Molecular Structures and Magnetic Properties of μ-Phenolato Binuclear Copper(II) Complexes Incorporating Chloro, Hydroxo, and Azido Exogenous Bridging Ligands

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The new binucleating ligand 2,6-bis[4-(2-benzimidazolyl)-2-thiabutyl]-4-methylphenol (H(L)) has been synthesized in the hope that its dicopper complexes would experience a strong antiferromagnetic coupling and exchange two electrons at positive potentials, two properties exhibited by the polyphenol oxidases. The X-ray structures of three complexes of general formula $Cu_2(L)(X)(Y)_2$ have been solved in which the exogenous ligand X is varied: **3**, X = Y = Cl; **4**, X = OH and Y = ClO_4; **5**, X = N_3 and Y = NO_3. Compound **3** crystallizes in the orthorhombic space group $Pna2_1$ with Z = 4 and a = 15.801 (5) Å, b = 23.15 (1) Å, and c = 8.190 (3) Å. Complex **4** crystallizes in the orthorhombic space group $Fdd2$ with Z = 8 and a = 26.30 (1) Å, b = 18.801 (8) Å, and c = 14.831 (9) Å. Compound **5** crystallizes in the orthorhombic space group $Pbcn$ with Z = 4 and a = 12.605 (6) Å, b = 14.024 (7) Å, and c = 17.003 (9) Å. All copper atoms are pentacoordinated with ligation from a sulfur, a nitrogen, and the bridging oxygen of the L⁻ ligand, the exogenous bridge, and a counteranion. But they differ in the symmetry of their environments. In **4** and **5**, both copper sites have the same symmetry, being square pyramidal in the first and trigonal bipyramidal in the second compound. In **3**, the two sites are different, one being square pyramidal and the other trigonal bipyramidal. Magnetic susceptibility measurements in the temperature range 6–300 K reveal the antiferromagnetic behavior of every complex. The differences in the values of the exchange integral (**3**, $-2J = 443$ cm⁻¹; **4**, $-2J = 809$ cm⁻¹; **5**, $-2J = 388$ cm⁻¹) can be explained, within the magnetic orbital concepts, by considering the symmetry properties of the various copper sites.

Introduction

The polyphenol oxidases are a group of copper enzymes that reduce molecular oxygen to water at the expense of a polyphenolic substrate (e.g. hydroquinone or catechol) or ascorbate.[1] The site of dioxygen interaction is a binuclear entity that, in its oxidized state, is strongly antiferromagnetically coupled and behaves as a two-electron acceptor operating at a high (positive) potential of the copper(I)/copper(II) couple.

Mimicking, simultaneously, the magnetic and the redox properties of the O_2-interacting site of the copper oxidases has attracted attention for years.[2–5] Very recent studies have shown that it is possible to duplicate these features with dicopper complexes of binucleating ligands that furnish, at the same time, a bridging network and a soft environment to the metal atoms. Accordingly, to mimic the copper oxidase active site, we decided to rely on ligand H(L) (Figure 1), which associates a phenolic moiety with a pair of complexing arms involving soft donor atoms (sulfur and aromatic nitrogen). Obviously, the role of the latter is to favor Cu^I, while the one of the former is to mediate the magnetic exchange between the two Cu^{II} ions. Moreover, the pentadentate nature of the ligand allows for the introduction of a variable exogenous bridging ligand. The aim of this paper is to describe the syntheses, the molecular structures, and the magnetic properties of a series of binuclear copper complexes of H(L) with various exogenous ligands: Cl⁻, OH⁻, and N_3^-. All these complexes exhibit very strong antiferromagnetic interactions, and electrochemical studies, to be reported in full in a forthcoming paper,[6] show that they all exchange electrons at rather positive potentials.[6]

The ligand used in the present study belongs to the class introduced by Robson[7] and Kida[8] in the early 1970s. Although a great number of ligands with nitrogen donors have been used since that time,[9–12] ligands incorporating sulfur donors have been scarcely reported.[6,9,13–15] Most of the time, these ligands possess an "external"[16] sulfur whose coordination in solution is not warranted. To eliminate this possible ambiguity, we chose to introduce the sulfur donor in an "internal" position. Dicopper complexes of a similar ligand with pyridines in place of benzimidazoles have been mentioned by Urbach,[9] but details of their obtention and characterization were not provided. It is worth noting that the present work complements the ones of several authors[15,17–19] who investigated the effect of dissimilar bridges in the transmission of magnetic exchange between two copper atoms. These types of systems are, actually, suitable to variation of the

exogenous bridging ligand without altering drastically the coordination of the metal atoms. This has led to the isolation of a great number of compounds with common structural framework such as A or B and various exogenous ligands.[9–12] It was anticipated that changing the nature of the exogenous bridge X in (μ-phenolato)(μ-X)dicopper species would help in understanding how each pathway contributes to the overall interaction.[18]

Experimental Section

Syntheses. 2-(2-Benzimidazolyl)ethanethiol (1). To a solution of 21 g of o-phenylenediamine in 200 mL of 3 N hydrochloric acid was added

(1) (a) Reinhammar, B.; Malmström, B. G. In *Copper Proteins*; Spiro, T. G., Ed.; Wiley: New York, 1981; Vol, 3, pp 109–149. (b) Reinhammar, B. In *Copper Proteins and Copper Enzymes*; Lontie, R., Ed.; CRC: Boca Raton, FL, 1984; Vol. III, pp 1–35.
(2) (a) Lintvedt, R. L.; Glick, M. D.; Tomlonovic, B. K.; Gavel, D. P.; Kuszaj, J. P. *Inorg. Chem.* **1976**, *15*, 1633–1645. (b) Fenton, D. E.; Lintvedt, R. L. *J. Am. Chem. Soc.* **1978**, *100*, 6367–6375.
(3) (a) Gisselbrecht, J. P.; Gross, M. *Adv. Chem. Ser.* **1982**, *No. 201*, 109–137. (b) Commarmond, J.; Plumer, P.; Lehn, J. M.; Agnus, Y.; Louis, R.; Weiss, R.; Kahn, O.; Morgenstern-Badarau, I. *J. Am. Chem. Soc.* **1982**, *104*, 6330–6340. (c) Agnus, Y.; Louis, R.; Gisselbrecht, J. P.; Weiss, R. *J. Am. Chem. Soc.* **1984**, *106*, 93–102.
(4) Tikkanen, W. R.; Krüger, C.; Bomben, K. D.; Jolly, W. L.; Kaska, W. C.; Ford, P. C. *Inorg. Chem.* **1984**, *23*, 3633–3638.
(5) (a) Mandal, S. K.; Thompson, L. K.; Hanson, A. W. *J. Chem. Soc., Chem. Commun.* **1985**, 1709–1711. (b) Mandal, S. K.; Woon, T. C.; Thompson, L. K.; Newlands, M. J.; Gabe, E. J. *Aust. J. Chem.* **1986**, *39*, 1007–1021.
(6) Benzekri, A.; Dubourdeaux, P.; Latour, J. M.; Laugier, J.; Rey, P. *J. Chem. Soc., Chem. Commun.* **1987**, 1564–1565.
(7) Robson, R. *Inorg. Nucl. Chem. Lett.* **1970**, *6*, 125–128.
(8) Okawa, H.; Kida, S. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 1172.
(9) Urbach, F. L. In *Metal Ions in Biological Systems*; Sigel, H., Ed.; Dekker: New York, 1981; Vol. 13, pp 73–115.
(10) Fenton, D. E. *Adv. Inorg. Bioinorg. Mech.* **1983**, *2*, 187–257.
(11) Zanello, P.; Tamburini, S.; Vigato, P. A.; Mazzochin, G. A. *Coord. Chem. Rev.* **1987**, *77*, 165–273.
(12) Latour, J. M. *Bull. Soc. Chim. Fr.*, in press.
(13) Drago, R. S.; Desmond, M. J.; Corden, B. B.; Miller, K. A. *J. Am. Chem. Soc.* **1983**, *105*, 2287–2296.
(14) Suzuki, M.; Uehara, A. *Inorg. Chim. Acta* **1984**, *87*, L29–L30.
(15) Nishida, Y.; Shimo, H.; Maehara, H.; Kida, S. *J. Chem. Soc., Dalton Trans.* **1985**, 1945–1951.
(16) By "external", we mean that the sulfur atom is the last donor in the chain.
(17) (a) Eduok, E. E.; O'Connor, C. J. *Inorg. Chim. Acta* **1984**, *88*, 229–233. (b) O'Connor, C. J.; Firmin, D.; Pant, A. K.; Babu, B. R.; Stevens, E. D. *Inorg. Chem.* **1986**, *25*, 2300–2307.
(18) (a) Mallah, T.; Boillot, M. L.; Kahn, O.; Gouteron, J.; Jeannin, S.; Jeannin, Y. *Inorg. Chem.* **1986**, *25*, 3058–3065. (b) Mallah, T.; Kahn, O.; Gouteron, J.; Jeannin, S.; Jeannin, Y.; O'Connor, C. J. *Inorg. Chem.* **1987**, *26*, 1375–1380. (c) Kahn, O.; Jeannin, Y., submitted for publication in *Inorg. Chem.*
(19) Karlin, K. D.; Farooq, A.; Hayes, J. C.; Cohen, B. I.; Rowe, T. M.; Sinn, E.; Zubieta, J. *Inorg. Chem.* **1987**, *26*, 1271–1280.
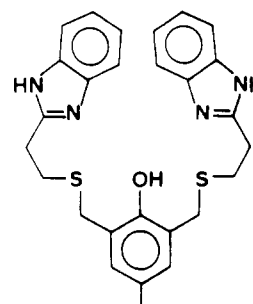
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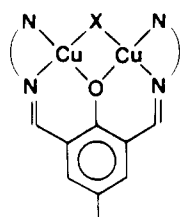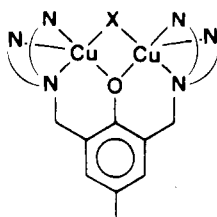
22 mL of mercaptopropionic acid, and the mixture was refluxed for 20 h. The blue solution was allowed to cool to room temperature and then was neutralized with an aqueous saturated solution of KHCO$_3$. The white precipitate was filtered under vacuum (32 g, yield 94%). As shown by NMR spectroscopy and TLC, this compound contained a small amount (1–8%) of bis(2-(2-benzimidazolyl)ethyl) disulfide. This product was used in the next step of the synthesis without any further purification.

2,6-Bis(chloromethyl)-4-methylphenol (2). 2,6-Bis(hydroxymethyl)-4-methylphenol (30 g) was dissolved in 300 mL of methanol, and HCl was bubbled through this solution for 4 h. The reaction mixture was then poured into 500 mL of 12 N aqueous HCl, and the resulting precipitate was filtered out under vacuum and dissolved in ligroin. After decantation of the aqueous phase, evaporation of the organic solution furnished a white solid, which upon recrystallization from hexane gave 29.3 g (69%) of pure **2**.

2,6-Bis(4-(2-benzimidazolyl)-2-thiabutyl)-4-methylphenol (H(L)). Compound **1** (10.3 g) was dissolved in 50 mL of ethanol and 30 mL of 4 N sodium hydroxide, and the mixture was brought to reflux. Compound **2** was added dropwise to this solution. Reflux was continued for 4 h, and the resulting orange solution was evaporated under vacuum. Extraction of the residue with dichloromethane gave the crude ligand (13.4 g), which was purified by column chromatography (5 g of **2**, 200 g of SiO$_2$, ethyl acetate). Yield: 21%.

Synthesis of the Copper Complexes. The following general procedure was used to prepare the copper complexes: H(L) (1 mmol) was first ionized with a base (triethylamine or KOH for **3** and **4**; NaN$_3$ for **5**) in methanol (30 mL), and this solution was added to the appropriate copper(II) salt (2 mmol) dissolved in the same solvent (30 mL). Crystals suitable for an X-ray diffraction study were obtained by slow diffusion of diethyl ether for **3** (Cu$_2$LCl$_3$·MeOH) and by slow evaporation for **4** (Cu$_2$L(OH)(ClO$_4$)$_2$·2MeOH) and **5** (Cu$_2$L(N$_3$)(NO$_3$)$_2$).

Anal. Calcd for Cu$_2$LCl$_3$·MeOH (**3**), C$_{28}$H$_{31}$N$_4$O$_2$S$_2$Cl$_3$Cu$_2$: C, 44.65; H, 4.15; N, 7.44; O, 4.25; S, 8.51; Cl, 14.12; Cu, 16.87. Found: C, 44.57; H, 3.82; N, 8.10; O 3.49; S, 8.65; Cl, 14.59; Cu, 17.14.

Anal. Calcd for Cu$_2$L(OH)(ClO$_4$)$_2$·2MeOH (**4**), C$_{29}$H$_{36}$N$_4$O$_{12}$S$_2$Cl$_2$Cu$_2$: C, 38.92; H, 4.05; N, 6.26; O, 21.45; S, 7.17; Cl, 7.93; Cu, 14.20. Found: C, 38.90; H, 3.95; N, 5.91; O, 21.12; S, 7.00; Cl, 8.46; Cu, 13.69.

Anal. Calcd for Cu$_2$L(N$_3$)(NO$_3$)$_2$ (**5**), C$_{27}$H$_{27}$N$_9$O$_7$S$_2$Cu$_2$: C, 41.54; H, 3.49; N, 16.14; O, 14.34;, S, 8.21; Cu, 16.28. Found: C, 41.81; H, 3.54; N, 16.04;, O, 14.45; S, 7.83; Cu, 16.10.

X-ray Data Collections and Structure Determinations. Orthorhombic unit cells were found for the three compounds by taking preliminary Laue and Weissenberg photographs. The same crystals were mounted on an Enraf-Nonius CAD-4 four-circle diffractometer equipped with graphite-monochromated Mo Kα radiation. Accurate cell dimensions were obtained by least-squares fitting of the setting angles of 25 reflections and are reported in Table I with other experimental parameters for the three complexes. The space groups *Pna2$_1$* for **3**, *Fdd2* for **4**, and *Pbcn* for **5** were established from systematic absences. The data were corrected for Lorentz and polarization effects, but not for absorption.

The three crystal structures were solved by conventional Patterson and Fourier methods using the SHELX-86 package. The copper positions were determined from sharpened Patterson functions, and the phases provided by these heavy atoms were used for successive Fourier difference syntheses that revealed the positions of the remaining non-hydrogen atoms. Structure refinements included anisotropic thermal parameters for all non-hydrogen atoms. These were introduced into the final refinement model in fixed and idealized positions and isotropic thermal parameters. The functions minimized were $R_w = [\sum w(F_o - F_c)^2 / \sum wF_o^2]^{1/2}$ and $R = \sum |F_o - F_c| / \sum |F_o|$.

In the case of **4**, the methanol solvate molecule has its carbon atom located on the 2-fold axis; this results in disorder of the hydroxyl group. Since the exact location of this group does not hamper the chemical meaning of the structure, no attempt was made to build a model with fractional occupancies.
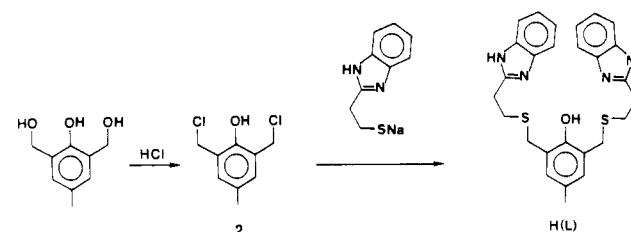
Atomic coordinates of compounds **3–5** are listed in Table II, IV, and VI, respectively. Anisotropic thermal parameters, bond distances, bond

Figure 1. Structure of ligand H(L).

Table I. Crystallographic Data for Complexes 3–5

chem formula	C$_{28}$H$_{29}$N$_4$O$_2$-S$_2$Cl$_3$Cu$_2$	C$_{27}$H$_{27}$N$_4$O$_{10}$-S$_2$Cl$_2$Cu$_2$	C$_{27}$H$_{27}$N$_9$O$_7$-S$_2$Cu$_2$
mol wt	738.1	829.7	648.9
space group	*Pna2$_1$*	*Fdd2*	*Pbcn*
a, Å	15.801 (5)	26.30 (1)	12.605 (6)
b, Å	23.15 (1)	18.801 (8)	14.024 (7)
c, Å	8.190 (3)	14.831 (9)	17.003 (9)
V, Å^3	2995.8	7334.3	3005.7
Z	4	8	4
ρ_{calcd}, g cm^{-3}	1.64	1.503	1.72
T, °C	20	22	22
λ, Å	0.7107	0.7107	0.7107
R	0.035	0.053	0.074
R_w	0.039	0.059	0.065

Scheme I

angles, and structure factors are collected in Tables S1–3, S4–6, S7–9, and S10–12 for **3–5**, respectively (supplementary material).

Magnetic Susceptibility Measurements. The magnetic susceptibilities of the three complexes were measured in the range 6–300 K with a superconducting SHE SQUID susceptometer at a field strength of 0.5 T. The data were corrected for the magnetization of the sample holder and for the diamagnetism of the constituent atoms estimated from Pascal's constants.

Results

Syntheses. The ligand H(L) has been synthesized in two steps (Scheme I) from the commercially available 2,6-bis(hydroxymethyl)-4-methylphenol. In the first reaction, the starting compound is converted by action of methanolic hydrogen chloride into its bis(chloromethyl) analogue, **2**. The latter is then reacted with the sodium salt of 2-(2-benzimidazolyl)ethanethiol (**1**).[20] the overall yield of the synthesis was 15%.

Description of the Structures. In spite of their chemical similarity, the three compounds are structurally very different owing to the various symmetries of the copper sites. This justifies a more detailed analysis of the copper coordination polyhedrons by the method of Muetterties and Guggenberger (M-G).[21] This approach compares the actual geometry of a metal site to ideal geometries by the way of a key shape-determining angle. For the pentacoordinate metal centers found in the present case, the two limiting geometries to be considered are the square-based pyramid and the trigonal bipyramid, for which the key angles e_3 are 0.0 and 53.1°, respectively.

(20) Phillips, M. A. *J. Chem. Soc.* **1928**, 172 and 2393.
(21) Muetterties, E. L.; Guggenberger, L. J. *J. Am. Chem. Soc.* **1974**, *96*, 1748–1756.

Table II. Atomic Coordinates (×10⁴) and Temperature Factors ($\text{Å}^2 \times 10^3$) for Compound 3

	x	y	z	B_{eq}		x	y	z	B_{eq}
Cu1	1292 (1)	1560 (0)	660 (2)	2.46	C9	201 (6)	1756 (4)	3723 (13)	5.93
Cu2	2084 (1)	2828 (0)	0 (0)	3.11	C10	−538 (6)	1402 (5)	3139 (12)	5.09
Cl1	940 (1)	2313 (1)	−1190 (3)	3.07	C11	−446 (6)	1134 (4)	1513 (12)	4.02
Cl2	2227 (1)	914 (1)	−658 (4)	4.46	C12	−893 (6)	634 (4)	−558 (14)	2.68
Cl3	1986 (2)	3332 (1)	2436 (3)	4.48	C13	−87 (5)	857 (4)	−927 (12)	2.95
S1	1181 (1)	1351 (1)	3502 (3)	3.04	C14	312 (6)	761 (4)	−2446 (13)	3.37
S2	3613 (1)	2825 (1)	−539 (3)	2.50	C15	−117 (7)	424 (4)	−3540 (14)	3.47
O1	2211 (3)	2097 (2)	1108 (7)	2.62	C16	−929 (7)	179 (4)	−3157 (18)	2.47
O2	2694 (4)	4664 (3)	3183 (10)	5.57	C17	−1316 (7)	280 (4)	−1693 (16)	3.16
N1	181 (4)	1172 (3)	422 (9)	3.15	C18	3818 (6)	2066 (4)	−307 (11)	2.62
N2	−1101 (4)	807 (3)	941 (11)	3.59	C19	3709 (6)	2956 (4)	−2725 (13)	5.06
N3	1951 (5)	3466 (3)	−1559 (10)	3.38	C20	2874 (6)	2987 (4)	−3604 (13)	4.08
N4	2219 (4)	3963 (3)	−3818 (9)	3.66	C21	2348 (6)	3470 (5)	−2996 (12)	3.11
C1	2879 (5)	1953 (4)	2097 (11)	1.95	C22	1689 (6)	4290 (4)	−2899 (14)	3.16
C2	2753 (6)	1815 (4)	3748 (12)	2.80	C23	1513 (6)	3984 (4)	−1499 (13)	4.80
C3	3438 (6)	1650 (4)	4703 (12)	2.99	C24	967 (8)	4192 (6)	−348 (16)	14.53
C4	4257 (6)	1647 (4)	4087 (14)	2.67	C25	637 (10)	4738 (6)	−653 (19)	18.87
C5	4384 (6)	1786 (4)	2447 (13)	2.87	C26	864 (9)	5063 (6)	−1993 (18)	12.43
C6	3697 (6)	1917 (4)	1440 (12)	3.51	C27	1375 (7)	4848 (5)	−3177 (15)	5.64
C7	5005 (6)	1478 (5)	5138 (14)	4.79	C28	2996 (13)	−166 (9)	−2792 (33)	15.39
C8	1877 (5)	1875 (4)	4429 (11)	2.18					

Table III. Selected Bond Lengths (Å) and Angles (deg) for Compound 3

Cu1–Cu2	3.255 (1)	Cl2–Cu1–N1	102.6 (2)
Cu1–Cl1	2.386 (2)	S1–Cu1–O1	90.1 (1)
Cu1–Cl2	2.372 (2)	S1–Cu1–N1	86.4 (2)
Cu2–Cl1	2.382 (2)	O1–Cu1–N1	165.7 (2)
Cu2–Cl3	2.322 (2)	Cu1–Cu2–Cl1	47.0 (0)
Cu1–S1	2.386 (3)	Cu1–Cu2–Cl3	106.9 (0)
Cu2–S2	2.461 (2)	Cu1–Cu2–S2	114.0 (0)
Cu1–O1	1.954 (4)	Cu1–Cu2–O1	33.4 (1)
Cu2–O1	1.941 (4)	Cu1–Cu2–N3	138.7 (2)
Cu1–N1	1.987 (6)	Cl1–Cu2–Cl3	123.8 (1)
Cu2–N3	1.972 (7)	Cl1–Cu2–S2	132.3 (0)
Cu2–Cu1–Cl1	46.9 (0)	Cl1–Cu2–O1	80.1 (1)
Cu2–Cu1–Cl2	105.1 (0)	Cl1–Cu2–N3	91.9 (2)
Cu2–Cu1–S1	112.1 (0)	Cl3–Cu2–S2	102.8 (1)
Cu2–Cu1–O1	33.2 (1)	Cl3–Cu2–O1	92.8 (1)
Cu2–Cu1–N1	137.5 (2)	Cl3–Cu2–N3	99.7 (2)
Cl1–Cu1–Cl2	108.8 (1)	S2–Cu2–O1	88.8 (1)
Cl1–Cu1–S1	138.9 (0)	S2–Cu2–N3	89.5 (2)
Cl1–Cu1–O1	79.8 (1)	O1–Cu2–N3	167.4 (2)
Cl1–Cu1–N1	93.8 (2)	Cu1–Cl1–Cu2	86.1 (0)
Cl2–Cu1–S1	111.2 (0)	Cu1–O1–Cu2	113.4 (2)
Cl2–Cu1–O1	91.6 (1)		
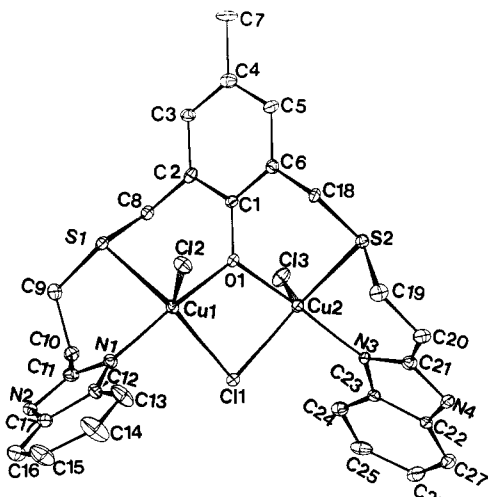
Figure 2. Molecular structure of **3**: ORTEP diagram showing 30% probability ellipsoids and the atom-numbering scheme.

Cu₂LCl₃·MeOH (3). The molecular structure of the chloride complex is illustrated in Figure 2, and the relevant bond lengths and angles are given in Table III. The two copper atoms are pentacoordinated; each one is bound to a nitrogen, a sulfur, and

Table IV. Atomic Coordinates (×10⁴) and Temperature Factors ($\text{Å}^2 \times 10^3$) for Compound 4

	x	y	z	B_{eq}
Cu	393 (1)	523 (1)	0 (0)	3.77
S	516 (3)	1119 (1)	912 (2)	4.25
Cl	2408 (3)	−327 (1)	184 (2)	5.32
O1	0 (0)	0 (0)	715 (6)	4.28
O2	0 (0)	0 (0)	−582 (7)	4.44
O6	1772 (10)	9310 (4)	−44 (9)	9.04
O4	3164 (9)	−342 (5)	−213 (11)	11.09
O5	2591 (15)	−364 (7)	875 (10)	13.34
O3	2013 (9)	152 (5)	157 (10)	10.20
N1	684 (9)	1021 (4)	−702 (6)	4.28
N2	427 (10)	1718 (5)	−1328 (7)	6.32
C1	0 (0)	0 (0)	1421 (8)	2.99
C2	−253 (9)	422 (6)	1824 (8)	4.54
C3	−225 (8)	423 (5)	2525 (8)	4.28
C4	0 (0)	0 (0)	2915 (11)	4.32
C5	0 (0)	0 (0)	3743 (11)	7.12
C6	−448 (12)	934 (5)	1419 (8)	5.40
C7	131 (11)	1715 (5)	545 (9)	5.39
C8	−354 (11)	1658 (5)	−185 (7)	4.64
C9	255 (9)	1452 (5)	−733 (7)	3.96
C10	1075 (13)	1420 (6)	−1712 (10)	6.69
C11	1236 (12)	978 (6)	−1316 (9)	5.65
C12	1834 (13)	629 (6)	−1553 (11)	6.79
C13	2240 (16)	712 (8)	−2180 (14)	9.45
C14	2069 (22)	1094 (8)	−2605 (17)	13.51
C15	1498 (20)	1471 (9)	−2398 (14)	12.81
O7	2531 (13)	2031 (7)	−279 (11)	12.23
C16	2500 (0)	2500 (0)	−823 (93)	43.60

the oxygen of the ligand and to two chloride anions. The phenolato oxygen and one chloride bridge the two metal centers, and the Cu–Cu distance is 3.255 Å. The angles around the bridging atoms are Cu1–O1–Cu2 = 113.4° and Cu1–Cl1–Cu2 = 86.1°. Nevertheless, the two metal sites differ drastically. The M-G approach gives e_3 values of 9.7 and 34.1° for Cu1 and Cu2, respectively. Therefore, the geometry around Cu1 can be described as a slightly distorted square pyramid with the basal plane occupied by O1, S1, N1, and Cl1. Cu1 lies 0.11 Å above this plane toward the apical chloride, Cl2. On the other hand, the intermediate value of its associated e_3 angle is of no utility to describe the coordination polyhedron around Cu2 by either of the two limiting geometries. However, from a close inspection of the bond lengths and angles, one can tentatively describe this polyhedron as a distorted trigonal bipyramid whose basal plane comprises S1, Cl1, and Cl3. The metal atom is close to the basal plane and slightly off the O1N3 axis of the bipyramid (O1–Cu2–N3 = 167.5°). The axial distances are shorter than the equatorial ones, and the angles for the atoms in the basal plane are far from the ideal value of 120° (Table III).
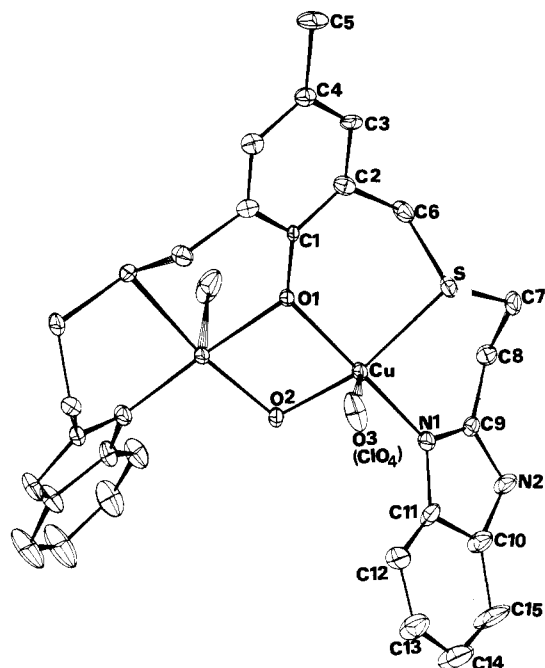
Figure 3. Molecular structure of **4**: ORTEP diagram showing 30% probability ellipsoids and the atom-numbering scheme.

Table V. Selected Bond Lengths (Å) and Angles (deg) for Compound **4**

Cu–Cu	2.994 (1)	Cu–Cu–N1	135.8 (2)
Cu–S	2.335 (3)	S–Cu–O1	90.0 (2)
Cu–O1	2.001 (6)	S–Cu–O2	164.0 (2)
Cu–O2	1.868 (6)	S–Cu–N1	91.9 (2)
Cu–O6	2.596 (10)	O1–Cu–O2	78.3 (3)
Cu–N1	1.911 (8)	O1–Cu–N1	175.8 (3)
Cu–Cu–S	130.6 (0)	O2–Cu–N1	99.1 (3)
Cu–Cu–O1	41.6 (2)	Cu–O1–Cu	96.9 (4)
Cu–Cu–O2	36.7 (2)	Cu–O2–Cu	106.5 (5)

Table VI. Atomic Coordinates ($\times 10^4$) and Temperature Factors (Å^2 $\times 10^3$) for Compound **5**

	x	y	z	B_{eq}
Cu	5484 (1)	2257 (1)	3526 (1)	2.77
S	4968 (2)	3152 (1)	4685 (2)	2.96
O1	5000 (0)	2949 (5)	2500 (0)	2.68
O2	7132 (6)	2538 (4)	3231 (5)	4.09
O3	8181 (7)	3008 (6)	2204 (7)	7.11
O4	7199 (8)	2051 (5)	1844 (6)	6.37
N1	5780 (6)	1458 (4)	4515 (5)	2.90
N2	5723 (7)	734 (5)	5824 (6)	3.75
N3	5000 (0)	1496 (7)	2500 (0)	4.26
N4	5000 (0)	793 (8)	2500 (0)	3.45
N5	5000 (0)	103 (7)	2500 (0)	4.85
N6	7499 (8)	2528 (6)	2423 (7)	4.05
C1	5000 (0)	3760 (7)	2500 (0)	2.54
C2	5466 (8)	4164 (5)	1754 (6)	3.10
C3	5442 (8)	4994 (6)	1767 (7)	3.67
C4	5000 (0)	5401 (10)	2500 (0)	4.28
C5	5000 (0)	6318 (9)	2500 (0)	6.61
C6	3982 (8)	3739 (6)	4044 (7)	3.76
C7	4032 (8)	2511 (6)	5311 (7)	4.11
C8	4648 (9)	1922 (6)	5927 (6)	4.01
C9	5377 (9)	1390 (6)	5372 (6)	3.49
C10	6406 (8)	354 (6)	5202 (7)	3.65
C11	6456 (8)	801 (6)	4374 (7)	3.53
C12	7084 (8)	589 (6)	3630 (8)	4.50
C13	7629 (9)	−124 (7)	3687 (10)	5.67
C14	7543 (10)	−585 (7)	4524 (10)	5.95
C15	6944 (9)	−368 (6)	5330 (10)	5.49

Cu$_2$L(OH)(ClO$_4$)$_2$·2MeOH (4). Figure 3 depicts the molecular structure of the hydroxo complex, **4**, and Table V summarizes important bond lengths and angles. The two copper atoms are bridged by the phenolato and hydroxo oxygens, O1 and O2,
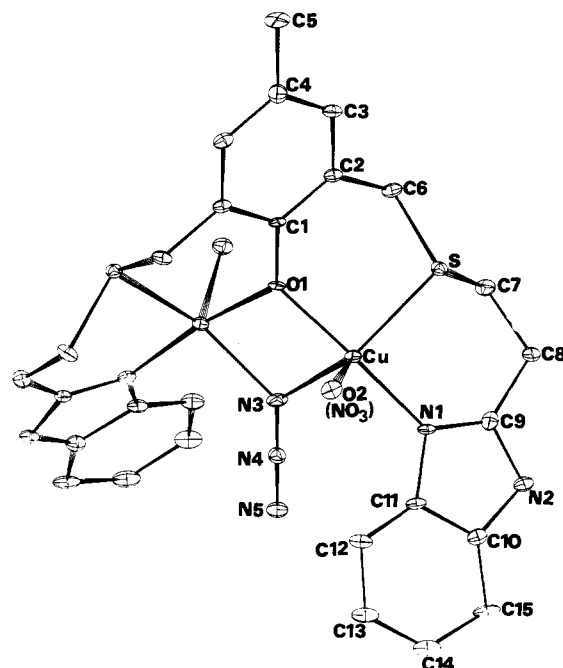

Figure 4. Molecular structure of **5**: ORTEP diagram showing 30% probability ellipsoids and the atom-numbering scheme.

Table VII. Selected Bond Lengths (Å) and Angles (deg) for Compound **5**

Cu–Cu	3.131 (3)	O1–Cu–O2	91.4 (2)
Cu–S	2.325 (2)	O1–Cu–N1	171.2 (2)
Cu–O1	1.960 (5)	O1–Cu–N3	76.7 (3)
Cu–O2	2.172 (7)	O2–Cu–N1	96.0 (2)
Cu–N1	1.981 (7)	O2–Cu–N3	107.0 (1)
Cu–N3	2.033 (7)	N1–Cu–N3	96.6 (3)
S–Cu–O2	104.9 (2)	S–Cu–O1	91.9 (1)
S–Cu–N1	90.7 (2)	Cu–O1–Cu	106.0 (4)
S–Cu–N3	146.3 (1)	Cu–N3–Cu	100.7 (5)

respectively. The Cu–Cu separation is 2.994 Å, and the angles around the bridging atoms are Cu–O1–Cu' = 96.9° and Cu–O2–Cu' = 106.5°. Moreover, the two coppers are crystallographically related by a C_2 axis running through the phenolato atoms C1, C4, C5, and O1 and the hydroxo oxygen O2. Therefore, the Cu–O1–Cu'–O2 core is perfectly planar. Each cupric ion is pentacoordinate with ligation to a sulfur, a nitrogen, and three oxygens coming from the two bridging ligands and a perchlorate. The M–G approach furnishes a shape-determining angle e_3 = 5.9°, in agreement with a slightly distorted square-pyramidal geometry. Thus, the coordination sphere of each copper belongs to the 4 + 1 type, with the four basal atoms O1, O2, S, and N1 and an apical perchlorate O3. All metal–ligand distances are in the range observed for analogous five-coordinate copper(II) complexes with tetragonal geometries.

Cu$_2$L(N$_3$)(NO$_3$)$_2$ (5). The molecular structure of the azido derivative is shown in Figure 4, and important bond lengths and angles are collected in Table VII. As in **4**, a crystallographic 2-fold axis is present, which passes through the phenolato atoms C1, C4, C5, and O1 and the three azido nitrogens, N3, N4, and N5. The two coppers are bridged by the phenolato oxygen, O1, and nitrogen N3 from the μ-1,1-azide. The Cu–Cu distance is 3.131 Å, and the angles within the bridge are Cu–O1–Cu' = 106.0° and Cu–N3–Cu' = 100.7°. The 2-fold symmetry requires that the azido ligand be coplanar with the bridging Cu–O1–Cu'–N3 unit. Each cupric ion is pentacoordinate with ligation to a sulfur, a nitrogen, and the phenolato oxygen of the organic ligand, an azido nitrogen, and an oxygen of a nitrate counterion. The M–G analysis produces a shape angle e_3 = 27.93°, which does not permit a straightforward determination of the coordination geometry of the copper atoms. Nevertheless, as in the case of **3**, a careful examination of the bond angles allows one to describe, tentatively, the copper coordination sphere as trigonal bipyramidal.
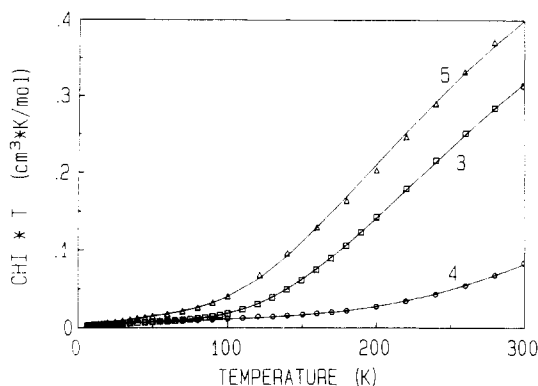
Figure 5. Temperature dependence of the product of the temperature multiplied by the molar susceptibility for **3–5**.
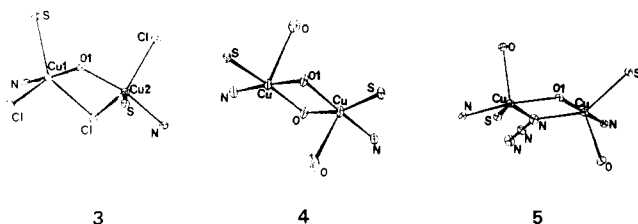

Figure 6. Copper coordination spheres of **3–5**.

Table VIII. Fitting Parameters of the Magnetic Data

compd	g	10^2P	10^6TIP	E_{ST}, cm^{-1}	10^3R
3	2.086	0.35	114	−443	0.36
4	1.953	0.93	80	−809	0.03
5	1.989	0.30	283	−388	0.16

The axis of the bipyramid passes through the O1 and N1 atoms, and its equatorial plane comprises N3, S, and O2. The copper atom is slightly off the axis of the bipyramid (O1–Cu–N1 = 171.2°). Bond lengths and angles are within the range expected for pentacoordinate copper(II) complexes.

Analysis of the Magnetic Data. The magnetic properties of **3–5** are illustrated in Figure 5 in the form of the temperature dependence of the product of the molar susceptibility multiplied by the temperature over the range 6–300 K. In the three cases, the value of χT at high temperature is lower than expected for two noninteracting $^1/_2$ spins. This value decreases with the temperature, as is typical for antiferromagnetically coupled species.

The above structural analyses have shown that the various complexes can be considered as discrete binuclear entities. Accordingly, their magnetic properties can be analyzed with the classical Bleaney–Bowers equation[22] for a pair of $^1/_2$ spins. When modified to include the presence of a mononuclear impurity, this equation takes the form

$$\chi T =$$
$$(Ng^2\beta^2/k)((1 - P)/(3 + \exp(-J/kT)) + P/4) + T(\text{TIP})$$

where TIP is the temperature-independent paramagnetism, $100P$ is the percentage of monomeric impurity, and the other symbols have their usual meaning. The g, J, and P values obtained from least-squares fittings of the experimental data are summarized in Table VIII. The singlet–triplet energy gaps are −443 cm^{-1} for **3**, −809 cm^{-1} for **4**, and −388 cm^{-1} for **5**.

Discussion

Structural Properties. When we consider the structures of the three complexes, the most striking feature is undoubtedly the variability of the copper coordination sphere. Actually, only half of these sites can be described as tetragonal, the other approaching a trigonal bipyramid. These differences appear clearly in Figure 6, which compares the environments of the copper ions in the three

Table IX. Selected Structural and Magnetic Data for (μ-Hydroxo)(μ-phenolato)dicopper Complexes

Cu–Cu, Å	Cu–OH–Cu, deg	Cu–OPh–Cu, deg	$-E_{ST}$, cm^{-1}	ref
3.05	102.5	101.4	525	24, 25[a]
3.053	103.6	101.9	420	23[c]
2.864	96.45	91.55	0	26[a]
3.014	101.3	100.9	516	27[a]
3.020	104.8	99.1	675	15[d]
2.947	100.44	99.18	364	17b[a]
2.991	102.2	99.9	499	17b[a]
2.924	99.3	97.4	367	18a[a]
2.957	99.3	98.3	493	28[a]
2.933	99.7	97.9	288	29[a]
3.018	106.3	100.6	852	29[a]
3.021	104.7	98.7	569	29[a]
3.082	104.4	102.5	600	19[c]
2.994	106.5	96.9	809	this work[b]

[a] Ligand type A, donor set ON$_4$. [b] Ligand type B, donor set ON$_2$S$_2$. [c] Ligand type B, donor set ON$_6$. [d] Ligand type B, donor set ON$_2$S$_4$.

Table X. Selected Structural and Magnetic Data for (μ-Chloro)(μ-phenolato)- and (μ-Azido)(μ-phenolato)dicopper Complexes

Cu–Cu, Å	Cu–X–Cu, deg	Cu–O–Cu, deg	$-E_{ST}$, cm^{-1}	ref
	X = Cl$^-$			
3.167	87.0	105.9	84	17a, 30[a]
3.265	89.6	111.4	335	19[c]
3.255	86.1	113.4	443	this work[b]
	X = N$_3^-$			
3.149	103.4	106.8	450	31[c]
2.972	100.0	98.7	87	18a[a]
2.993	99.7	100.5	161	18b[a]
3.120	104.5	102.9	534	29, 32[a]
2.952	99.2	98.1	84	29[a]
3.185	103.6	107.9	440	19, 33[c]
3.131	100.7	106.0	388	this work[b]

[a] Ligand type A, donor set ON$_4$. [b] Ligand type B, donor set ON$_2$S$_2$. [c] Ligand type B, donor set, ON$_6$. [d] Ligand type B, donor set ON$_2$S$_4$.

compounds. Such distortions have already been observed in several instances,[15,23] but in the nitrogen analogs of H(L), tetragonality of the metal sites is the rule.[12] We believe that two factors can concur to cause the observed distortions. First, the aliphatic tetraatomic (ethylthio)methyl chain is far more flexible than the usual (alkylamino)methyl linkage, and also, it is not restricted by conjugation to coplanarity with the phenolic moiety. Moreover, owing to its larger size, the sulfur atom introduces tensions in the six-membered chelate rings, and these constraints are reflected in the deformations observed within these units. Second, sulfur is not a strong donor to copper(II), and a balance between the various ligands can operate. The latter effect is dependent on the nature of the coligands of the metal, in particular, the exogenous bridging ligand. Along these lines, one can interpret the tetragonality of the copper sites of the hydroxo complex **4** as resulting from the fact that hydroxide is a strong donor to Cu^{II}. As the other two exogenous ligands are weaker donors, the geometry around the copper atom is less definite.

The presence of the sulfur atom has another structural effect that will prove of interest to explain the magnetic behavior of the complexes. For every compound, there is within the central Cu–O–Cu–X core, an angle wider than 106°. In the chloro and azido derivatives, this angle is the Cu–O—Cu angle at the phenolato oxygen, while, in the hydroxide, the Cu–O(H)—Cu angle is wider. It is worth noting that such wide angles are found also for complexes of heptadentate ligand systems such as B;[19] in this case again, the simplest way to lessen the steric constraints within the ligand is probably to pull the two metal atoms aside, and this

(22) Bleaney, B.; Bowers, K. D. *Proc. R. Soc. London, A* **1952**, *A214*, 451–465.

(23) Sorrell, T. N.; Jameson, D. L.; O'Connor, C. J. *Inorg. Chem.* **1984**, *23*, 190–195.
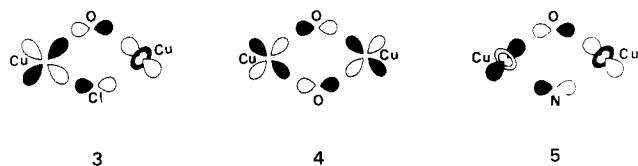
3   4   5

Figure 7. Magnetic orbitals of **3–5**.

makes the bridge angles more obtuse.

Magnetic Properties. Examination of Tables IX and X, which summarize relevant structural and magnetic properties of (μ-phenolato)(μ-X)dicopper complexes, shows that the antiferromagnetic interactions exhibited by the present compounds are among the strongest in each series of products. In line with this observation, one can note that a μ-phenolato μ-hydroxo complex of a heptadentate ligand with four thioether functions[15] is also in the upper range of these compounds, and the same is true for a μ-phenolato μ-azido derivative of a similar sulfur ligand.[18c] It thus appears that the presence of sulfur in the coordination sphere of the copper atoms is always associated with strong antiferromagnetic interactions between the two cupric ions, stronger than generally observed for dicopper complexes of the corresponding nitrogen ligands. This fact had already been noted in other series of dicopper complexes.[34,35] An attractive explanation of this effect has been advanced by Kahn and co-workers:[18c,34] the s and p orbitals of the sulfur atom, which are more diffuse than the s and p orbitals of the nitrogen, contribute to making the magnetic orbitals also more diffuse. This would increase the overlap between the latter and, in turn, would also increase the antiferromagnetic contribution to the exchange; at the same time, this would decrease the Coulombic repulsion between the odd electrons and, thus, decrease the ferromagnetic contribution. Nevertheless, another, more prosaic, interpretation can be proposed that takes into account the structural properties of the various compounds. Actually, as revealed by Tables IX and X, all dicopper complexes of these series involving thioether donors possess wide Cu–O–Cu angles. Since the early study of bis(μ-hydroxo)dicopper derivatives,[36] it is known that a wide angle at the bridging ligand leads to an important antiferromagnetic component of the exchange interaction. The two interpretations of the experimental observations are not at all exclusive. Both aspects concur to cause the same effect; therefore, it is difficult to estimate which contributes more to the overall effect.

One can now try to get a deeper understanding of the interactions operating in the compounds described in the present study, and in order to do so, it is necessary to come back to the precise description of the symmetry of the copper sites. In this respect, the most important feature is the trigonal-bipyramidal geometry

of Cu2 in the chloride **3** and of both coppers of the azide **5**. Such a change of symmetry from tetragonal to trigonal produces a switching of the metal-based magnetic orbital.[37] In the case of copper(II) ions, the odd electron, which occupies a $d_{x^2-y^2}$ orbital in a tetragonal environment, is located in the d_{z^2} orbital in a trigonal one. Therefore, the relative orientation of the metallic part of the magnetic orbitals of the three compounds can be represented as depicted in Figure 7.

The case of the hydroxide **4** is the most straightforward. As is generally observed for this kind of compound, the tetragonality of both copper sites makes both oxygen bridges similarly active in the exchange process. The complementarity[38] of the two bridging ligands toward the exchange allows one to predict a strong antiferromagnetic interaction, which is observed in the present case also. Examination of Table IX shows that this series of compounds obeys the following general trend:[36] the wider the bridge angles, the stronger the antiferromagnetic interaction. In agreement with this trend, **4**, which has the widest Cu–O(H)–Cu angle in the series, has also one of the highest singlet–triplet gaps.

The magnetic coupling of (μ-azido)dicopper complexes has attracted much interest recently owing to the following peculiarity. It was observed that this ligand can induce either a ferromagnetic or an antiferromagnetic exchange between the two coppers, depending on whether it bridges in the μ-1,1 or the μ-1,3 modes, respectively.[39] This dual behavior has been explained with the spin-polarization concept.[40] In the present azido derivative, **5**, both copper sites are trigonal and the axis of the bipyramid, which coincides with the axis of the magnetic orbital, points toward the phenolato oxygen. This situation ensures that the latter bridge will contribute most to the magnetic exchange, since the azido bridge interacts only with the prolate lobe of the d_{z^2} orbital. In other words, the antiferromagnetic contribution transmitted by the oxygen bridge must dominate the ferromagnetic one associated with the μ-1,1-azide. This explains the observation of a moderately strong antiferromagnetic interaction.

Similar lines of reasoning can be applied to the chloride, **3**. In this case, the two copper sites are dissymmetrical, as illustrated in Figure 6. Owing to the small angle at the chloride bridge (Cu1–Cl1–Cu2 = 86.1°), it is likely that the latter will have a ferromagnetic contribution.[41] However, this interaction involves the prolate lobe of the d_{z^2} orbital on Cu2, which will lessen its importance. Accordingly, the antiferromagnetic interaction mediated by the oxygen bridge must overwhelm the above ferromagnetic contribution, in agreement with the observed overall antiferromagnetic exchange.

Conclusion

In summary, this work has shown, in a series of (μ-phenolato)(μ-X)dicopper complexes, that the introduction of thioether functions into Robson type ligands leads to enhanced stabilization of the singlet level. Through the use of the magnetic orbital concept, it has been possible to rationalize the importance of the various pathways conducive to affecting the exchange coupling. However, it is not possible to unambiguously attribute the origin of the enhanced singlet stabilization to the diffuseness of the sulfur orbitals, since in all complexes structural factors are acting in the same direction.

This series of complexes is the first to give rise to such high antiferromagnetic interactions whatever the nature of the ex-

(24) Gagne, R. R.; McCool, M. W.; Marsh, R. E. Acta. *Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1980**, *B36*, 2420–2422.
(25) Grzybowski, J. J.; Merrell, P. H.; Urbach, F. L. *Inorg. Chem.* **1978**, *17*, 3078–3082.
(26) Fallon, G. D.; Murray, K. S.; Spethmann, B.; Yandell, J. K.; Hodgkin, J. H.; Loft, B. C. *J. Chem. Soc., Chem. Commun.* **1984**, 1561–1563.
(27) Lorösch, J.; Haase, W. *Inorg. Chim. Acta* **1985**, *108*, 35–40.
(28) Bailey, N. E.; Fenton, D. E.; Lay, J.; Roberts, P.; Latour, J. M.; Limosin, D. *J. Chem. Soc., Dalton Trans.* **1986**, 2681–2689.
(29) Lorösch, J.; Quotschalla, U.; Haase, W. *Inorg. Chim. Acta* **1987**, *131*, 229–236.
(30) Majeste, R. J.; Klein, C. L.; Stevens, E. D. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1983**, *C39*, 52–54.
(31) Sorrell, T. N. In *Biological and Inorganic Copper Chemistry*; Karlin, K. D., Zubieta, J., Ed.; Adenine: Guilderland, NY, 1985; Vol. II, pp 41–56.
(32) Lorösch, J.; Paulus, H.; Haase, W. *Inorg. Chim. Acta* **1985**, *106*, 101–108.
(33) Karlin, K. D.; Cohen, B. I.; Hayes, J. C.; Farooq, A.; Zubieta, J. *Inorg. Chem.* **1987**, *26*, 147–153.
(34) (a) Girerd, J. J.; Jeannin, S.; Jeannin, Y.; Kahn, O. *Inorg. Chem.* **1978**, *17*, 3034–3040. (b) Chauvel, C.; Girerd, J. J.; Jeannin, Y.; Kahn, O.; Lavigne, G. *Inorg. Chem.* **1979**, *18*, 3015–3020.
(35) Mikuriya, M.; Okawa, H.; Kida, S. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 2871–2877.
(36) Crawford, V. H.; Richardson, H. W.; Wasson, J. R.; Hodgson, D. J.; Hatfield, W. E. *Inorg. Chem.* **1976**, *15*, 2107–2110.

(37) (a) Girerd, J. J.; Kahn, O.; Verdaguer, M. *Inorg. Chem.* **1980**, *19*, 274–276. (b) Verdaguer, M.; Michalowicz, A.; Girerd, J. J.; Alberding, N.; Kahn, O. *Inorg. Chem.* **1980**, *19*, 3271–3279.
(38) (a) Nishida, Y.; Takeuchi, M.; Takahashi, K.; Kida, S. *Chem. Lett.* **1985**, 631–634. (b) McKee, V.; Zvagulis, M.; Reed, C. A. *Inorg. Chem.* **1985**, *24*, 2914–2919.
(39) (a) Kahn, O.; Sikorav, S.; Gouteron, J.; Jeannin, S.; Jeannin, Y. *Inorg. Chem.* **1983**, *22*, 2877–2883. (b) Sikorav, S.; Bkouche-Waksman, I.; Kahn, O. *Inorg. Chem.* **1984**, *23*, 490–495.
(40) Charlot, M. F.; Kahn, O.; Chaillet, M.; Larrieu, C. *J. Am. Chem. Soc.* **1986**, *108*, 2574–2581.
(41) Roundhill, S. G. N.; Roundhill, D. M.; Bloomquist, D. R.; Landee, C.; Willett, R. D.; Dooley, D. M.; Gray, H. B. *Inorg. Chem.* **1979**, *18*, 831–835.

ogenous bridging ligand. Preceding examples have concerned only single types of bridging networks; thus, in the present system, this feature appears as an intrinsic property and not as the result of a combination of factors.

Stepwise Metal-Assisted Conversion of η²-CSe₂ to η¹-Se₂CPEt₃, η²-Se₂CO, and η²-Se₂. Crystal Structures of the Complexes [(triphos)Rh(Se₂CO)]BPh₄·0.5CH₂Cl₂·0.5C₄H₉OH and [(triphos)Rh(μ-Se₂)₂Rh(triphos)](BPh₄)₂·2DMF [triphos = MeC(CH₂PPh₂)₃]

Claudio Bianchini,* Dante Masi, Carlo Mealli, Andrea Meli, Michal Sabat, and Francesco Vizza

The reaction of (triphos)RhCl(η²-CSe₂) (1) in CH₂Cl₂ with PEt₃ gives the phosphoniodiselenoformate complex (triphos)RhCl-(Se₂CPEt₃) (2). Compound 2 reacts at room temperature in CH₂Cl₂ solution with dioxygen to yield OPEt₃ and (triphos)-RhCl(Se₂CO) (3). The chloride ligand can be removed from 3 in CH₂Cl₂ by NaBPh₄ in 1-butanol to give the 16-electron complex [(triphos)Rh(Se₂CO)]BPh₄·0.5CH₂Cl₂·0.5C₄H₉OH (4), which photochemically or thermally undergoes the chelotropic elimination of CO to form the bis(μ-diselenium) complex [(triphos)Rh(μ-Se₂)₂Rh(triphos)](BPh₄)₂·2DMF (5b). The crystal structures of 4 and 5b have been determined by X-ray crystallography. 4 crystallizes in the triclinic system, space group P1̄, with *a* = 18.853 (6) Å, *b* = 16.744 (5) Å, *c* = 11.021 (3) Å, α = 69.45 (2)°, β = 81.23 (2)°, γ = 77.35 (2)°, and *Z* = 2. The structure was refined to an R factor of 0.071 (*R*ᵥ = 0.072) for 4093 unique reflections. The structure consists of monomeric complex cations [trip-hos)Rh(Se₂CO)]⁺, BPh₄⁻ anions, and some amount of CH₂Cl₂ and 1-butanol molecules of crystallization. The metal atom is five-coordinated by the three phosphorus atoms of triphos and by the two selenium atoms of the diselenocarbonate ligand in a distorted-square-pyramidal environment. 5b crystallizes in the triclinic system, space group P1̄, with *a* = 16.950 (5) Å, *b* = 13.710 (4) Å, *c* = 13.379 (4) Å, α = 90.19 (1)°, β = 98.53 (2)°, γ = 104.03(2)°, and *Z* = 1. The structure was refined to a final R factor of 0.053 (*R*ᵥ = 0.057) for 5458 unique reflections. The structure consists of binuclear [(triphos)Rh(μ-Se₂)₂Rh(triphos)]²⁺ cations, BPh₄⁻ anions, and DMF molecules of crystallization. The system consists of two (triphos)Rh(η²-Se₂) fragments related by a crystallographic inversion center. Each rhodium atom is coordinated by the three phosphorus atoms of triphos, an η²-diselenium molecule, and one selenium atom from the other (triphos)Rh(η²-Se₂) moiety.

Introduction

Over the past decade there has been increasing interest in metal complexes containing selenium ligands because of their implication in catalysis and biology and their potential application in organic and organometallic synthesis.[1–4] A large number of preparative routes have been developed to introduce selenium into a complex framework,[5,6] including the reaction of CSe₂ with metal frag-

ments.[7] This method is perhaps the most versatile and leads very frequently to η²-CSe₂ derivatives. The latter complexes exhibit a rich ligand-centered reactivity, which is mainly due to the dual nature of the metal–η²-CSe₂ moiety, i.e. electrophilic at the carbon atom and nucleophilic at the uncoordinated selenium atom.[7]

In this article we describe the stepwise metal-promoted transformation of the ligand CSe₂ within (triphos)RhCl(η²-CSe₂) (1) into a variety of selenium-containing species such as η¹-Se₂CPEt₃, η²-Se₂CO, and η²-Se₂ [triphos = MeC(CH₂PPh₂)₃]. The structure of the first metal diselenocarbonate [(triphos)Rh-(Se₂CO)]BPh₄·0.5CH₂Cl₂·0.5C₄H₉OH (4) and that of the di-selenium complex [(triphos)Rh(μ-Se₂)₂Rh(triphos)](BPh₄)₂·2DMF (5b) have been determined by X-ray methods. The latter complex is of particular interest because it exhibits a novel bonding mode of the diselenium unit.

A preliminary account of part of this work has already been published.[8]

Results and Discussion

Synthesis and Characterization of Se₂CPEt₃ and Se₂CO²⁻ Complexes. In previous MO studies on the bonding capabilities of heteroallene molecules,[9] we emphasized the percentage contribution of the heteroallene orbitals to the frontier orbitals as a very important tool to interpret the chemical reactivity. In

(1) Gates, B. C.; Katzer, J. R.; Schmit, G. C. A. *Chemistry of Catalytic Processes*; McGraw-Hill: New York, 1979.
(2) For a general view on selenium topics, see: Klayman, D. L.; Gunther, W. H. H. *Organic Selenium Compounds: Their Chemistry and Biology*; Wiley: New York, 1973.
(3) McCleverty, J. A. *Prog. Inorg. Chem.* **1968**, *10*, 49.
(4) Hoots, J. E.; Lesch, D. A.; Rachfuss, T. B. *Inorg. Chem.* **1984**, *23*, 3130 and references therein.
(5) For a general view on the synthesis of metal complexes containing selenium, see: Gysling, H. J. In *The Chemistry of Organic Selenium and Tellurium Compounds*; Patai, S., Rappaput, Z., Wiley: New York, 1986; Vol. 1, Chapter 16.
(6) (a) Farrar, D. H.; Grundy, K. R.; Payne, N. C.; Roper, W. R. *J. Am. Chem. Soc.* **1979**, *101*, 6577. (b) Brunner, H.; Wachter, J.; Wintergerst, H. *J. Organomet. Chem.* **1982**, *235*, 77. (c) Ginsberg, A. P.; Lindsell, W. E.; Sprinkle, C. R.; West, K. W.; Cohen, R. L. *Inorg. Chem.* **1982**, *21*, 3666. (d) Ginsberg, A. P.; Osborne, J. H.; Sprinkle, C. R. *Ibid.* **1983**, *22*, 1781. (e) Hoots, J. E.; Rauchfuss, T. B. *Ibid.* **1983**, *22*, 2806. (f) Goh, L. Y.; Wei, C.; Sinn, E. *J. Chem. Soc., Chem. Commun.* **1985**, 462. (g) Belin, C.; Makani, T.; Roziere, J. *Ibid.* **1985**, 118. (h) Gautheron, B.; Tainturier, G.; Pouly, S.; Theobald, F.; Viviev, H.; Laarif, A. *Organometallics* **1984**, *3*, 1495. (i) Benelli, C.; Di Vaira, M.; Noccioli, G.; Sacconi, L. *Inorg. Chem.* **1977**, *16*, 182. (j) Gautheron, B.; Tainturier, G.; Degrand, C. *J. Am. Chem. Soc.* **1985**, *107*, 5579. (k) Cecconi, F.; Ghilardi, C. A.; Midolini, S. *Inorg. Chem.* **1983**, *22*, 3802. (l) Bolinger, C. M.; Rauchfuss, T. B. *Inorg. Chem.* **1982**, *21*, 3947. (m) Hieber, H.; Gruber, J. *Z. Anorg. Allg. Chem.* **1958**, *296*, 91. (n) Herrmann, W. A.; Rohrmann, J.; Noth, H.; Nanila, Ch. K.; Bernal, I.; Draux, M. *J. Organomet. Chem.* **1985**, *284*, 189. (o) Kuhn, N.; Schumann, H. *J. Organomet. Chem.* **1985**, *287*, 345. (p) Bremer, G.; Boese, R.; Keddo, M.; Kruck, T. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1986**, *41B*, 981. (q) Dean, P. A. W.; Carson, G. K. *Can. J. Chem.* **1983**, *61*, 1800. (r) Kopf, H.; Klapotke, Z. *Naturforsch., B: Anorg. Chem., Org. Chem.* **1986**, *41B*, 971.

(7) (a) Kawakami, K.; Ozaki, Y.; Tanaka, T. *J. Organomet. Chem.* **1974**, *69*, 151. (b) Clark, G. R.; Grundy, K. R.; Harris, R. O.; James, S. M.; Roper, W. R. *Ibid.* **1975**, *90*, C37. (c) Roman, E.; Catheline, D.; Astruc, D. *Ibid.* **1982**, *236*, 229. (d) Roper, W. R.; Town, K. G. *Ibid.* **1983**, *252*, C97. (e) Werner, H.; Ebner, M. *Ibid.* **1983**, *258*, C52. (f) Bianchini, C.; Mealli, C.; Meli, A.; Sabat, M. *J. Chem. Soc., Chem. Commun.* **1984**, 1647. (g) Kolb, O.; Werner, H. *J. Organomet. Chem.* **1984**, *258*, 49. (h) Werner, H.; Ebner, M.; Bertleff, W. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1985**, *40B*, 1351.
(8) Bianchini, C.; Mealli, C.; Meli, A.; Sabat, M. *J. Am. Chem. Soc.* **1985**, *107*, 5317.
(9) (a) Mealli, C.; Hoffmann, R.; Stockis, A. *Inorg. Chem.* **1984**, *23*, 56. (b) Bianchini, C.; Masi, D.; Mealli, C.; Meli, A. *Ibid.* **1984**, *23*, 2838.