [μ(Mo Kα) = 12.0 cm^{-1}] by using an empirical method based on the measurement of the intensity of a suitable reflection in different azimuthal orientations. Atomic scattering factors for neutral atoms were taken from ref 13 with corrections for real and imaginary anomalous dispersion. The structure was solved with use of the MULTAN direct-methods package and refined with full-matrix least-squares techniques.[14] The function minimized was $\sum w(|F_o| - k|F_c|)^2$ with $w = \{[\sigma(F)]^2 + (0.01|F_o|)^2\}^{-1}$ and $\sigma(F) = \sigma(I)/(2|F_o|(Lp))$, Lp being the Lorentz and polarization correction factor. All nonhydrogen atoms could be located in a series of refinements followed by difference Fourier syntheses. The hydrogen atoms were placed at their calculated positions with fixed isotropic temperature factors ($B = 5.0$ Å^2, C–H = 0.95 Å, N–H = 0.87 Å[15]). The structure contains two disordered ethanol molecules, which were isotropically refined in distinct adjacent partially occupied positions (see Description of the Structure). Anisotropic refinement of all other atoms resulted in a residual R value $\sum||F_o| - k|F_c|| / \sum|F_o| = 0.071$; the weighted R value was $[\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2} = 0.053$. A final difference Fourier synthesis showed no residual densities above 0.5 e Å^{-3}. The atomic parameters of nonhydrogen atoms are listed in Table I. A list of positions of hydrogen atoms and a table of observed and calculated structure factors is available as supplementary material.

Description of the Structure and Comparison with Related Structures

The solid-state structure of $[Cu(BBDH)Cl]Cl \cdot 2C_2H_5OH$ consists of discrete $[Cu(BBDH)Cl]^+$ ions, a Cl^- counterion, and two disordered ethanol molecules. The $[Cu(BBDH)Cl]^+$

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(13) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 71–102.

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Table I. Fractional Positional, Thermal,[a] and Occupancy[b] Parameters for $[Cu(BBDH)Cl]Cl \cdot 2C_2H_5OH$[c]

Atom	10^4x	10^4y	10^4z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	7658(1)	3346(1)	3806(1)	2.66(4)	3.41(4)	3.89(4)	0.03(4)	0.64(3)	-0.64(4)
S(1)	7055(1)	3539(1)	5780(2)	3.5(1)	4.2(1)	3.2(1)	0.6(1)	0.5(1)	0.3(1)
S(2)	6404(1)	4204(1)	2682(2)	4.0(1)	4.1(1)	3.3(1)	0.4(1)	0.6(1)	0.4(1)
Cl(1)	8725(1)	2692(1)	2946(2)	4.6(1)	5.0(1)	10.9(2)	0.4(1)	3.9(1)	-1.9(1)
Cl(2)	3668(1)	3831(1)	3621(2)	4.3(1)	7.4(1)	6.8(1)	0.4(1)	0.4(1)	-1.0(1)
N(1)	8689(4)	5356(4)	5423(7)	3.4(3)	4.5(4)	6.3(4)	0.5(3)	-0.8(3)	-1.3(3)
N(2)	8336(4)	4303(3)	4292(5)	3.0(3)	3.1(3)	4.3(3)	-0.3(2)	0.3(3)	-0.4(3)
N(3)	6730(4)	2531(3)	3453(5)	2.9(3)	3.3(3)	3.8(3)	-0.3(2)	0.3(2)	-1.1(3)
N(4)	5408(4)	2019(4)	2746(5)	2.9(3)	5.5(4)	3.7(3)	-1.0(3)	0.3(2)	-1.1(3)
C(1)	9086(5)	5459(5)	4355(9)	3.1(4)	2.8(4)	7.6(6)	0.9(3)	-1.0(4)	0.4(4)
C(2)	8864(5)	4785(5)	3637(8)	2.5(3)	3.7(4)	5.7(5)	0.6(3)	-0.1(3)	0.5(4)
C(3)	9146(5)	4700(5)	2458(8)	3.2(4)	5.6(5)	5.8(5)	-0.0(4)	-0.2(4)	0.8(4)
C(4)	9643(6)	5314(7)	2043(9)	4.6(5)	6.7(6)	8.0(6)	-0.2(5)	0.6(4)	3.6(5)
C(5)	9865(6)	5971(7)	2766(14)	3.5(5)	5.6(7)	14(1)	-0.7(4)	0.6(6)	4.8(7)
C(6)	9592(6)	6059(5)	3916(11)	3.9(5)	3.2(5)	11.9(8)	-0.1(4)	-0.6(5)	1.0(5)
C(7)	8246(5)	4670(4)	5348(7)	3.0(4)	3.1(4)	5.1(4)	0.3(3)	-0.5(3)	-1.2(3)
C(8)	7727(5)	4365(4)	6337(7)	3.3(4)	6.4(5)	4.1(4)	0.5(4)	0.4(3)	-2.0(4)
C(9)	5986(4)	3982(4)	5169(6)	3.0(3)	5.2(4)	3.3(3)	0.6(3)	0.4(3)	-0.1(3)
C(10)	5984(5)	4545(4)	4086(6)	4.1(4)	4.2(4)	3.6(4)	1.5(3)	0.2(3)	0.2(3)
C(11)	5652(4)	3415(5)	2173(6)	3.3(3)	5.0(4)	3.6(3)	0.3(3)	0.2(3)	-0.5(3)
C(12)	5934(5)	2666(5)	2793(6)	3.2(4)	4.3(4)	3.1(4)	-0.3(3)	0.9(3)	-1.3(3)
C(13)	5887(5)	1445(5)	3406(6)	4.7(4)	4.4(5)	2.9(3)	-0.2(4)	0.9(3)	-0.7(3)
C(14)	5683(6)	661(6)	3638(6)	6.8(6)	4.8(5)	4.8(5)	-2.0(4)	1.2(4)	-0.9(4)
C(15)	6325(8)	223(5)	4306(9)	10.3(8)	3.4(5)	5.8(5)	-1.9(5)	1.8(5)	0.1(4)
C(16)	7165(7)	550(5)	4789(7)	7.6(6)	4.0(5)	4.7(4)	0.4(4)	0.9(4)	0.8(4)
C(17)	7375(5)	1331(5)	4571(7)	5.2(4)	4.1(4)	4.2(4)	-0.6(4)	0.2(4)	-0.5(3)
C(18)	6725(5)	1764(4)	3854(6)	3.6(4)	3.3(4)	3.3(3)	0.0(3)	0.8(3)	-0.9(3)

Ethanol molecules:

Atom	Occupancy	10^4x	10^4y	10^4z	B_{iso}
C(A1)	1.00	2957(9)	1566(8)	3122(13)	12.0(4)
C(A2I)	0.50	2936(15)	1654(15)	1735(22)	5.4(5)
C(A2II)	0.25	2882(26)	1347(22)	2300(43)	5.6(9)
C(A2III)	0.25	2989(28)	1990(24)	1618(38)	5.2(11)
O(AI)	0.50	3820(8)	1527(7)	1515(11)	4.4(3)
O(AII)	0.50	3840(10)	1817(9)	1119(13)	7.5(4)
C(B1I)	0.50	9250(16)	6701(14)	9330(21)	9.0(6)
C(B1II)	0.50	8547(16)	6383(13)	9086(21)	9.2(6)
C(B2)	1.00	8948(13)	6806(10)	8165(17)	16.8(5)
O(BI)	0.50	8321(10)	6170(9)	7631(14)	8.6(4)
O(BII)	0.50	8402(9)	6510(9)	6960(13)	8.4(4)

[a] Temperature factors are of the form $\exp[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$ and $\exp[-B_{iso}(\sin^2\theta)/\lambda^2]$. [b] All atom positions are fully occupied unless indicated otherwise. [c] Estimated standard deviations in parentheses.

ion has no crystallographic symmetry. The Cu^{II} atom in the structure is in a distorted trigonal-bipyramidal coordination geometry (see Figure 2). The axial positions are occupied by nitrogen donor atoms of two benzimidazole groups; two thioether sulfur atoms and a chloride ion are the ligands in the equatorial plane. Relevant interatomic distances and angles are presented in Table II; the atomic numbering is shown in Figure 2.

The most obvious deviations from ideal trigonal-bipyramidal coordination geometry are the N(2)–Cu–N(3) angle of 165.9 (2)° (ideally 180°) and the S(1)–Cu–S(2) angle of 90.39 (6)° (ideally 120°). The latter is a consequence of the presence of an ethylene bridge between the two S atoms. The S–Cu–S

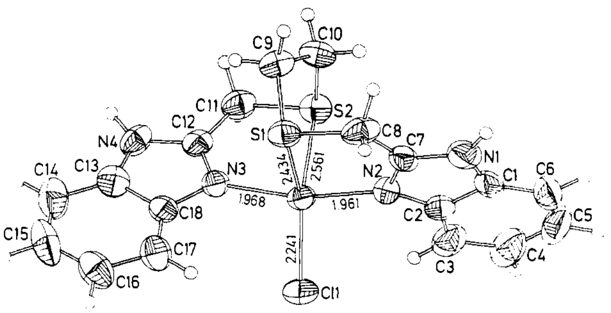

Figure 2. Structure of the $[Cu(BBDH)Cl]^+$ ion, showing the atomic numbering and the anisotropic thermal motion of the atoms.

Table II. Interatomic Distances (Å) and Angles (deg) in [Cu(BBDH)Cl]Cl·$2C_2H_5OH$[a]

The $[Cu(BBDH)Cl]^+$ ion:

Atoms	Distance	Atoms	Distance	Atoms	Distance
Cu-N(2)	1.961(6)	N(4)-C(12)	1.36(1)	C(9)-C(10)	1.51(1)
Cu-N(3)	1.968(6)	N(4)-C(13)	1.36(1)	C(10)-S(2)	1.807(7)
Cu-Cl(1)	2.241(2)	C(1)-C(2)	1.41(1)	S(2)-C(11)	1.798(8)
Cu-S(1)	2.434(2)	C(2)-C(3)	1.40(1)	C(11)-C(12)	1.48(1)
Cu-S(2)	2.561(2)	C(3)-C(4)	1.39(1)	C(13)-C(14)	1.41(1)
N(1)-C(1)	1.37(1)	C(4)-C(5)	1.38(2)	C(14)-C(15)	1.35(1)
N(1)-C(7)	1.35(1)	C(5)-C(6)	1.36(2)	C(15)-C(16)	1.41(2)
N(2)-C(2)	1.40(1)	C(6)-C(1)	1.39(1)	C(16)-C(17)	1.40(1)
N(2)-C(7)	1.32(1)	C(7)-C(8)	1.49(1)	C(17)-C(18)	1.38(1)
N(3)-C(12)	1.33(1)	C(8)-S(1)	1.793(8)	C(18)-C(13)	1.40(1)
N(3)-C(18)	1.38(1)	S(1)-C(9)	1.813(7)		

Atoms	Angle	Atoms	Angle
S(1)-Cu-S(2)	90.39(6)	N(2)-C(2)-C(1)	108.4(7)
S(1)-Cu-Cl(1)	142.18(8)	N(2)-C(2)-C(3)	130.9(7)
S(1)-Cu-N(2)	83.6(2)	C(1)-C(2)-C(3)	120.7(7)
S(1)-Cu-N(3)	86.4(2)	C(2)-C(3)-C(4)	116.6(8)
S(2)-Cu-Cl(1)	127.29(8)	C(3)-C(4)-C(5)	122.2(9)
S(2)-Cu-N(2)	88.2(2)	C(4)-C(5)-C(6)	121(1)
S(2)-Cu-N(3)	82.0(2)	C(1)-C(6)-C(5)	117.8(9)
N(2)-Cu-N(3)	165.9(2)	N(1)-C(7)-N(2)	111.3(6)
N(2)-Cu-Cl(1)	99.0(2)	N(1)-C(7)-C(8)	124.0(7)
N(3)-Cu-Cl(1)	95.0(2)	N(2)-C(7)-C(8)	124.7(7)
Cu-S(1)-C(8)	98.4(3)	C(7)-C(8)-S(1)	110.9(5)
Cu-S(1)-C(9)	98.4(2)	S(1)-C(9)-C(10)	117.6(5)
C(8)-S(1)-C(9)	102.8(3)	S(2)-C(10)-C(9)	118.3(5)
Cu-S(2)-C(10)	95.7(2)	S(2)-C(11)-C(12)	112.4(5)
Cu-S(2)-C(11)	96.0(2)	N(3)-C(12)-C(11)	125.3(6)
C(10)-S(2)-C(11)	103.2(3)	N(4)-C(12)-C(11)	124.0(6)
C(1)-N(1)-C(7)	108.8(7)	N(3)-C(12)-N(4)	110.7(6)
Cu-N(2)-C(2)	131.7(5)	N(4)-C(13)-C(14)	132.1(7)
Cu-N(2)-C(7)	121.4(5)	N(4)-C(13)-C(18)	106.7(6)
C(2)-N(2)-C(7)	106.3(6)	C(14)-C(13)-C(18)	121.2(7)
Cu-N(3)-C(12)	122.8(5)	C(13)-C(14)-C(15)	118.0(8)
Cu-N(3)-C(18)	130.0(5)	C(14)-C(15)-C(16)	120.9(9)
C(12)-N(3)-C818)	107.1(6)	C(15)-C(16)-C(17)	121.6(8)
C(12)-N(4)-C(13)	107.9(6)	C(16)-C(17)-C(18)	116.8(7)
N(1)-C(1)-C(2)	105.1(7)	C(17)-C(18)-C(13)	121.4(7)
N(1)-C(1)-C(6)	133.7(8)	N(3)-C(18)-C(13)	107.7(6)
C(2)-C(1)-C(6)	121.2(8)	N(3)-C(18)-C(17)	130.9(7)

[a] The dimensions of the ethanol molecules are shown in Figure 2. Estimated standard deviations are in parentheses.

angle in a square-pyramidal Cu^{II} compound of 1,8-diamino-3,6-dithiaoctane ($H_2N(CH_2)_2S(CH_2)_2S(CH_2)_2NH_2$) is 86.3 (1)°.[16] A wide range of Cu^{II}–S(thioether) bond lengths has been reported in the literature. The Cu^{II}–S bond length appears to be strongly dependent on the position (axial or equatorial) of the S atom in trigonal-bipyramidal, square-pyramidal or elongated octahedral coordination geometry. In the latter two symmetries the $d_{x^2-y^2}$ orbital is half-filled and the *equatorial* bonds tend to be shorter than the analogous axial bonds.

In the square-pyramidal Cu^{II} compound (1,8-diamino-3,6-dithiaoctane)(1-methylimidazole)copper(II) perchlorate[16] the equatorial Cu^{II}–S bond is 2.414 (2) Å, whereas the axial Cu^{II}–S bond is 2.560 (2) Å long. In (1,11-diamino-3,6,9-trithiaundecane)copper(II) bromide the Cu^{II} atom is in a distorted octahedral coordination geometry.[17] In this compound the equatorial and axial Cu^{II}–S bond lengths are 2.349 (6) and 2.576 (9) Å, respectively. The equatorial bond lengths in $Cu(H_3CS(CH_2)_2SCH_3)_2(BF_4)_2$[18] are 2.315 (2) and 2.319 (2) Å, and Cu^{II}–S is 2.366 (1) Å in $Cu(H_2N(CH_2)_2SCH_3)_2(ClO_4)_2$.[19]

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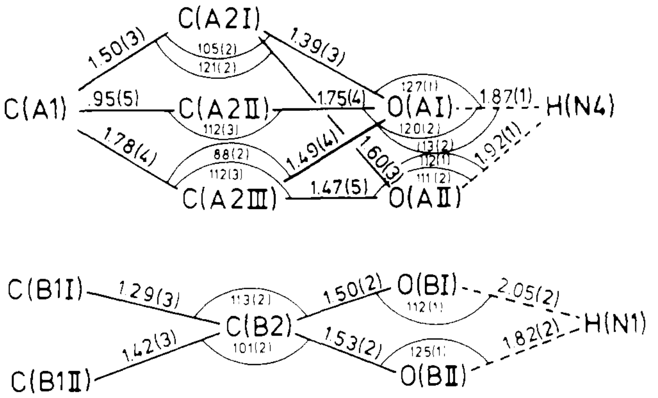

Figure 3. Molecular dimensions of the disordered ethanol molecules in the $[Cu(BBDH)Cl]Cl{\cdot}2C_2H_5OH$.

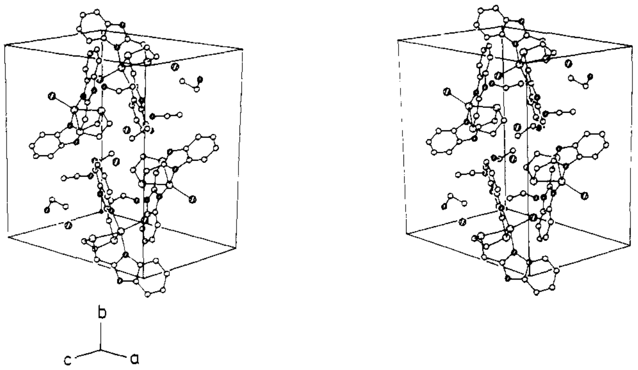

Figure 4. Stereodrawing of the unit cell of $[Cu(BBDH)Cl]Cl{\cdot}2C_2H_5OH$. Only one orientation of the disordered ethanol molecules is shown.

In trigonal-bipyramidal coordination geometry the Cu d_{z^2} orbital is half-filled and the *axial* bonds tend to be slightly shorter than analogous equatorial bonds.[20] In [(2-pyridylmethyl)bis(2-(ethylthio)ethyl)amine]copper(II) sulfate[21] the Cu^{II} atom is in a trigonal-bipyramidal coordination geometry. The two equatorial Cu^{II}–S bonds are 2.385 (1) and 2.461 (2) Å long. The Cu^{II}–S bond lengths of 2.434 (2) and 2.561 (2) Å in the present compound are slightly longer, possibly as a result of the strong Cu–N(benzimidazole) binding or the bulky character of the ligand. We are not aware of any compounds of Cu^{II} in trigonal-bipyramidal geometry with axially coordinated thioether S atoms.

The Cu–N(benzimidazole) bond lengths of 1.961 (6) and 1.968 (6) Å in the present compound are in the usual range.[7a,b]

The equatorial Cu–Cl bond length of 2.241 (2) Å in the $[Cu(BBDH)Cl]^+$ ion is slightly shorter than the equatorial Cu–Cl bond lengths in trigonal-bipyramidal $[Cu(bpy)_2Cl]X{\cdot}nH_2O$, where Cu–Cl = 2.292 (4) Å for X = $S_5O_6^-$ and n = 3,[22] Cu–Cl = 2.356 Å for X = $CuCl_2^-$ and n = 0,[23] and Cu–Cl = 2.361 (4) Å for X = Cl and n = 6.[24]

The disordered ethanol molecules in the structure are described with a split-atom model. The bond lengths between atoms in the partially occupied positions are shown in Figure 3. Occupancies and thermal parameters are listed in Table I.

Table III. Hydrogen Bonds in $[Cu(BBDH)Cl]Cl{\cdot}2C_2H_5OH$[a] (Distances in Å, Angles in Deg; Standard Deviations in Parentheses[b]

N(1)···O(BI)	2.87 (2)	N(4)···O(AI)	2.70 (1)
H(N1)···O(BI)	2.05 (2)	H(N4)···O(AI)	1.87 (1)
N(1)···O(BII)	2.65 (2)	N(4)···O(AII)	2.76 (2)
H(N1)···O(BII)	1.82 (1)	H(N4)···O(AII)	1.92 (1)
Cl(2)···O(AI′)	3.16 (1)	Cl(2)···O(BII″)	3.13 (1)
Cl(2)···O(BI″)	3.10 (1)	Cl(2)···O(AII″)	2.89 (1)
N(1)–H(N1)···O(BI)	155.6 (6)	N(4)–H(N4)···O(AI)	160.0 (6)
N(1)–H(N1)···O(BII)	157.5 (6)	N(4)–H(N4)···O(AII)	163.6 (6)

[a] Hydrogen atoms are labeled with the names of the atoms to which they are bonded. Superscripts indicate the following symmetry operations: none = x, y, z; ′ = $x, \frac{1}{2} - y, \frac{1}{2} + z$; ″ = $1 - x, 1 - y, 1 - z$. [b] The estimated standard deviations for the hydrogen bond lengths are based on those of the positional parameters of the nonhydrogen atoms.

A stereodrawing of the unit cell contents is shown in Figure 4.

The structure is stabilized by hydrogen bonds between N–H groups of the $[Cu(BBDH)Cl]^+$ ions and oxygen atoms of ethanol molecules (see Figure 3 and Table III), and between the separate Cl^- counterion and the O–H groups of the ethanol molecules (see Table II). As all hydrogen bonds involve ethanol molecules, it is not surprising that loss of ethanol of crystallization leads to complete deterioration of the crystals.

Spectroscopic Properties

NMR Spectra. The Cu^I BBDH compounds are diamagnetic. In $(CH_3)_2SO$ solution they do not react readily with dioxygen and they could be studied by NMR spectroscopy without special precautions. The NMR spectral data are presented in Table IV together with those of the free ligand and of diamagnetic Ag^I and Zn^{II} compounds for comparison. A $Cu^I(BBDH)ClO_4$ solution was kept in an open NMR tube for 24 h and then remeasured. The solution had changed from colorless to pale green (much paler than a $Cu^{II}(BBDH)(ClO_4)_2$ solution of the same concentration). The spectrum showed only a decrease in intensity, but there were no appreciable changes in δ values or line width. This suggests that there is no fast exchange of Cu between $Cu^I(BBDH)^+$ and Cu^{II} compounds in the solution on the NMR time scale.

The presence of well-resolved N–H resonances in the NMR spectra of the Cu^I and Ag^I compounds indicates Cu(Ag)–N binding,[25] preventing fast exchange of protons between both N atoms of a single benzimidazole group. Although the NMR parameters of the Zn^{II} compound are quite similar to those of the Cu^I and Ag^I compounds, its coordination geometry must be quite different (see Table IV). The conductivity of the Zn^{II} BBDH complex (Table V) shows that the chloride ions in this compound are bonded to the Zn atom. Coordination of Zn^{II} by two benzimidazole N atoms and two Cl^- ions with possibly additional semicoordination by the two thioether S atoms seems likely.

ESR and Ligand Field Spectra and Conductivity. The physical properties of all solid Cu^{II} BBDH compounds are all entirely consistent with trigonal-bipyramidal coordination of the ligand atoms around the metal. Cu^{II} compounds of this geometry often show either one absorption band with a shoulder on the high-energy slope of the band or two separate bands, the low-intensity band being found at higher frequency

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(25) We recently solved the crystal structure of a Cu^I compound of a related ligand with a trimethylene group present between the two thioether S atoms, rather than an ethylene group. The Cu^I atom in this compound is essentially linearly coordinated by two imidazole N atoms (Cu–N = 1.918 (2) Å, N–Cu–N = 168.5°): Schilstra, M. J.; Birker, P. J. M. W. L.; Verschoor, G. C.; Reedijk, J., submitted for publication in *Inorg. Chem.*

Table IV. NMR Data for the BBDH Ligand and Its Diamagnetic Coordination Compounds[a]

compd	aromatic protons	$C(1)H_2$	$C(2)H_2$	NH
BBDH·2HCl	7.82 (m, 4), 7.58 (m, 4)	4.43 (s, 4)	3.02 (s, 4)	10.28 (b, 4)
BBDH	7.51 (m, 4), 7.15 (m, 4)	3.98 (s, 4)	2.80 (s, 4)	absent
$Cu^I(BBDH)ClO_4$	7.57 (m, 4), 7.29 (m, 4)	4.35 (s, 4)	3.19 (s, 4)	13.07 (b, 2)
$Cu^I(BBDH)NO_3$	7.62 (m, 4), 7.30 (m, 4)	4.25 (s, 4)	3.08 (s, 4)	13.70 (b, 2)
$Ag^I(BBDH)NO_3$	7.78 (m, 4), 7.38 (m, 4)	4.23 (s, 4)	2.94 (s, 4)	~13.7 (b)
$Zn(BBDH)Cl_2·2C_2H_5OH$[b]	7.84 (m, 4), 7.32 (m, 4)	4.23 (s, 4)	2.63 (s, 4)	absent[c]

[a] All data in ppm vs. $Si(CH_3)_4$. All measurements were carried out on $(CD_3)_2SO$ solutions. The abbreviations b, m, s, t, and q indicate broad, multiplet, singlet, triplet, and quartet resonances, respectively. Relative intensities are also shown in parentheses. The atomic numbering is as follows: $(C_7H_5N_2-C(1)H_2-S-C(2)H_2-)_2$. [b] The ethanol resonances are found at 1.03 (t, 3) and 3.43 (q, 2) ppm. [c] The NH resonances are not observed, probably due to fast exchange with ethanol OH protons.

Table V. Spectroscopic Data and Conductivity of BBDH Compounds

	ligand field spectra[a]			ESR parameters						
compd	ν_1	ν_2		g_1	g_2	g_3	A_1-(Cu)	A_3-(N)[f]		conductivity[g]
$Cu(BBDH)Cl_2·H_2O$	14.9 (w)	11.2 (str)	$MgCO_3$[b]	2.13 ($g_\perp$), 2.02 ($g_\parallel$)					X band; powder[d]	43 (DMF)
	15.4 (390)	11.4 (260)	Me_2SO[c]	2.21	2.06	2.00	131	17	X band; glass[e]	84 (CH_3OH)
	15.4 (390)	11.4 (260)	CH_3OH[c]							
$Cu(BBDH)(ClO_4)_2·H_2O$	14.9 (w)	10.5 (str)	$MgCO_3$[b]	2.21	2.13	2.00[h]			X band; powder[d]	193 (CH_3OH)[i]
	15.1 (150)	11.4 (100)	Me_2SO[c]	2.21	2.13	2.00			Q band; powder[d]	
$Cu(BBDH)(BF_4)_2·H_2O$	14.5 (w)	10.5 (str)	$MgCO_3$[b]	2.27	2.08	2.02	138	14	X band; glass[e]	149 (CH_3OH)
	14.9 (120)	11.4 (80)	Me_2SO[c]							
$Cu(BBDH)Br_2·H_2O$	14.9 (w)	11.1 (str)	$MgCO_3$[b]	2.14	2.08	2.04			X band; powder[d]	94 (CH_3OH)
	15.1 (550)	11.3 (260)	Me_2SO[c]	2.18	2.10	2.04			Q band; powder[d]	
$Zn(BBDH)Cl_2·C_2H_5OH$										4 (DMF)

[a] All frequencies in 1000 cm^{-1}; extinction coefficients (in dm^3 mol^{-1} cm^{-1}) of solutions or relative intensities of absorption bands in reflectance spectra are given in parentheses (w = weak; str = strong). [b] Reflectance spectra measured on solid powders diluted in $MgCO_3$. [c] Measured in solution in the indicated solvent. [d] Measured at 77 K. [e] Measured in a $(CH_3)_2SO/C_2H_5OH$ glass at 77 K. [f] Cu and N hyperfine coupling constants in gauss. [g] Molar conductance in Ω^{-1} cm^2 mol^{-1}, measured in methanol or dimethylformamide (DMF) as indicated; concentration 5 × 10^{-4} mol dm^{-3}. [h] The ESR spectra of the BF_4^- and ClO_4^- derivatives are identical. [i] We observed that the molar conductance of the perchlorate salt of an anion of comparable size, $Cu(EDTB)^{2+}$,[7a] was 177 Ω^{-1} cm^2 mol^{-1} under the same conditions (20.0 °C).

than the high-intensity band. The two components of the visible absorption have been assigned to $d_{xz},d_{yz} \rightarrow d_{z^2}$ (weak) and $d_{xy},d_{x^2-y^2} \rightarrow d_{z^2}$ (strong) transitions.[2] Table V shows that the solid-state reflectance spectra of Cu^{II} BBDH compounds indeed have a strong absorption band around 11 000 cm^{-1} and a weaker band at about 15 000 cm^{-1}. Five-coordination is achieved by the four ligand donor atoms and a halogenide ion in the chloride and bromide compounds (see X-ray structure above). In the BF_4^- and ClO_4^- salts the fifth coordination position is most likely occupied by the water molecule in the structure.[26] The infrared spectra of these compounds did not show any evidence for coordination of the ClO_4^- or BF_4^- ions. In solution however the relative intensities of the visible bands at 11 000 and 15 000 cm^{-1} are reversed. This indicates that the coordination geometry is different in solution, as a result of a rearrangement of ligand atoms and/or of an increase in coordination number by binding of solvent molecules. It is known that Cu(II) compounds with a coordination geometry intermediate between square pyramidal and trigonal bipyramidal can show ESR spectra that are quite similar to the spectra of our compounds measured in frozen solutions.[27] Similar variations in structures of different stereochemistries, deduced from ligand field spectra of Cu^{II} compounds, have recently been described.[28]

The extinction coefficients of the absorption bands in the visible spectra of solutions of $Cu(BBDH)Cl_2·H_2O$ and $Cu(BBDH)Br_2·H_2O$ are considerably higher than those of the compounds with the noncoordinating ClO_4^- and BF_4^- counterions. This indicates that a halogenide ion remains in the coordination sphere of Cu in the chloride and bromide derivatives in solution. The same conclusion must be drawn from a comparison of the molar conductances, showing that the Cu BBDH halogenides behave as 1:1 electrolytes whereas the conductivities of the BF_4^- and ClO_4^- salts are more consistent with 1:2 electrolyte behavior.

The ESR spectra of Cu BBDH compounds measured on solid powders yield *g* values that obey the criteria given by Hathaway[2] (Table V) for trigonal-bipyramidal coordination (lowest $g < 2.03$; $g_\parallel < g_\perp$) or distorted trigonal-bipyramidal coordination (three *g* values; lowest $g < 2.03$). It is therefore assumed that the compounds with composition $Cu^{II}(BBDH)X_2·H_2O$ have a solid-state structure similar to that of $[Cu(BBDH)Cl]Cl·2C_2H_5OH$.[26] The fact that the values of g_1 for the chloride and the bromide compounds are relatively low is a further indication for the covalent character of the Cu–X bond.[2] The ESR spectra in frozen solution have different *g* values, which is again consistent with a change in coordination geometry. The values found for *A*(Cu) in solution are too high for trigonal-bipyramidal geometry and are in fact again close to the values for the compounds with intermediate geometry mentioned above.[27]

Concluding Remarks

The present work shows that it is possible to obtain stable Cu^I and Cu^{II} compounds with bulky chelating ligands. The steric requirements of the BBDH ligand lead to trigonal-bipyramidal coordination of Cu^{II} in the solid state. The ESR and ligand field spectra of solid Cu^{II} compounds are consistent with this coordination geometry. The spectral properties of solutions of these Cu^{II} compounds indicate a different coordination geometry, either due to additional solvation or geometrical changes. Further work will deal with analogues of

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(26) After submission of the paper we solved the crystal structure of a related compound, $[Cu^{II}(L)H_2O](ClO_4)_2·5C_2H_5OH$ (L = the analogon of BBDH with a *o*-phenylene bridge between the two S atoms), which indeed contains a coordinated water molecule. The trigonal-bipyramidal coordination consists of CuN_2S_2O, having again imidazoles as axial ligands (manuscript in preparation).

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Inorg. Chem. **1982**, *21*, 363–368

the present ligand having different steric constraints.

Registry No. Cu(BBDH)$Cl_2 \cdot 2C_2H_5OH$, 79682-06-7; Cu(BBDH)Cl_2, 76683-99-3; Cu(BBDH)Br_2, 79682-07-8; Cu(BBDH)$(ClO_4)_2 \cdot H_2O$, 76684-01-0; Cu(BBDH)$(BF_4)_2 \cdot H_2O$, 76831-39-5; Cu(BBDH)ClO_4, 76761-70-1; Cu(BBDH)BF_4, 79682-08-9; Cu(BBDH)NO_3, 79682-09-0; Ag(BBDH)NO_3, 79682-11-4; Zn(BBDH)Cl_2, 79682-12-5; BBDH, 57698-70-1; BBDH·2HCl, 79664-66-7; 3,6-dithiaoctanedioic acid, 7244-02-2; 1,2-diaminobenzene, 95-54-5.

Supplementary Material Available: A listing of observed and calculated structure factors and a table with calculated positions for hydrogen atoms (7 pages). Ordering information is given on any current masthead page.

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Electron Transfer in Authentic Triangular Copper(II) Trimers with a Cu_3X (X = O or OH) Core. The $Cu^{II}{}_2Cu^{III}$–$Cu^{II}{}_3$ and $Cu^{II}{}_3$–$Cu^{I}Cu^{II}{}_2$ Couples

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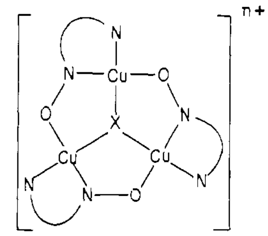
Trinuclear triangular copper(II) complexes of pyridine-2-carbaldoxime (HPL) and isonitrosoketimine ligands of type RNC(R′)C(R′)NOH (R = Et, *n*-Pr, *n*-Bu, Ph; R′ = Me, Ph) have been examined electrochemically. These strongly antiferromagnetic complexes are of types $[Cu_3O(\text{ligand})_3]^+$ and $[Cu_3OH(\text{ligand})_3]^{2+}$, having Cu_3O and Cu_3OH cores, respectively. The known structure of $[Cu_3OH(PL)_3]^{2+}$ provides an authentic reference point for data analyses. Cyclic voltammetry and constant-potential electrolysis (platinum working electrode) show that complexes with a Cu_3O core uniformly display a one-electron-transfer process characterized by the oxidation-state description $Cu^{III}Cu^{II}{}_2 + e^- \rightleftharpoons Cu^{II}{}_3$ with $E°_{298}$ in the range 0.3–0.6 V vs. SCE in acetonitrile and dimethylformamide. The species with a Cu_3OH core do not have this electrochemical response. On the other hand, such species show a novel one-electron-transfer process of the type $Cu^{II}{}_3 + e^- \rightleftharpoons Cu^{II}{}_2Cu^{I}$ with $E°_{298}$ in the range −0.3 to −0.45 V vs. SCE at a hanging-mercury-drop electrode in acetonitrile. The Cu_3O core does not display this process. In effect the electrochemical behaviors of the two cores are complementary: the Cu_3O core undergoes oxidation while the Cu_3OH core undergoes reduction. Thus the core proton acts in a valvelike fashion in controlling the direction of electron transfer. Addition of an acid ($HClO_4$) converts the Cu_3O species to the Cu_3OH species. Conversely, addition of a base (NEt_3) converts Cu_3OH to Cu_3O. The electrochemical responses change accordingly with addition of acid or base. The interconversion reactions are also useful at preparative levels.

Introduction

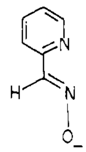
The triangular Cu_3X (X = OH, O) core is now known to be present in three[1–3] related groups of copper(II) complexes. The structural feature common to all the groups is the presence of three oximato functions spanning peripheral bridging positions and of three nitrogen atoms binding terminally (**1**). The three groups differ in having different types of terminal nitrogen. The ligands and their abbreviations are shown in **2**–**4**. The presence of **1** in the complexes of PL and AL is conclusively demonstrated by X-ray diffraction works. In the case of RL(RL′) complexes, the proof is based on analogy. All complexes are strongly antiferromagnetic, and only the $S = {}^1/_2$ state is populated.[1–3]

Recently we reported[4] certain aspects of the electrochemistry of the trinuclear complexes of RL and RL′ (isonitrosoketimines). The redox process (eq 1) was thoroughly characterized. The existence of the couple (eq 2) was also briefly

$$\mathbf{5b} + e^- \rightleftharpoons \mathbf{5a} \tag{1}$$

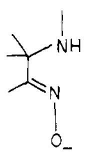


1



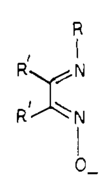
PL

2



AL

3



R′=Me, RL
R′=Ph, RL′

4

$[Cu_3X(RL \text{ or } RL')_3]^{n+}$

5a X = O, n = 1
5b X = O, n = 2
6a X = OH, n = 2
6b X = OH, n = 1

$[Cu_3X(PL)_3]^{n+}$

7a X = O, n = 1
7b X = O, n = 2
8a X = OH, n = 2
8b X = OH, n = 1

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