

stitution is small, since the solvation of the NH protons by 1,2-dichloroethane is weaker than that by nitrobenzene. Therefore, K_a of the N,N' -dmen complex in 1,2-DCE becomes smaller compared to that of the en complex, in contrast to the result in PhNO_2 . Thus, the K_a values of the chelate electrolyte in 1,2-DCE decrease with the decrease in the number of NH protons, monotonously.

In conclusion, the difference in the conductance behavior of $[\text{Co}(\text{acac})_2(\text{diamine})]\text{ClO}_4$ in PhNO_2 and 1,2-DCE can be interpreted in terms of specific ion-solvent interactions involving hydrogen bonding through the NH protons, its activation by the introduction of the N -methyl groups in PhNO_2 , and the π - π interaction between the bpy ligand and nitrobenzene molecules. Particularly, the difference in both solvents could be monitored from mobility data.

Acknowledgment. The author expresses his deep gratitude to Professor Yuroku Yamamoto of Hiroshima University and Dr. Etsuro Iwamoto for helpful discussions in the course of

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Registry No. $[\text{Co}(\text{acac})_2(\text{en})]\text{ClO}_4$, 15611-02-6; $[\text{Co}(\text{acac})_2(\text{pn})]\text{ClO}_4$, 86647-00-9; $[\text{Co}(\text{acac})_2(N,N\text{-dmen})]\text{ClO}_4$, 86647-02-1; $[\text{Co}(\text{acac})_2(N,N'\text{-dmen})]\text{ClO}_4$, 86647-04-3; $[\text{Co}(\text{acac})_2(N,N,N'\text{-trimen})]\text{ClO}_4$, 86647-06-5; $[\text{Co}(\text{acac})_2(N,N,N',N'\text{-tmen})]\text{ClO}_4$, 22732-31-6; $[\text{Co}(\text{acac})_2(2\text{-ampy})]\text{ClO}_4$, 86647-08-7; $[\text{Co}(\text{acac})_2(\text{bpy})]\text{ClO}_4$, 14896-36-7; $[\text{Co}(\text{acac})_2(\text{en})]\text{I}$, 76377-41-8; $[\text{Co}(\text{acac})_2(\text{pn})]\text{I}$, 86647-09-8; $[\text{Co}(\text{acac})_2(\text{bpy})]\text{I}$, 14651-98-0; PhNO_2 , 98-95-3; $[\text{Co}(\text{acac})_2(\text{en})]^+$, 46934-01-4; $[\text{Co}(\text{acac})_2(\text{pn})]^+$, 64234-29-3; $[\text{Co}(\text{acac})_2(N,N\text{-dmen})]^+$, 86647-01-0; $[\text{Co}(\text{acac})_2(N,N,N'\text{-trimen})]^+$, 86647-05-4; $[\text{Co}(\text{acac})_2(N,N,N',N'\text{-tmen})]^+$, 47245-76-1; $[\text{Co}(\text{acac})_2(2\text{-ampy})]^+$, 86647-07-6; $[\text{Co}(\text{acac})_2(\text{bpy})]^+$, 47515-61-7; $[\text{Co}(\text{acac})_2(N,N'\text{-dmen})]^+$, 86647-03-2; 1,2-dichloroethane, 107-06-2.

Supplementary Material Available: Tables of chemical analysis for $[\text{Co}(\text{acac})_2(\text{diamine})]\text{X}$ and the equivalent conductance data at various concentrations of the salts employed (6 pages). Ordering information is given on any current masthead page.

Contribution from the Laboratoire de Spectrochimie des Eléments de Transition, ERA No. 672, Université de Paris Sud, 91405 Orsay, France, and Laboratoire de Chimie des Métaux de Transition, ERA No. 608, Université Pierre et Marie Curie, 75232 Paris, France

Crystal Structure and Magnetic Properties of $(\mu\text{-Azido})(\mu\text{-hydroxo})\text{bis}[(N,N,N',N'\text{-tetramethylethylenediamine})\text{copper(II)}]\text{Perchlorate}$, a Copper(II) Dinuclear Complex with a Large Ferromagnetic Interaction

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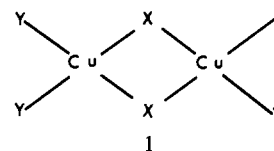
The title compound has been synthesized and its structure has been solved at room temperature. It crystallizes in the tetragonal system, space group $P4_2/mnm$. Its lattice constants are $a = b = 9.50 \pm 0.02 \text{ \AA}$ and $c = 13.94 \pm 0.03 \text{ \AA}$ with $Z = 2$. The structure consists of $[\text{Cu}_2(\text{tmen})_2(\text{N}_3)(\text{OH})]^{2+}$ dinuclear cations and perchlorate anions. In each cationic unit, the copper(II) ions are four-coordinated with planar surroundings; they are bridged by an azido group in an end-on fashion and by a hydroxo group. The bridging network is disordered. The $\text{Cu}-\text{N}_{\text{P}_1}$ distance is $1.960(9) \text{ \AA}$, and the $\text{Cu}-\text{N}_{\text{P}_1}-\text{Cu}$ angle is $99.4(6)^\circ$, N_{P_1} being the $\text{N}_{0.5}\text{O}_{0.5}$ composite bridging atom. The magnetic properties of the title compound have been investigated in the 2-300 K temperature range. $\chi_{\text{M}}T$, the product of the molar magnetic susceptibility and the temperature, is equal to $1.02 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 295 K, increases up to $1.15 \pm 0.02 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 150 K, and then remains constant down to 20 K. This behavior shows that the ground state is the spin triplet and that the excited spin singlet state is so high in energy that it is only weakly populated, even at room temperature. This singlet-triplet energy gap is estimated to be larger than 200 cm^{-1} . The specific ability of the end-on azido bridge to favor the triplet state in dinuclear copper(II) complexes is emphasized. An interpretation based on a spin polarization effect is proposed. The magnetic properties of the title compound are compared to those of $[\text{Cu}(\text{tmen})(\text{N}_3)_2]_2$, where the two copper(II) ions are noncoupled.

Introduction

Until now, two strategies have been described to achieve a ferromagnetic interaction between two metal ions belonging to the same molecular entity, namely the strict orthogonality or the accidental orthogonality of the magnetic orbitals.²

The strict orthogonality occurs when the magnetic orbitals around a metal center transform as the Γ_i irreducible representations of the molecular symmetry group, and the magnetic orbitals around the other metal center transform as Γ_j with $\Gamma_i \neq \Gamma_j$ for any i and j . These conditions are realized in $\text{Cu}^{\text{II}}\text{VO}^{\text{III}}$ and $\text{Cu}^{\text{II}}\text{Cr}^{\text{III}}$ heterobinuclear complexes.^{2,3} The accidental orthogonality between two magnetic orbitals ϕ_A and ϕ_B of the same symmetry, characterized by $\langle \phi_A | \phi_B \rangle = 0$, can occur for very peculiar values of the structural parameters.

In this case, around each bridge, the positive lobes of the overlap density $\rho(i) = (\phi_A(i))(\phi_B(i))$ exactly compensate the negative lobes.⁴ It has been shown that this accidental orthogonality could be realized in planar dinuclear copper(II) complexes like 1.⁴⁻⁷ Thus, when Y is a nitrogen atom of a



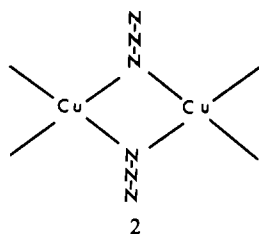
diamine and X is the hydroxo group, the accidental orthogonality is expected for a value of the bridging angle close to 90° .

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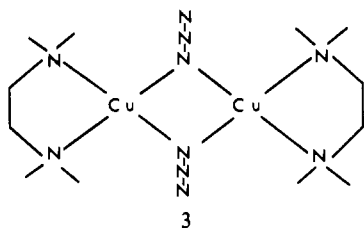
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Experimentally, for Cu–O–Cu < 97.5°, the ground state is actually a triplet state. In principle, the accidental orthogonality is destroyed by a small structural change like a modification of the value of the bridging angles. This is observed in the bis(μ -hydroxo) copper(II) complex where, for Cu–O–Cu > 97.5°, the singlet state is lower in energy.⁶ For instance, in [Cu(tmen)(OH)]₂(ClO₄)₂, the value of Cu–O–Cu is 101.6° and the energy gap between singlet ground state and triplet state is ca. 360 cm⁻¹.^{6,8} A crossover between singlet and triplet states has also been observed in series of bis(μ -chloro) copper(II) species.^{9–10}

Recently, we have described a bis(μ -azido) copper(II) complex of formula [Cu₂(N₃)₄(C₁₆H₃₄N₂O₆)(H₂O)] where the azido ligands bridge in an end-on fashion as shown in 2.¹¹ The



average value of Cu–N–Cu is 103.55°, and the ground state is the triplet state with $J = 70 \pm 20$ cm⁻¹. We wanted to know whether, in μ -azido (end-on) complex, the coupling could be antiferromagnetic, and for that we endeavored to synthesize new complexes of this kind. Trying to prepare 3, we actually



obtained the title compound with mixed bridges, of formula [Cu₂(tmen)₂(N₃)(OH)](ClO₄)₂. In this paper, we describe its crystal structure and its magnetic properties. This study led to a quite spectacular result. Not only is the ground state a triplet state but also the excited singlet state is so high in energy that it is almost depopulated, even at room temperature. To explain the specific ability of the end-on azido bridge to favor the triplet state, we shall introduce the concept of spin polarization.

In this paper, we shall also compare the title compound to another dinuclear copper(II) compound obtained in the same synthesis process, of formula [Cu(tmen)(N₃)₂]₂ where, in contrast, the interaction between the copper(II) ions is negligible.¹³

Experimental Section

Synthesis. A 369-mg (10⁻³ mol) amount of copper(II) perchlorate and 116 mg (10⁻³ mol) of tmen (=tetramethylethylenediamine) were

dissolved in 10 mL of water. Then, a solution of 65 mg (10⁻³ mol) of NaN₃ dissolved in 5 mL of water was added. After a few seconds, [Cu(tmen)(N₃)₂] precipitated (about 60 mg). The solution was then filtered, and [Cu₂(tmen)₂(N₃)(OH)](ClO₄)₂, which is much more soluble, was obtained as well-shaped dark blue single crystals by slow evaporation. Anal. Calcd for C₁₂H₃₃N₇O₉Cl₂Cu₂: C, 23.34; H, 5.39; N, 15.88; Cl, 11.48; Cu, 20.58. Found: C, 23.48; H, 5.36; N, 15.80; Cl, 11.52; Cu, 20.5. [Cu(tmen)(N₃)₂]₂ was more conveniently obtained by using 2 times the above amount of NaN₃ (130 mg, 2 × 10⁻³ mol), as described elsewhere.¹³

Crystallographic Data Collection and Refinement of the Structure.

The air-stable crystal selected for X-ray analysis had roughly a parallelepipedal shape with 1 × 0.48 × 0.15 mm dimensions. Preliminary Laue and precession photographs led to a tetragonal unit cell with $a = b = 9.50 \pm 0.02$ Å, $c = 13.94 \pm 0.03$ Å, and $Z = 2$ dinuclear units. ρ_{meas} (floatation in a chlorobenzene/1,2-dibromoethane mixture) = 1.65 g cm⁻³, and ρ_{calcd} = 1.63 g cm⁻³, with $V = 1258$ Å³. Three space groups were possible from systematic absences: centrosymmetric $P4_2/mnm$ and noncentrosymmetric $P4n2$ or $P4_2nm$. Statistical tests of MULTAN suggested $P4_2/mnm$. The conditions of intensity data collection were as follows: diffractometer, laboratory-made automatic three-circle diffractometer; radiation, Mo K α ; Monochromator, graphite monochromator set in front of the counter; 2θ range, 3.0–54.0°; scan type, coupled θ (crystal)– 2θ (counter); scan speed, 1.5° min⁻¹; scan range, $(1.6 + 0.345 \tan \theta)^\circ$; background, stationary crystal, stationary counter, at beginning and end of scan, each of one-seventh of the scan time; reflections collected, 731 independent, at room temperature; standard reflections, 505 and 040 every 50 reflections.

The intensities were corrected for Lorentz–polarization. The absorption coefficient was equal to 19.2 cm⁻¹; corrections were calculated and intensities corrected, and transmission factors varied from 0.40 to 0.74. For every observed structure factor F_o , a standard deviation σ was computed: $\sigma = F_o(\Delta C)/2C$, where C is the integrated intensity and ΔC the error. A total of 168 reflections for which integrated intensities were lower than 3σ were excluded. Atomic form factors were taken from ref 12b Tables for all the atoms. Refinements were carried out with the SHELX 76 computing program, which minimizes the R_w factor

$$R_w = \left[\sum_i (w_i |F_o - F_c|^2) / \sum_i (w_i F_o^2) \right]^{0.5}$$

where w is $1/\sigma$. A three-dimensional Patterson map showed copper and chlorine atoms. Refinement of their coordinates gave $R = 0.31$. Successive Fourier syntheses and refinements dropped R to 0.218 with isotropic temperature factors and to 0.117 with anisotropic temperature factors. It must be pointed out that refinement was possible only by constraining several interatomic distances: Cl–O (1.40 Å) and O–O (2.26 Å) in the ClO₄⁻ anion, N–CH₃ (1.47 Å) and N–CH₂ (1.47 Å) in the ligand tmen. All these constraints were then released at the end of the refinement.

Introduction of hydrogen atoms coordinates led to $R = 0.110$. Fourteen reflections for which $|F_o - F_c|/\sigma$ was higher than 3 were excluded from refinement. A secondary extinction factor was introduced and refined: R dropped to 0.095. At this stage, it must be pointed out that the carbon atoms of the CH₂ groups (x, x, z positions) appeared in the mirror plane from the Fourier synthesis, with a CH₂–CH₂ distance of 1.30 Å. This unrealistic result clearly revealed that the CH₂ groups, and consequently also the CH₃ groups, were disordered. In the following, we took into account this disorder by considering that the CH₂ groups were shifted away from mirror plane. Several trials were carried out, with the coordinates of the CH₂ carbon atoms fixed at six different values from which the CH₃ carbon coordinates were computed in each case with use of a nitrogen tetrahedral surrounding and a 1.47 Å C–N distance. By an increase of the distance of CH₂ from the crystallographic mirror plane, R_w decreased down to a significant minimum of 0.063 and the CH₂–CH₂ distance then was 1.51 ± 0.01 Å. Moreover, when one looks at the carbon thermal ellipsoid of CH₂ group when it was in the mirror plane, the longest axis was perpendicular to this plane, which supported the assumption of a disorder. When CH₂ was out of the mirror plane, the volume of the thermal ellipsoid was decreased by 19% and its longest axis was no longer oriented perpendicular with regard to the mirror plane.

Final factors are as follows: nonweighted R (excluding zeros), 0.0862; weighted R (excluding zeros), 0.0563; $F(000) = 628$. The atomic parameters are given in Table I and the anisotropic thermal parameters in Table II.

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Table I. Atomic Coordinates^a

atom	x/a	y/b	z/c
Cu	0.1112 (1)	0.1112 (1)	0.0000
Cl	0.7457 (3)	-0.7457 (3)	0.0000
O ₃	0.683 (2)	-0.683 (2)	-0.072 (2)
O ₁	0.888 (1)	-0.7168 (9)	0.0000
N	0.2232 (6)	0.2232 (6)	0.0982 (9)
Np ₁	0.0000	0.0000	-0.091 (1)
Np ₂	0.0000	0.0000	-0.176 (3)
Np ₃	0.0000	0.0000	-0.260 (3)
CH ₃	0.1270	0.2790	0.1710
CH ₃ *	0.3270	0.1307	0.1440
CH ₂	0.2950	0.3390	0.0500

^a Standard deviations in the least significant figures are given in parentheses.

Magnetic Measurements. These were carried out with a Faraday type magnetometer equipped with a helium continuous-flow cryostat working in the temperature range 2–300 K. Two samples of the title compound and one sample of [Cu(tmen)(N₃)₂]₂ were studied. These samples weighing about 6 mg were prepared with crystals carefully picked up under a binocular lens and slightly broken to avoid the anisotropy. Independence of the magnetic susceptibility vs. the magnetic field was checked at both room temperature and 4.2 K. Mercury tetrakis(thiocyanato)cobaltate was used as a susceptibility standard. Diamagnetism corrections were estimated at $-252 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ for the title compound and $-234 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ for [Cu(tmen)(N₃)₂]₂.

Description of the Structures

The unit cell for the title compound contains two dinuclear [Cu₂(tmen)₂(N₃)(OH)]²⁺ cations and four perchlorate anions. The copper(II) environment is planar; each copper atom is coordinated to the two nitrogen atoms of tmen and to two bridging atoms. The centrosymmetric *P4₂/mnm* space group involves a composite N_{0.5}O_{0.5} atom, denoted Np₁, as bridging atom. The metal-bridging atom distance is then found to be equal to 1.960 (9) Å, and the bridging angle is found to be equal to 99.4 (6)°. With such a space group, a crystallographic inversion center relates the two parts of each dinuclear unit. A perspective view of this unit, with and without the disorder in the bridging network, is shown in Figure 1. Main interatomic distances and bond angles are given in Table III.

The symmetrical bridge may be questioned. Many attempts were carried out in the *P4₂nm* group, which involves an asymmetrical double bridge, i.e. Cu–N₃–Cu on one side and Cu–OH–Cu on the other side. These refinements did not converge. In *P4₂/mnm*, either the crystal contains a mixture of N₃⁻ double-bridged units and of OH⁻ double-bridged units or it contains disordered asymmetrical N₃⁻–OH⁻ mixed-bridge units. In the first case, the composition of the mixture can be refined and there is no reason to find exactly a 50%–50% mixture. Five refinements were carried out with different occupation factors for the bridging atoms. The *R* minimum

Table II. Atomic Thermal Parameters^a

atom	B ₁₁	B ₂₂	B ₃₃	B ₁₂	B ₁₃	B ₂₃
Cu	4.16 (5)	4.16 (5)	6.54 (9)	-0.75 (7)	0.0000	0.0000
Cl	4.7 (1)	4.7 (1)	17.3 (5)	0.0 (1)	0.0000	0.0000
O ₃	21.1 (11)	21.1 (11)	18.3 (15)	0.0000	3.8 (27)	3.8 (27)
O ₁	5.0 (5)	5.1 (4)	50.2 (28)	-0.2 (4)	0.0000	0.0000
N	7.4 (3)	7.4 (3)	7.7 (7)	-2.7 (4)	-0.0 (3)	-0.0 (3)
Np ₁	7.8 (4)	7.8 (4)	5.5 (7)	0.0000	0.0000	0.0000
Np ₂	6.3 (9)	6.3 (9)	5.8 (18)	0.0000	0.0000	0.0000
Np ₃	14.6 (19)	14.6 (19)	6.5 (21)	0.0000	0.0000	0.0000
CH ₃	27.0 (62)	22.7 (40)	12.8 (23)	-3.5 (43)	-5.2 (33)	-10.9 (27)
CH ₃ *	12.0 (16)	9.2 (15)	24.5 (36)	-3.1 (14)	-13.2 (22)	-0.3 (20)
CH ₂	7.8 (11)	7.2 (8)	13.8 (14)	-0.2 (10)	-2.6 (8)	-1.7 (8)

^a The anisotropic thermal parameters have units of Å². They enter the expression for the structure factor in the form $\exp[-0.25 \cdot (B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + B_{12}hka^*b^* + 2B_{23}klb^*c^* + 2B_{13}hla^*c^*)]$. Standard deviations in the least significant figures are given in parentheses.

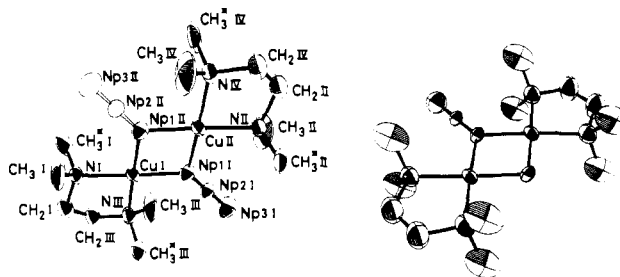
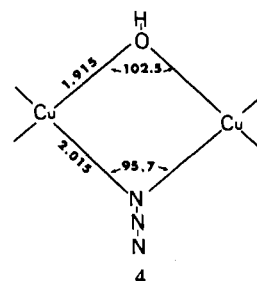


Figure 1. Left: Perspective view of the structure of the [Cu₂(tmen)₂(N₃)(OH)]²⁺ cation with the disorder on the bridges. Right: Perspective view of the structure without the disorder.

value rigorously corresponds to 50% oxygen and 50% nitrogen. Thus, the bridging network is mixed and the dinuclear unit has to be formulated as [Cu₂(tmen)₂(N₃)(OH)]²⁺. This unit is disordered, and each bridge crystallographically appears as an average between end-on N₃⁻ and OH⁻. In the related bis(μ-hydroxo) complex [Cu(tmen)(OH)]₂(ClO₄)₂, the Cu–O bridging distances⁸ are 1.897 and 1.931 Å; the average is 1.914 Å. In the recently described [Cu₂(N₃)₄(C₁₆H₃₄N₂O₆)(H₂O)], a dinuclear copper(II) cryptate with two end-on azido bridges,¹¹ the average Cu–N bridging distance is 2.013 Å. For our compound, a refinement was carried out by keeping constant the z coordinates of the bridging N and O atoms. The starting positions of the copper atoms were such that Cu–O = 1.91 Å and Cu–N = 2.01 Å. After three least-squares cycles of refinement, the bridging distances and angles were found as Cu–O = 1.915 (1) Å, Cu–N = 2.015 (1) Å, Cu–O–Cu = 102.5 (1)°, and Cu–N–Cu = 95.7 (1)°. The actual uncertainties in these lengths and angles are likely much larger than the error values, which are biased by the chosen model for this refinement. It follows that the geometry of the double-bridged network in [Cu₂(tmen)₂(N₃)(OH)](ClO₄)₂ is likely close to that shown in 4. Concerning the perchlorate anions, an

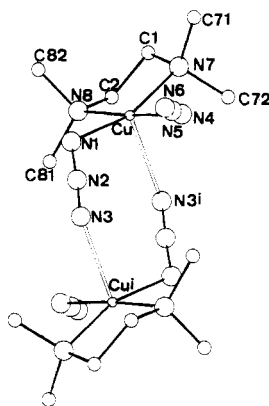


oxygen atom of each ClO₄⁻ group is located in the apical position with regard to the planar copper environment with a copper–oxygen distance of 2.68 (1) Å. The copper atom strictly remains in the basal plane, suggesting a negligible copper–perchlorate interaction.^{12a}

Table III. Main Interatomic Distances (Å) and Bond Angles (deg)^a

Copper Environment			
Cu-N	2.03 (1)	Cu-N _{P₁}	1.960 (9)
N _{P₁} -Cu-N _{P₁}	80.6 (6)	N-Cu-N _{P₁}	97.4 (6)
N-Cu-N	84.6 (6)		
Double Bridge			
N _{P₁} -N _{P₂}	1.18 (3)	Cu-Cu	2.988 (3)
N _{P₂} -N _{P₃}	1.17 (4)		
Cu-N _{P₁} -Cu	99.4 (6)	Cu-N _{P₁} -N _{P₂}	130.3 (3)
Ligand			
N-CH ₂	1.46 (1)	N-CH ₃ [*]	1.467 (5)
N-CH ₃	1.465 (9)	CH ₂ -CH ₂	1.51 (fixed)
Cu-N-CH ₂	109.2 (7)	CH ₂ -N-CH ₃	109.8 (3)
Cu-N-CH ₃	109.2 (4)	CH ₂ -N-CH ₃ ^{*b}	109.8 (4)
Cu-N-CH ₃ ^{*b}	109.3 (3)	CH ₃ -N-CH ₃ ^{*b}	109.5 (8)
Perchlorate Anion			
Cl-O ₁	1.38 (1)	Cl-O ₃	1.31 (2)
Cl-O ₂		Cl-O ₄	
O ₁ -Cl-O ₃	111.0 (6)	O ₃ -Cl-O ₄	99 (2)
O ₁ -Cl-O ₂	112.6 (8)		

^a Standard deviations in the least significant figures are given in parentheses. ^b Starred atoms as shown in Figure 1.

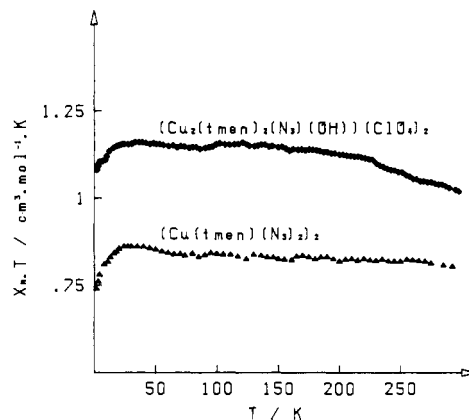
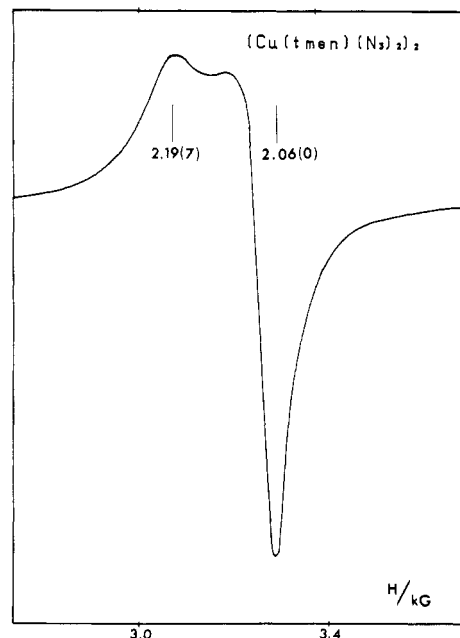
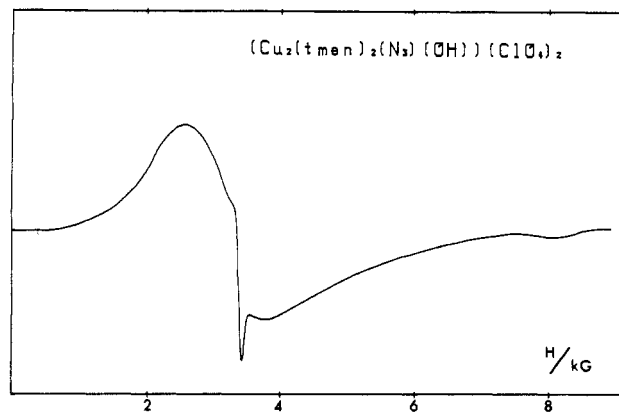
Figure 2. View of the structure [Cu(tmen)(N₃)₂]₂.

The structure of [Cu(tmen)(N₃)₂]₂, described elsewhere,¹³ is recalled in Figure 2. It consists of centrosymmetric dimeric units with two asymmetric end-to-end azido bridges. Each copper(II) ion is five-coordinated in the form of a slightly distorted square-based pyramid, CuN₅. The apical position is occupied by a nitrogen atom of the azido bridge with a Cu-N apical bond of 2.456 (6) Å. The Cu-N bond distance with the azido bridge in the basal plane is 1.979 (5) Å. The intradimer Cu...Cu distance is 5.004 (2) Å.

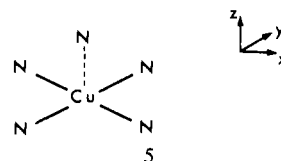
Magnetic Properties

The magnetic behavior of [Cu₂(tmen)₂(N₃)(OH)]ClO₄ and [Cu(tmen)(N₃)₂]₂ is shown in Figure 3 in the form of the variation of $\chi_M T$ vs. the temperature T , χ_M being the molar magnetic susceptibility for the dinuclear unit. At first glance, the curves of Figure 3 are not spectacular. In fact, the magnetic data for [Cu₂(tmen)₂(N₃)(OH)]ClO₄ reveal a quite unusual situation.

Let us start with [Cu(tmen)(N₃)₂]₂. $\chi_M T$ is nearly constant and equal to $0.85 \pm 0.02 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ in the whole temperature range down to 15 K and then slightly decreases. This Curie constant corresponds to two noncoupled copper(II) ions with an average g factor of 2.13 ($\chi_M T = N\beta^2 g^2 / 2k$). The EPR spectrum of this compound, shown in Figure 4, is typical of a noncoupled copper(II) ion in an axially elongated tetragonal surrounding with $g_{\parallel} = 2.19(7)$ and $g_{\perp} = 2.06(0)$. The average g value is then 2.10(7), in satisfying agreement with the value deduced from the magnetic data. The interpretation of the absence of interaction is straightforward. Let us define

Figure 3. Temperature dependence of $\chi_M T$ for [Cu₂(tmen)₂(N₃)(OH)]ClO₄ and [Cu(tmen)(N₃)₂]₂.Figure 4. X-Band EPR spectra of powdered samples of [Cu₂(tmen)₂(N₃)(OH)]ClO₄ and [Cu(tmen)(N₃)₂]₂.

the reference drawn in 5 for each CuN₅ chromophore, where the apical position is occupied by the terminal atom of a semibringing azido group.



Each magnetic orbital is of the d_{xy} type with a small admixture of d_{z^2} . It follows that the two magnetic orbitals are essentially localized in parallel planes separated by more than 5 Å. Such a relative orientation is particularly unfavorable for the interaction. The overlap density between the magnetic orbitals is negligible in any point of the space. A quite similar situation has been recently described.¹¹

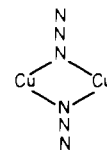
Concerning [Cu₂(tmen)₂(N₃)(OH)](ClO₄)₂, $\chi_M T$ is equal to 1.02 cm³ mol⁻¹ K at room temperature, then very smoothly increases when the complex cools down, reaches a plateau around 150 K with $\chi_M T = 1.15 \pm 0.02$ cm³ mol⁻¹ K, is nearly constant down to about 20 K, and finally decreases when the complex is cooled down to pumped liquid-helium temperature to reach 1.10 cm³ mol⁻¹ K at 2 K. We can notice first that this behavior rules out the hypothesis of a mixture of N₃⁻ double-bridged units and OH⁻ double-bridged units. Indeed, the bis(μ -hydroxo) dimer with bridging angles of 102.5° would be strongly antiferromagnetically coupled ($J \approx -370$ cm⁻¹ from ref 6) and whatever the sign and the magnitude of the interaction in the bis(μ -azido) dimer may be, the resulting magnetic curve would be completely different from that shown in Figure 3. The quasi Curie law exhibited by the compound corresponds neither to two noncoupled copper(II) ions nor to accidentally degenerate singlet and triplet states ($J = 0$). Indeed, the average values of the g factor for each doublet state in the former case and for the triplet state in the latter case would be 2.51 ($\chi_M T = N\beta^2 g^2 / 2k$), which is a quite unrealistic value. Therefore, the magnetic behavior corresponds to a triplet ground state very separated in energy from the excited singlet state. The plateau for $\chi_M T$ is obtained in the temperature range where only the ground state is significantly populated. The average value of the g factor for the triplet state can be deduced from the value of the plateau ($\chi_M T = 2N\beta^2 g^2 / 3k$). This gives $g = 2.14$, which is now a reasonable value. The magnetic data at the very low temperatures may be influenced by the combined effect of the zero-field splitting of the triplet ground state and the intermolecular interactions.

The situation encountered in [Cu₂(tmen)₂(N₃)(OH)](ClO₄)₂ with a triplet ground state and the large singlet-triplet separation J is quite interesting from a conceptual viewpoint but is also the worst situation to determine accurately the energy gap J from the magnetic data. We already emphasized that, in copper(II) dinuclear species, the theoretical variation of the magnetic susceptibility is much more sensitive to small changes of J for negative J (singlet ground state) than for positive J (triplet ground state).¹¹ Our opinion is that many authors have overestimated the accuracy of the J values deduced from magnetic data in the case of ferromagnetic coupling. This is particularly true when J is so large that the singlet excited state is only weakly populated even at room temperature. In the present case, we are unable to propose a J value from the magnetic data. We can only give a lower limit by comparing these data with the theoretical expression: $\chi_M T = 2N\beta^2 g^2 / (k(T - \Theta)) [3 + \exp(-J/kT)]^{-1}$ where the Θ Weiss correction accounts for intermolecular effects. J is certainly larger than 200 cm⁻¹.

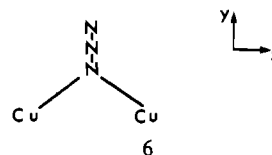
The X-band EPR of a powdered sample of [Cu₂(tmen)₂(N₃)(OH)](ClO₄)₂ at 4.2 K, shown in Figure 4, is badly resolved. It exhibits a very broad feature centered at 3120 G ($g = 2.17$) and a much smaller feature near 8000 G. In addition, a sharp feature at 3200 G is most likely due to a dilute copper(II) impurity. When the sample is heated up, the intensity of the spectrum quickly diminishes. Above 100 K, only the signal due to the impurity remains detectable. The poor quality of this spectrum precludes a more thorough investigation.

Discussion: Spin Polarization in μ -Azido Copper(II) Complexes

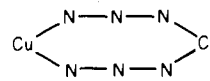
To the best of our knowledge, only one dinuclear copper(II) complex with end-on azido ligands has already been structurally characterized¹¹ with a



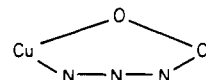
bridging network located inside a cryptate cavity. The average value of the Cu-N bridging distances is 2.013 Å, and the average value of the Cu-N-Cu bridging angle is 103.55°. The magnetic properties of this copper(II) cryptate have revealed that the ground state was a triplet state with a singlet-triplet separation of 70 ± 20 cm⁻¹. A weak stabilization of the triplet state has already been reported for [Cu(acac)(N₃)₂]₂, where end-on bridging azido groups were postulated.¹⁴ End-on azido bridges have also been found in copper(II) azides with complicated polymeric structures.¹⁵⁻¹⁷ In [Cu₂(tmen)₂(N₃)(OH)](ClO₄)₂, with one end-on azido bridge, the triplet state is again stabilized with regard to the singlet state. In a forthcoming paper, we shall describe a new bis(μ -azido)-(end-on) copper(II) dimer with a triplet ground state and a large singlet-triplet energy gap. The question at hand is *why the end-on azido bridge has such an ability to stabilize the triplet state in structures like 6*. The problem appears



fascinating when realizing that the symmetrical end-to-end azido bridge has exactly the opposite ability; it strongly stabilizes the singlet state. Two copper(II) complexes of this kind have already been described.¹⁸ The first one contains the planar



network inside a cryptate cavity;¹⁹ the second one contains a nearly planar



network with the oxygen atom belonging to an alkoxide bridge.²⁰ Both complexes are diamagnetic. The comparison between this second complex and [Cu₂(tmen)₂(N₃)(OH)]²⁺

(14) Barroclough, C. G.; Brookes, R. W.; Martin, R. L. *Aust. J. Chem.* **1974**, *27*, 1843.

(15) Agrell, I. *Acta Chem. Scand.* **1966**, *20*, 1281; **1967**, *21*, 2647.

(16) Agrell, I.; Lamnevik, S. *Acta Chem. Scand.* **1968**, *22*, 2038.

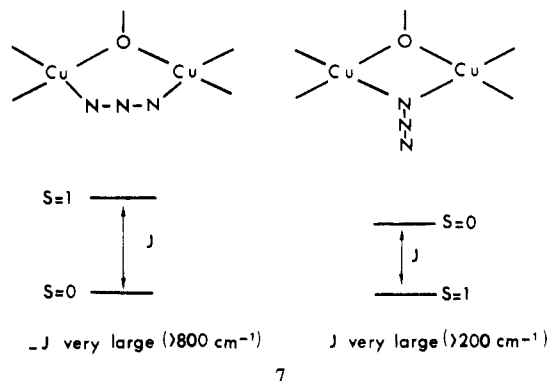
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(18) Drew, G. B.; McCann, M.; Nelson, S. M. *J. Chem. Soc., Chem. Commun.* **1979**, 481. The μ -azido binuclear macrocyclic copper(II) complex described here does not enter in the frame of this comparison. Indeed, the two terminal nitrogen atoms of the bridging azido group occupy the apical positions around the copper(II) ions in distorted square-pyramidal environments, with rather long Cu-N distances (2.25 (2) and 2.20 (3) Å). It follows that N₃⁻ is perpendicular to the basal planes in which the magnetic orbitals are localized.

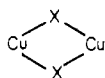
(19) Agnus, Y.; Louis, R.; Weiss, R. *J. Am. Chem. Soc.* **1979**, *101*, 3381.

(20) McKee, V.; Dagdigian, J. V.; Bau, R.; Reed, C. A. *J. Am. Chem. Soc.* **1981**, *103*, 7000.

is particularly spectacular since they differ essentially by the way the azido group bridges. This comparison is specified in 7. We have recently attributed the ferromagnetic interaction



in $[\text{Cu}_2(\text{N}_3)_4(\text{C}_{16}\text{H}_{34}\text{N}_2\text{O}_6)(\text{H}_2\text{O})]$ to the accidental orthogonality of the xy -type magnetic orbitals.¹¹ More generally, in a



bridging network, this orthogonality occurs for a value of the Cu-X-Cu bridging angle close to 90° when X is very electronegative. When X is made less electronegative, the orthogonality is realized for larger values of Cu-X-Cu. An extended Hückel-type calculation had shown that the orthogonality was expected for Cu-X-Cu = 103° when X = N_3 . In $[\text{Cu}_2(\text{N}_3)_4(\text{C}_{16}\text{H}_{34}\text{N}_2\text{O}_6)(\text{H}_2\text{O})]$, the average value of the bridging angle is effectively close to 103° . However, it seems that, whatever the value of Cu-N-Cu may be, an end-on azido bridge leads to a ferromagnetic interaction. In the title compound, Cu-N-Cu is about 95.7° . Moreover, the hydroxo bridge is such that Cu-O-Cu = 101.6° , a value which should favor an antiferromagnetic interaction. In our previous paper on the azido bridges,¹¹ we made an observation that could explain this behavior of the end-on azido group: for any Cu-N-Cu value in the range 90 – 110° , the splitting Δ between the two molecular orbitals built from the xy -type magnetic orbitals, as determined by extended Hückel calculation, remained very weak, in contrast with what is observed for X = OH. In the orbital model of the exchange interaction we have proposed,^{2,4} the J singlet-triplet energy gap in copper(II) dimers is expressed as the sum of two antagonistic contributions J_{AF} and J_{F} favoring the antiferromagnetic and the ferromagnetic interactions, respectively, according to

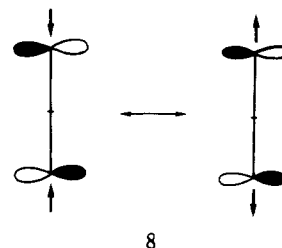
$$J = J_{\text{AF}} + J_{\text{F}} \quad J_{\text{AF}} = -2\Delta S \quad J_{\text{F}} = 2C \quad (1)$$

where S is the overlap integral and C the two-electron exchange integral between the magnetic orbitals. If Δ remains very weak whatever the value of Cu-N-Cu may be, the antiferromagnetic contribution is also very weak and never compensates for the ferromagnetic contribution.

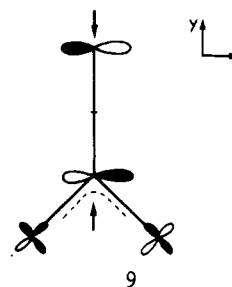
At this stage of the discussion, we could conclude that we have justified in a satisfying way the ability of the end-on azido bridge to stabilize the triplet state. In fact, we have the feeling that another factor, more striking, occurs in addition to the already presented factors, namely the *spin polarization*.²¹

In this paper, we restrict ourselves to some qualitative considerations on the spin polarization by the azido bridges. The *ab initio* calculation of the electronic structure of N_3^- has shown that, in the $^1\Sigma_g^+$ ground state, the highest occupied level

$(\pi_g)^4$ was very separated in energy from the level located immediately below. The energy gap is 6.68 eV (ca. $54\,000\text{ cm}^{-1}$).²² Thus, the π_g^x molecular orbital (MO) in the plane of the bridging network (see 6) plays a dominant role in the interaction between the copper(II) ions through the azido bridge. At a given instant, in π_g^x , an electron with the α spin is localized around one of the terminal nitrogen atoms and the other electron with the β spin is localized around the other terminal atom as shown in 8. When N_3^- bridges in an end-on

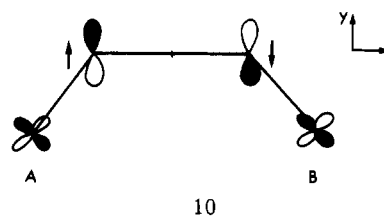


fashion, the electron on the bridging nitrogen (e.g. with the α spin) is partially delocalized toward the d_{xy} metallic orbitals in a bonding MO schematized in 9. This delocalization is



a function of the overlap $\langle (d_{xy})_{\text{Cu}} | (p_x)_{\text{N}} \rangle$ and of the energy gap between d_{xy} and π_g . It gives an instantaneous density of the α spin in each of the two d_{xy} metal orbitals. Therefore, each unpaired electron localized in its magnetic orbital with a preponderant metallic character will have a probability of β spin larger than 0.5. This favors the triplet state.

One can notice that the same phenomenon of spin polarization with an end-to-end azido bridge favors the singlet state. Indeed, π_g^y gives the bonding MO shown in 10. If an α



electron is partially delocalized toward $(d_{xy})_{\text{A}}$, a β electron is symmetrically delocalized toward $(d_{xy})_{\text{B}}$. Hence, the unpaired electron around A will have a probability of β spin larger than 0.5 and the unpaired electron around B will have a probability of α spin larger than 0.5, which effectively favors the singlet state.

It is important to point out that the spin polarization is in no way a new model of the exchange interaction. It is a new factor, which adds itself to the J_{AF} and J_{F} contributions defined in (1). Till now, we had only taken into account the magnetic orbitals and the molecular orbitals constructed from the magnetic orbitals, with a preponderant metallic character. This is likely justified when the bonding MO's with preponderant bridging ligand characters are very low in energy with regard to the metal orbitals. For the first time, here, we

(21) See for instance: Salem, L. "Electrons in Chemical Reactions: First Principles"; Wiley: New York, 1982; Chapter 7. de Loth, P.; Cassoux, P.; Daudey, J. P.; Malrieu, J. P. *J. Am. Chem. Soc.* **1981**, *103*, 4007.

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qualitatively account for the role of these low-energy, doubly occupied MO's. Later on, we shall propose a quantitative approach of the spin polarization in coupled systems. We can already notice that, in this respect, the situation encountered with the end-on azido bridge is quite peculiar. The quasi-absence of overlap density in π_g pushes away the two paired electrons occupying the same MO toward the extremities of the system. This could be the cornerstone of the large ferromagnetic interaction observed in μ -azido (end-on) copper(II) dinuclear complexes.

Acknowledgment. We are most grateful to L. Salem, J. P. Malrieu, P. de Loth, J. P. Daudey, and our colleagues of the Laboratoire de Spectrochimie des Eléments de Transition for very helpful discussions on the spin polarization.

Registry No. $[\text{Cu}_2(\text{tmen})_2(\text{N}_3)(\text{OH})](\text{ClO}_4)_2$, 86645-78-5; $[\text{Cu}(\text{tmen})(\text{N}_3)_2]_2$, 86667-98-3.

Supplementary Material Available: Listings of structure factor amplitudes and magnetic data (7 pages). Ordering information is given on any current masthead page.

Contribution from the School of Chemistry,
University of New South Wales, Kensington, NSW 2033, Australia

Planar Bridging Thiolate in $(\text{Ph}_3\text{P})_2\text{Cu}(\mu\text{-SPh})_2\text{Cu}(\text{PPh}_3)_2$

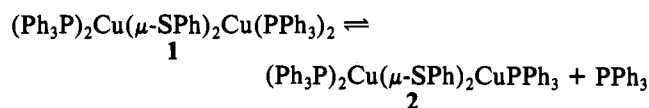
IAN G. DANCE,* PHILIP J. GUERNEY, A. DAVID RAE, and MARCIA L. SCUDDER

Received December 9, 1982

Pale yellow $(\text{Ph}_3\text{P})_2\text{Cu}(\mu\text{-SPh})_2\text{Cu}(\text{PPh}_3)_2$ has been crystallized from a mixture of CuSPh and Ph_3P in chloroform/propanol. The pseudotetrahedra around the equivalent copper atoms are linked at the common edge formed by the bridging thiolate ligands, such that the four phosphorus atoms and the two copper atoms are virtually coplanar. The molecule contains a crystallographic twofold axis that passes through both benzenethiolate ligands, and accordingly, the stereochemistry at sulfur is strictly planar. This is the first reported instance of planar stereochemistry at sulfur in a thiolate ligand bridging two metal atoms. There is crowded packing of the phenyl rings of the four Ph_3P ligands around the equatorial girdle of the molecule, an effect that restricts any movement of the axial SPh ligands away from planarity at sulfur and also increases the separation between the two copper atoms. Key dimensions: Cu-S, 2.344 (4), 2.415 (4) Å; Cu-P, 2.304 (2), 2.308 (2) Å; S-Cu-S, 79.3 (2)°; P-Cu-P, 118.3 (1)°; Cu-Cu, 3.662 (2) Å. Crystal data: prisms, $\text{C}_{84}\text{H}_{70}\text{Cu}_2\text{P}_4\text{S}_2$, mol wt 1394.6, tetragonal, $a = 14.071$ (1) Å, $c = 17.720$ (2) Å, $P4_2/m$ (disordered structure), $Z = 2$, Mo K α radiation, 1775 observed data, $R = 0.064$, $R_w = 0.077$.

Introduction

Reichle¹ has reported that CuSPh reacts with triphenylphosphine to form $(\text{Ph}_3\text{P})_2\text{CuSPh}$. Osmometric data for this compound in chlorobenzene solution indicate that either it is monomeric or, if dimeric, it is in dissociative equilibrium:



Precedent for the dissociated structure type exists in $(\text{Ph}_3\text{P})_2\text{CuCl}_2\text{CuPPh}_3$ (3).²

As part of our investigation of the coordination chemistry of fundamental thiolate ligands, particularly with copper,³ we have determined the crystal structure of $(\text{Ph}_3\text{P})_2\text{Cu}(\mu\text{-SPh})_2\text{Cu}(\text{PPh}_3)_2$ (1). A second reason for this investigation derived from the considerable crowding of phenyl groups, which appeared to be unavoidable in such a dimeric structure. This compound was therefore expected to be significant in our evaluation of the stereochemical properties of bridging thiolates, where the configurational isomerism due to inversion of pyramidal sulfur and the surface packing of substituents may influence the structures of homoleptic metal thiolate cages.³⁻⁵ This significance was established when the structure of 1 was revealed as the first example of doubly bridging thiolate with planar stereochemistry at sulfur.

Table I. Details of Diffraction Analysis of $(\text{Ph}_3\text{P})_2\text{Cu}(\text{SPh})_2\text{Cu}(\text{PPh}_3)_2$

formula, mass	$\text{C}_{84}\text{H}_{70}\text{Cu}_2\text{P}_4\text{S}_2$, 1394.6
cryst description	capped prisms; {101}, {011}
space group	$P4_2/m$
$a, b/\text{Å}$	14.071 (1)
$c/\text{Å}$	17.720 (2)
$V/\text{Å}^3$	3508.4
Z	2
$d_{\text{obsd}}/\text{g cm}^{-3}$	1.32 (1)
$d_{\text{calc}}/\text{g cm}^{-3}$	1.32
temp/ $^{\circ}\text{C}$	21
radiation, $\lambda/\text{Å}$	Mo K α , 0.710 69
scan mode	$\theta/2\theta$
$2\theta_{\text{max}}/\text{deg}$	50
μ/cm^{-1}	7.98
cryst dimens/mm	$0.17 \times 0.20 \times 0.21$
max and min transmissn coeff	0.890, 0.793
no. of intens measurements	3476
std intens decay	nil
criterion for obsd refln	$I/\sigma(I) > 3$
no. of indep obsd reflns	1775
no. of reflns (m) and variables (n)	1775, 156
in final refinement	
$R = \sum \Delta F / \sum F_o $	0.064
$R_w = [\sum w \Delta F ^2 / \sum w F_o ^2]^{1/2}$	0.077
$[\sum w \Delta F ^2 / (m - n)]^{1/2}$	2.27

Experimental Section

CuSPh was prepared from copper(II) nitrate in ethanol with a small excess of benzenethiol and tertiary amine. The insoluble yellow product was thoroughly washed and vacuum dried.

$(\text{Ph}_3\text{P})_2\text{Cu}(\mu\text{-SPh})_2$ (1). CuSPh (1.0 g, 5.8 mmol) was added to a solution of triphenylphosphine (3.04 g, 11.6 mmol) in chloroform (30 mL) under nitrogen, and the mixture was stirred and warmed until all solid had dissolved. After filtration the pale yellow solution was diluted with propanol (50 mL) and stored at 0 $^{\circ}\text{C}$. The large,

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(4) Dance, I. G. *J. Chem. Soc., Chem. Commun.* 1980, 818.

(5) Dance, I. G.; Scudder, M. L., to be submitted for publication.