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Synthesis, X-ray Diffraction Structure, Magnetic Properties, and MO Analysis of a Binuclear (μ-Tetrathiooxalato)copper(II) Complex, $(AsPh_4)_2[(C_3OS_4)CuC_2S_4Cu(C_3OS_4)]$

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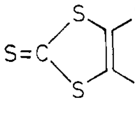
The synthesis, crystal and molecular structures, magnetic properties, and molecular orbital analysis for $(AsPh_4)_2[(C_3OS_4)Cu(\mu\text{-}C_2S_4)Cu(C_3OS_4)]$, the first μ-C_2S_4–copper(II) complex, are reported. It crystallizes in the triclinic space group $P\bar{1}$. Cell dimensions: a = 12.880 (3) Å, b = 11.904 (2) Å, c = 11.333 (2) Å, α = 97.65 (2)°, β = 111.16 (2)°, γ = 112.69 (2)°, Z = 1. The structure was solved by Patterson and Fourier methods and refined to an R(unweighted) value of 0.061 (R(weighted) = 0.062). The complex consists of centrosymmetric dinuclear units well separated from each other. Each copper atom shows distorted square-planar coordination with α = 28.3°, still far from a pseudotetrahedral (α = 90°) coordination. This deviation from planarity can be explained as a second-order Jahn–Teller distortion, and the degree of distortion can be correlated with the carbon–carbon bond length of the bridging C_2S_4 ligand. The proposed value of J, $|J| > 800\ \mathrm{cm^{-1}}$, is the largest one in a series of similar bisbidentate bridges: oxalato, oxamido, dithiooxamido. It can be understood in the light of a molecular orbital model: the overlap between the sulfur p orbitals is very large, creating a large gap, Δ, between the singly occupied molecular orbitals and, hence, a large antiferromagnetic coupling constant.

Introduction

The use of sulfur-containing molecules as precursors for conductive[2] or superconductive[3] materials or as bridging ligands for highly coupled magnetic materials[4] has been developed in the past few years. On the one hand, sulfur is expected to give π-overlap within the stacks of electron-donor molecules such as tetrathiofulvalene (TTF). Coupled with suitable electron acceptors, TTF gives rise to conductive molecular stacks. On the other hand, peripheral sulfur atoms allow interstack contacts and electron–phonon coupling and can give rise to superconductivity. Indeed, using TTF^+ and $[Ni(dmit)_2]^{2-}$ (**1**) as precursors, Cassoux et al. recently obtained nickel(II) complexes that have conductive[2] or superconductive[3] properties. Finally, dithiooxalate[4a–c] or dithiooxamide[4d–f] bridging ligands allow large antiferromagnetic coupling between remote paramagnetic ions in molecular complexes such as **2**, where X, Y, Z, and W can be O, N, or S.



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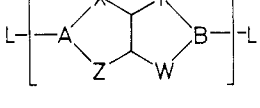

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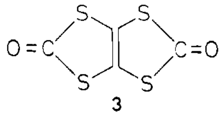
Up to now, few binuclear complexes with $C_2S_4^{n-}$ bridging ligands were reported.[5,6] In particular, no μ-$C_2S_4Cu^{II}$ binuclear complex has been synthesized, and it has been predicted to present a very large antiferromagnetic interaction.[7] Indeed, when molecular bridges between two copper(II) ions in the series oxalato (X = Y = Z = W = O),[8] oxamato (X = Y = Z = O; W = N),[9] oxamido (X = W = N; Y = Z = O),[9,10] and dithiooxamido (X = W = N; Y = Z = S)[4d–f] are used with similar planar geometries for the Cu–bridge–Cu unit, increasing coupling constants up to 600 $\mathrm{cm^{-1}}$ are found, for Cu–Cu distances larger than 5 Å. It is therefore tempting to verify if the C_2S_4 bridge behaves as expected,[7] with a larger interaction than found with the previously studied bridges.

Nevertheless, the chemistry of sulfur-rich molecules such as C_2S_4[6,11] or entities like **3** and **4**,[12,13] potential precursors of materials with the expected physical properties, is difficult.



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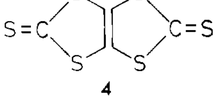

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For example, the real nature of the hydrolysis products of molecules **3** and **4** is not known. One solution this question is to stabilize the hydrolyzed products by complexation with a transition metal such as Cu(II). In this way, it appears possible to synthesize μ-C_2S_4 complexes of Cu(II). We report in this paper the synthesis, the crystal and molecular structures, the magnetic and spectroscopic properties, and an MO analysis of a binuclear complex containing two products of hydrolysis of molecule **3**: the C_2S_4

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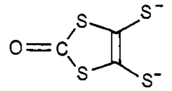
Table I. Selected Bands of the IR (Top) and Electronic Absorption Spectra (Solid Phase) (Bottom) of the Title Compound

bands, cm^{-1}	assignt
1600 (m), 1610 (s)	C=O and C=C stretching
1100 (m), 1010 (m)	deformation in-plane Ar—H
910 (m)	C—S stretching
750 (s), 695 (s)	deformation out-of-plane Ar—H
λ_{max}, nm	assignt
1100 (vbr)	d–d (Cu(II))
720 (sh)	π(S) → Cu(II)
560 (s)	σ(S) → Cu(II)
460 (vw)	σ(S) → Cu(II)

ligand, which bridges the two copper(II) ions in a bisbidentate manner, and the 2-oxo-1,3-dithiole-4,5-dithiolate dianion, **5**.



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The reader should be aware that C_2S_4 is a noninnocent ligand, and one could consider it either as $C_2S_4^{2-}$ (tetrathiooxalato) or $C_2S_4^{4-}$ (ethylenetetrathiolato). Hence, we will name this ligand as C_2S_4, without making any judgement on its formal charge, and this point will be discussed later in light of the crystallographic data and an MO analysis.

Experimental Section

Synthesis of Tetraphenylarsonium (μ-Tetrathiooxalato(2−))bis[(2-oxo-1,3-dithiole-4,5-dithiolato(2−))cuprate(II)], $(AsPh_4)_2[Cu_2(\mu$-$C_2S_4)(C_3OS_4)_2]$. When 1,3,4,6-tetrathiapentalene-2,5-dione[14] was treated under inert atmosphere at room temperature with 4 mol of sodium methoxide followed by addition of a slight excess of tetraphenylarsonium chloride and aqueous $CuCl_2$, in this order, a blue microcrystalline powder of $(AsPh_4)_2[Cu(C_3OS_4)_2]$ precipitated.[15] This solid was dissolved in acetone:ethanol (1:1) and the solution left in air at room temperature for several days. The resulting blue crystals of the title compound were collected by filtration, washed with ethanol, and air-dried. The new complex was characterized by chemical analysis, IR and visible spectra, and an X-ray structural determination. Anal. Calcd (found): C, 47.82 (48.0); H, 2.87 (2.9).

Techniques. Infrared spectra were recorded on a Beckman IR 20A spectrophotometer purged with dry air. Samples were prepared by using the KBr technique. The susceptibility of the complex was measured with a Faraday-type magnetometer, equipped with a helium flow cryostat. The measurements were performed in the 4.2–300 K temperature range. The X-band EPR spectra were recorded with a Brucker ER200 spectrometer, in the same temperature range.

Crystal Structure Determination. A small prismatic crystal (0.1 × 0.1 × 0.14 mm) was selected and mounted on a Philips PW-1100 four-circle diffractometer; the unit cell parameters were determined from 25 reflections ($4 \leq \theta \leq 9°$) and refined by least squares. Intensities were collected with graphite-monochromatized Mo K_α radiation by using the ω-scan technique (scan width 1°; scan speed 0.03° s^{-1}). Three reflections were measured every 2 h as orientation and intensity controls; significant variation was not observed. A total of 3852 intensities were measured in the range $2 \leq \theta \leq 25°$, 3840 of which were assumed as observed by applying the condition $I \geq 2.5\sigma(I)$. Lorentz–polarization but no absorption corrections were made.

The Cu and As atoms were located from a Patterson synthesis and the remaining non-hydrogen atoms from a weighted Fourier synthesis. The structure was isotropically and anisotropically refined by full-matrix least-squares methods using the SHELX76 computer program.[16a] The function minimized was $\sum w||F_o| - |F_c||^2$, where $w = (\sigma^2(F_o) + 0.0061|F_o|^2)^{-1}$. f, f', and f'' were taken from ref 16b. The 20 H atoms were located from a difference synthesis and refined with an overall isotropic temperature coefficient. The final R value was 0.061 (R_w = 0.062), for all observed reflections. Maximum shift/esd = 0.3 in y of H(45). The maximum peak in final difference synthesis was 0.3 e$Å^{-3}$.

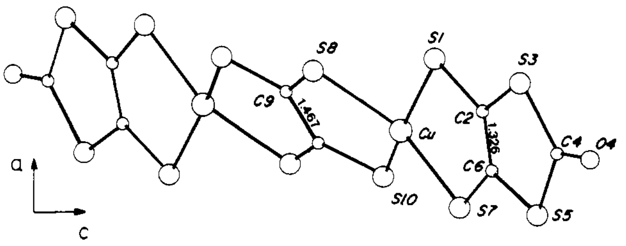

Figure 1. Projection of the molecular structure of $[(C_3OS_4)Cu(\mu$-$C_2S_4)Cu(C_3OS_4)]^{2-}$ anion down the b axis.

Crystal Data for the Title Compound: M_r = 1343.1, triclinic, a = 12.880 (3) Å, b = 11.904 (2) Å, c = 11.333 (2) Å, α = 97.65 (2)°, β = 111.16 (2)°, γ = 112.69 (2)°, V = 1418.2 (8) $Å^3$, D_{exptl} = 1.572 g cm^{-3}, space group $P\bar{1}$, Z = 1; $F(000)$ = 679, λ (Mo K_α) = 0.71069 Å, μ(Mo K_α) = 20.87 cm^{-1}, room temperature.

Results

IR and Electronic Spectra. The most characteristic bands in the IR spectrum are given in Table I with their assignments. The bands at 1660–1610 cm^{-1} are easily assigned to the C=O stretching, as we have previously reported for $[M(C_3OS_4)(Phos)_2]$ (M = Ni, Pd, Pt).[17] The ν(C–S) band at 905 cm^{-1} is also found. The electronic spectrum of the new compound is given in Table I with the assignments of the bands. These assignments are made according to the literature data for similar complexes of Cu(II) with four sulfur atoms in the ligands.[18]

Magnetic Results. The thermal variation of the molar susceptibility is not shown since it exhibits practically a Curie-law behavior. Starting at a value of 600 × 10^{-6} cm^3 mol^{-1} at room temperature ($\chi_m T$ = 0.17 cm^3 mol^{-1} K), the susceptibility increases monotonically down to 4.2 K ($\chi_m T$ at 4.2 K = 0.16 cm^3 mol^{-1} K). The expected value of $\chi_m T$ for 1 mol of dimer with uncoupled Cu(II) ions is 2.66 cm^3 mol^{-1} K. No rise of the molar susceptibility per copper ion toward a maximum at high temperature can be safely detected, given the low absolute values of the susceptibility and the inaccuracy of the large diamagnetic corrections, estimated from Pascal constants to be 680 × 10^{-6} cm^3 mol^{-1}. This behavior is further analyzed in the Discussion. It can be qualitatively understood as follows: the copper(II) ions are so coupled in the binuclear complex through the C_2S_4 bridge that the singlet state is largely stabilized and the triplet state is very weakly populated at room temperature. The singlet–triplet gap J cannot be computed since the paramagnetic impurities mask the coupled species. An estimate of the percentage of uncoupled spins is 9%, with g = 2.16 and $|J| > 800$ cm^{-1}.

EPR Spectra. The recorded spectra do not shown the broad triplet signal centered around g = 2, present in analogous binuclear units and disappearing at low temperatures.[4d-f] As in the susceptibility measurements, we detect only weak intensity signals, attributed to uncoupled paramagnetic species (Cu(II) surrounded by four sulfur atoms, for example) diluted in the diamagnetic lattice of strongly coupled dimers. Such an example was recently reported.[19]

Discussion

The structure consists of discrete ions. Each $[(C_3OS_4)Cu(C_2S_4)Cu(C_3OS_4)]^{2-}$ ion is surrounded by six tetraphenylarsonium cations, with shortest interionic distances $H(23)^{i}\cdots S(1)$ = 2.54 (6), $H(23)^{i}\cdots S(8)$ = 2.76 (6), $H(32)^{ii}\cdots S(5)$ = 2.80 (6), $H(36)^{iii}\cdots S(3)$ = 2.79 (6), and $H(46)^{ii}\cdots S(7)$ = 2.93 (6) Å (symmetry code: i = $-x, -y, -z - 1$; ii = $-x, 1 - y, -z$; iii = $-x, 1 - y, -z - 1$). The molecular structure of the anion is shown in Figure 1, together with the atom-labeling scheme. The inversion center is located at the middle of the C–C bond of the C_2S_4 bridging ligand.

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Table II. Final Atomic Coordinates ($\times 10^4$; Cu and As $\times 10^5$)

	x/a	y/b	z/c	B_{eq}, Å^2
Cu	15240 (6)	24453 (6)	−4555 (7)	3.36 (3)
S(1)	2236 (2)	2825 (1)	−1959 (2)	4.81 (8)
C(2)	3142 (5)	4478 (5)	−1243 (6)	3.36 (23)
S(3)	4091 (2)	5318 (2)	−1930 (2)	4.59 (8)
C(4)	4686 (6)	6864 (6)	−868 (6)	4.41 (27)
O(4)	5386 (5)	7830 (5)	−954 (6)	6.49 (25)
S(5)	4112 (2)	6819 (2)	335 (2)	5.77 (8)
C(6)	3168 (5)	5154 (5)	−193 (6)	3.82 (24)
S(7)	2359 (2)	4507 (2)	682 (2)	5.24 (8)
S(8)	64 (1)	417 (1)	−1766 (1)	3.81 (6)
C(9)	−293 (4)	−338 (5)	−716 (5)	2.91 (20)
S(10)	1390 (1)	1885 (1)	1319 (1)	3.85 (6)
As	−26080 (4)	26280 (4)	−40340 (5)	2.68 (2)
C(11)	−1245 (4)	4268 (5)	−3642 (5)	2.87 (19)
C(12)	−56 (5)	4352 (6)	−3363 (6)	3.91 (25)
C(13)	911 (5)	5514 (6)	−3159 (6)	4.22 (26)
C(14)	719 (6)	6557 (6)	−3213 (6)	4.15 (25)
C(15)	−436 (7)	6472 (6)	−3488 (7)	4.57 (28)
C(16)	−1434 (5)	5314 (5)	−3681 (6)	3.74 (25)
C(21)	−2760 (5)	1432 (5)	−5482 (5)	3.09 (20)
C(22)	−1869 (6)	985 (6)	−5215 (6)	4.12 (27)
C(23)	−1916 (7)	206 (7)	−6274 (8)	5.14 (33)
C(24)	−2835 (7)	−155 (6)	−7565 (7)	4.66 (29)
C(25)	−3703 (6)	273 (6)	−7793 (6)	4.28 (25)
C(26)	−3702 (5)	1077 (6)	−6751 (6)	3.67 (23)
C(31)	−4132 (4)	2761 (5)	−14519 (5)	2.92 (21)
C(32)	−4794 (5)	2413 (6)	−3802 (6)	3.54 (22)
C(33)	−5891 (6)	2551 (7)	−4140 (7)	4.73 (28)
C(34)	−6284 (6)	2995 (7)	−5165 (8)	5.01 (32)
C(35)	−5620 (6)	3341 (7)	−5887 (7)	4.34 (29)
C(36)	−4537 (5)	3228 (6)	−5563 (6)	3.92 (25)
C(41)	−2294 (5)	2037 (5)	−2537 (5)	3.13 (22)
C(42)	−2955 (6)	771 (6)	−2683 (7)	4.18 (26)
C(43)	−2801 (6)	387 (8)	−1544 (9)	5.05 (36)
C(44)	−1996 (7)	1276 (9)	−315 (8)	5.44 (40)
C(45)	−1317 (8)	2536 (9)	−145 (7)	5.33 (38)
C(46)	−1467 (6)	2938 (7)	−1277 (6)	4.18 (26)

Table III. Selected Bond Distances (Å) and Angles (deg)

S(1)–Cu	2.227 (2)	O(4)–C(4)	1.199 (8)
S(7)–Cu	2.228 (2)	S(5)–C(4)	1.767 (7)
S(8)–Cu	2.258 (2)	C(6)–S(5)	1.751 (6)
S(10)–Cu	2.245 (2)	S(7)–C(6)	1.730 (6)
C(2)–S(1)	1.736 (6)	C(9)–S(8)	1.673 (5)
S(3)–C(2)	1.747 (5)	C(9)–C(9)	1.467 (10)
C(6)–C(2)	1.326 (8)	C(9′)–S(10)	1.678 (5)
C(4)–S(3)	1.755 (8)		

S(7)–Cu–S(1)	95.1 (1)	C(4)–S(3)–C(2)	97.3 (3)
S(8)–Cu–S(1)	92.6 (1)	O(4)–C(4)–S(3)	124.2 (6)
S(8)–Cu–S(7)	160.1 (1)	S(5)–C(4)–S(3)	111.5 (3)
S(10)–Cu–S(1)	158.9 (1)	S(5)–C(4)–O(4)	124.3 (6)
S(10)–Cu–S(7)	90.4 (1)	C(6)–S(5)–C(4)	97.3 (3)
S(10)–Cu–S(8)	89.0 (1)	S(5)–C(6)–C(2)	116.5 (4)
C(2)–S(1)–Cu	97.8 (2)	S(7)–C(6)–C(2)	124.8 (4)
S(3)–C(2)–S(1)	118.6 (3)	S(7)–C(6)–S(5)	118.7 (4)
C(6)–C(2)–S(1)	124.1 (4)	C(6)–S(7)–Cu	97.7 (2)
C(6)–C(2)–S(3)	117.4 (4)	C(9)–S(8)–Cu	104.6 (2)

Final atomic coordinates are given in Table II; mean bond distances and angles are given in Table III.

The central Cu(C_2S_4)Cu core is practically planar (Cu, S(8), C(9), S(10), and the inversion-related atoms), the largest deviation from the mean plane being 0.015 (2) Å for the Cu atoms. It is noteworthy that the free anion $C_2S_4^{2-}$ in the tetraphenylphosphonium tetrathiooxalate is far from planar (torsion angle around the C–C bond = 79.5°)[11]. The C(9)–C(9′) distance, 1.467 (10) Å, is equal to that reported in the literature for the free ion in the above-mentioned salt, 1.461 (19) Å,[11] and smaller than the one recently reported for C_2S_4 acting as a side-on bridging ligand in a Cu(I) complex (1.531 (8) Å).[6] This fact indicates that the C_2S_4 bridge in the title compound can be formally considered as $C_2S_4^{2-}$ and not as the $C_2S_4^{4-}$ anion. Effectively, in other C_2S_4 complexes in which the C_2S_4 bridge can be formally considered as $C_2S_4^{4-}$, the C–C bond distance is clearly shorter: 1.332 (13) Å in $[Fe_4(CO)_{12}C_2S_4]$[5a,b] and 1.360 (11) Å in $[Ni(\eta^5\text{-}C_5Me_5)(C_2S_4)]$.[5a,c]

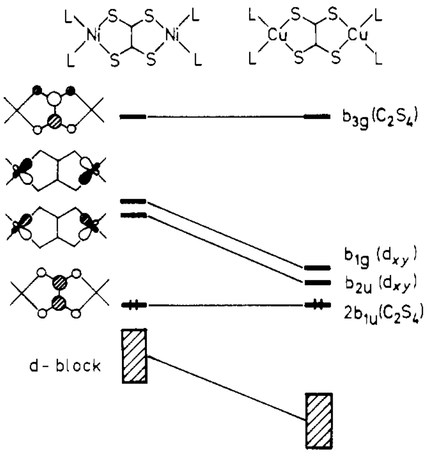

Figure 2. Frontier orbitals of a dinuclear $[L_2M(\mu\text{-}C_2S_4)ML_2]$ complex. Only the major contributions are depicted; the $2b_{1u}$ and b_{3g} orbitals are π-type orbitals. For a detailed description of those orbitals see ref 22.

The average C(9)–S bond length is 1.675 (6) Å, similar to the same distance in the Cu(I) complex[6] and slightly smaller than in the free ion (1.702 (10) Å).[11] The Cu–S(8) bond length (2.258 (2) Å) is significantly larger than the chemically equivalent Cu–S(10) bond distance (2.245 (2) Å). The same fact is found in the previously reported Cu(I) complex:[6] bond distances of 2.308 (2) and 2.275 (2) Å.

The external $C_3OS_4^{2-}$ ligands (S(1), S(7), C(2), C(6), S(3), S(5), C(4), and O(4)) are also practically planar, the largest deviation from the mean plane being that of S(3) (0.050 Å). The Cu atom is 0.161 Å away from this plane. The C(2)–C(6) bond length is 1.326 (8) Å, practically corresponding to a double bond typical of dithiolato ligands. This distance is shorter than in the analogous thione compounds $[Ni(C_3S_5)_2]^{n-}$ (ranging from 1.35 (1) to 1.435 (3) Å, depending on n = 2, 1, 0).[20,21] The average bond lengths for the C–S bonds in the terminal C_3OS_4 ligands are 1.755 (7) Å for the S atoms bound to the CO group and 1.733 (6) Å for the Cu-bonded ones, significantly larger than the corresponding distances in the bridging C_2S_4 ligand (C(9)–S(8) = 1.673 (5) Å and C(9′)–S(10) = 1.678 (5) Å. It is interesting to notice that there is a slight twisting of the C_3OS_4 ligand around the C–C bond (dihedral angle between both CS_2 moieties of 2.6°), while in the bridging C_2S_4 ligand, with a longer C–C bond length, this twist is negligible (dihedral angle of 0.03°).

The coordination sphere of each copper atom is formed by two S atoms of the bridging C_2S_4 ligand and two S atoms of a terminal C_3OS_4 ligand. The dihedral angle between the Cu–S(8)–S(10) and Cu–S(1)–S(7) planes is α = 28.3°, clearly distorted from an ideal square-planar coordination around Cu (α = 0°), but still far from a pseudotetrahedral (α = 90°) coordination.

All these crystallographic data, especially the C–C distance in both C_2S_4 and C_3OS_4 ligands, allow us to propose that the ligands are formally $C_2S_4^{2-}$ and $C_3OS_4^{2-}$. Therefore, taking into account the existence of two $AsPh_4^+$ cations, the two central copper atoms must be considered as Cu(II).

MO Analysis. A detailed study of the molecular orbitals of the C_2S_4 ligand has been previously reported.[22] The interaction of such a ligand with two NiL_2 fragments was considered and a

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(20) (a) Lindqvist, O. P.; Andersen, L.; Sieler, J.; Steinmecke, G.; Hoyer, E. *Acta Chem. Scand., Ser. A* **1982**, *A36*, 855. (b) Kato, R.; Mori, T.; Kobayashi, A.; Sasaki, K. *Chem. Lett.* 1984, 1. (c) Lindqvist, O. P.; Andersen, L.; Sieler, J.; Steinmecke, G.; Hoyer, E. *Acta Chem. Scand., Ser. A* **1979**, *A33*, 455.

(21) (a) Valade, L.; Bousseau, M.; Gleizes, A.; Cassoux, P. *J. Chem. Soc., Chem. Commun.* **1983**, 110. (b) Bousseau, M.; Valade, L.; Cassoux, P.; Garbauskas, M.; Interrante, L.; Kasper, J. *Nouv. J. Chim.* **1984**, *8*, 3. (c) Valade, L.; Legros, J. P.; Bousseau, M.; Cassoux, P.; Garbauskas, M.; Interrante, L. V. *J. Chem. Soc., Dalton Trans.* **1985**, 783.

(22) Alvarez, S.; Vicente, R.; Hoffmann, R. *J. Am. Chem. Soc.* **1985**, *107*, 6253.

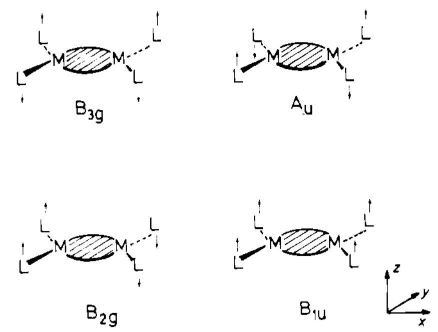
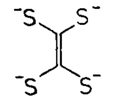


Figure 3. Possible out-of-plane distortion models for a planar dinuclear $[L_2M(bridge)ML_2]$ compound.

planar $[L_2Ni(\mu\text{-}C_2S_4)NiL_2]$ compound predicted to be stable. No such nickel compound is known so far, but a related platinum derivative, $(\mu\text{-}C_2S_4Me_2)Pt_2X_2L_2$ is indeed planar.[23] In essence, the frontier molecular orbitals are depicted in Figure 2 (left) and its salient features are (a) a large HOMO-LUMO gap exists, (b) the $2b_{1u}$ orbital of C_2S_4, essentially the carbon-carbon π-bonding orbital, is occupied, and (c) the symmetric and antisymmetric combinations of the M-d_{xy} orbitals are empty. All this points to a description of the hypothetical nickel complex as one of Ni(II) and $C_2S_4^{4-}$ (**6**). For the hypothetically planar copper dimer, Figure 2 would imply its formulation as a complex of Cu(III) and $C_2S_4^{4-}$.



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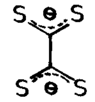

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In this context it is surprising to find that our isoelectronic copper compound is not planar and that the carbon-carbon bond distance corresponds roughly to a single bond, suggesting a Cu(II) plus $C_2S_4^{2-}$ (**7**) situation. A closer look at the electronic structure of this compound is hence worthwhile. Our qualitative molecular orbital study was done with the help of extended Hückel calculations on the model dimer $[H_2Cu(\mu\text{-}C_2S_4)CuH_2]^{2-}$, with a carbon-carbon bond distance of 1.34 Å, as found for other C_2S_4 complexes, since we expect to find the electronic reasons for a longer C-C bond without introducing it as a parameter in our calculations (See Appendix for computational details).

When Ni is substituted by Cu in the planar dinuclear complex, while the electron count constant is kept, the increased electronegativity of the metal produces lowering in the energy of the d orbitals as schematically shown in Figure 2, while $2b_{1u}$, mostly a π orbital of C_2S_4, changes little in energy. For Cu the HOMO-LUMO gap is small and a second-order Jahn-Teller effect[24] can be expected.[25] Let us look at some of the possible distortions, those related with out-of-plane displacement of the terminal ligands; they are represented in Figure 3, together with their symmetry species. The first two (B_{3g} and A_u) correspond to rotations of the outer ML_2 groups, in their way toward a tetrahedral coordination sphere. The other two (B_{2g} and B_{1u}) modes would produce a bending of the molecule toward a chair or a boat conformation, respectively, while keeping the metals in square-planar environments. In our case, only the B_{3g} and A_u distortions can stabilize the compound: the B_{3g} mode allows mixing of $2b_{1u}(C_2S_4)$ occupied and $b_{2u}(d_{xy})$ empty orbitals. The A_u distortion, on the other hand, allows mixing of $2b_{1u}$ and $b_{1g}(d_{xy})$, but it is expected to produce less stabilization due to a poorer energy match, as found in our calculations (Figure 4). The B_{2g} distortion is present in dinuclear copper(II) oxalato-bridged complexes[26] as well as in a tetrathionaphthalene-platinum derivative.[27]

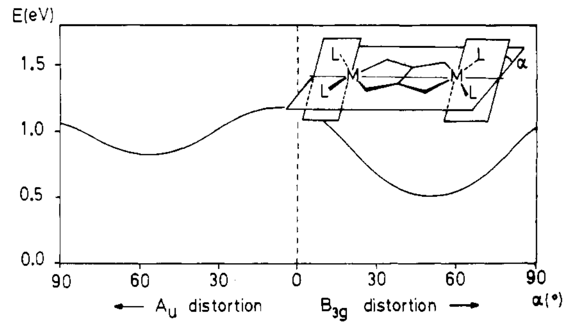

Figure 4. One-electron energy of the model dinuclear compound $[H_2Cu(\mu\text{-}C_2S_4)CuH_2]^{2-}$ along two of the distortion modes of Figure 3. The $\alpha = 0°$ situation corresponds to a square-planar environment for the metal atoms, while for $\alpha = 90°$ the coordination of both metals is approximately tetrahedral.

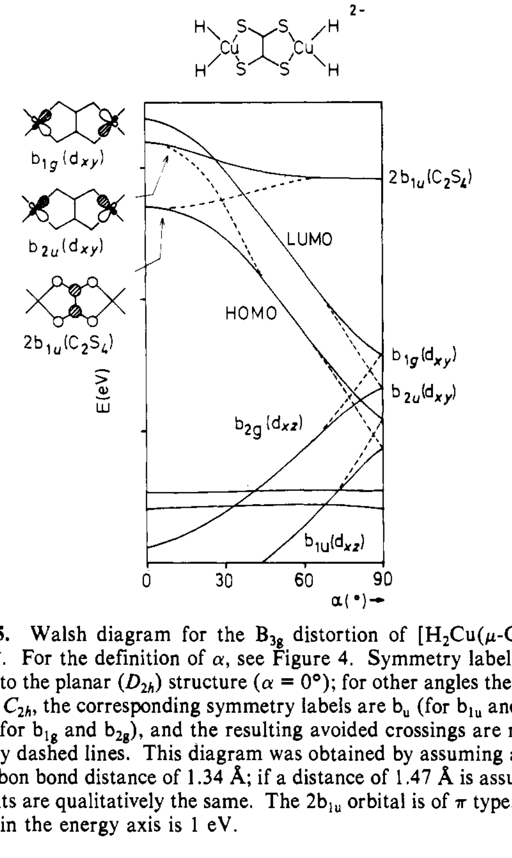

Figure 5. Walsh diagram for the B_{3g} distortion of $[H_2Cu(\mu\text{-}C_2S_4)CuH_2]^{2-}$. For the definition of α, see Figure 4. Symmetry labels correspond to the planar (D_{2h}) structure ($\alpha = 0°$); for other angles the point group is C_{2h}, the corresponding symmetry labels are b_u (for b_{1u} and b_{2u}) and b_g (for b_{1g} and b_{2g}), and the resulting avoided crossings are represented by dashed lines. This diagram was obtained by assuming a carbon-carbon bond distance of 1.34 Å; if a distance of 1.47 Å is assumed, the results are qualitatively the same. The $2b_{1u}$ orbital is of π type. The spacing in the energy axis is 1 eV.

Examination of a Walsh diagram is useful to understand the energy curves in Figure 4. Such a diagram is presented in Figure 5. First of all, one sees the step decrease in energy of both combinations of d_{xy} orbitals, as they loose their σ-antibonding character upon rotation. σ bonds are retained, of course, but they involve progressively the d_{xz} orbitals (increasing their energies with α at the lower part of the Walsh diagram), which, unlike d_{xy}, are not hybridized and overlap less with the ligand donor orbitals (**8**). Hence, rotation results in a weakening of the Cu-C_2S_4 σ bond.

Simultaneously, $2b_{1u}$ starts mixing with $b_{2u}(d_{xy})$, increasingly forming a π bond (**9**; $\alpha = 90°$), especially for small rotation angles,

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[23] Cetinkaya, B.; Hitchcock, P. B.; Lappert, M. F.; Pye, P. L.; Shaw, D. B. *J. Chem. Soc., Dalton Trans.* **1979**, 434.

[24] For a description of the second-order Jahn-Teller effect see, e.g.: Burdett, J. K. *Molecular Shapes*; Wiley: New York, 1980.

[25] In this regard it is irrelevant to worry about the relative energies of these orbitals. In any case they are close in energy, one will be occupied and two empty, and the second-order Jahn-Teller effect will be operative.

[26] (a) Julve, M.; Verdaguer, M.; Gleizes, A.; Philoche-Levisalles, M.; Kahn, O. *Inorg. Chem.* **1984**, *23*, 3808. (b) Julve, M.; Faus, J.; Verdaguer, M.; Gleizes, A. *J. Am. Chem. Soc.* **1984**, *106*, 8306. (c) Julve, M.; Faus, J.; Verdaguer, M.; Gleizes, A.; Kahn, O., submitted for publication.

[27] Teo, B. K.; Snyder-Robinson, P. A. *Inorg. Chem.* **1978**, *17*, 3489.

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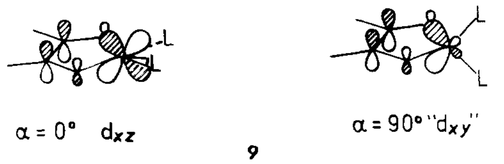

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when their difference in energy is small. This new π bond is much more important than that existing in the planar molecule (**9**; $\alpha = 0°$) due to both hybridization and electronegativity reasons. There is competition between the strengthening of the π(M–L) interaction and the weakening of a σ(M–L) interaction, finally avoiding the distortion to go all the way toward the tetrahedral conformation. In our model calculations with hydride as terminal ligands, the minimum is found at $\sim 50°$. It is clear that different terminal ligands or the choice of parameters may shift the position of the minimum, but the qualitative prediction of a B_{3g} distortion would hold.

There is still another important consequence of the orbital mixing discussed above. As can be seen in Figure 5, the $2b_{1u}$ orbital would be occupied for $\alpha = 0°$ but empty for $\alpha = 90°$. In between, its contribution to the HOMO decreases when α increases due to an avoided crossing with $b_{2u}(d_{xy})$ and, consequently, the electron population of $2b_{1u}$ decreases from ~ 2 to ~ 0 (Figure 6, top), while that of $b_{2u}(d_{xy})$ increases. These changes in orbital populations result in a change in the formal oxidation state of the copper ions to Cu(II) and in the charge of the bridging ligand to $C_2S_4^{2-}$.

Let us now recall that $2b_{1u}$ is mainly the carbon–carbon π-bonding orbital, and its depopulation must produce a lengthening of the C–C bond as indicated by the decrease in overlap population (Figure 6, bottom). $2b_{1u}$ has also some C–S antibonding character and its depopulation produces a strengthening of the C–S bonds. In agreement with the M–L nonbonding character of $2b_{1u}$, Cu–S is slightly sensitive to the degree of rotation.

If the geometry of the bridging C_2S_4 is adjusted to the new situation (lengthening of C–C and shortening of C–S bonds), the expected geometry closely resembles the experimental one, and the joint structural/MO analysis is in good agreement with a formal description of the complex as formed by two Cu(II) ions bridged by a $C_2S_4^{2-}$ (tetrathiooxalato) group.

Notice that on the basis of the Walsh diagram (Figure 5), a rotated structure should also be expected for a compound with two more electrons, as found in the recently reported[6] compound $[Cu_2(\mu\text{-}C_2S_4)(PR_3)_4]$. As the $b_{1g}(d_{xy})$ orbital is not involved in the second-order distortion, occupation of this orbital does not alter the conclusions on the twist angle/carbon–carbon bond distance correlation.

Hence, the data in Table IV for the three known complexes of the type $[L_2M(\mu\text{-}C_2S_4)ML_2]$ provide the experimental confirmation of the nice theoretical correlation found between the twist angle (α) and the C–C and C–S bond lengths.

Magnetic Properties. Another important point of interest is the magnetic behavior of the complex. As we already pointed out, the thermal variation of the suceptibility denotes mainly the presence of uncoupled species. This is a frequently encountered problem in binuclear complexes with a large antiferromagnetic coupling, where the determination of $|J|$ is difficult.[4d-f] In our case, the amount of impurities allows us only to propose a lower limit for $|J|$ as $|J| > 800$ cm^{-1}. This large coupling through the tetrathioxalato bridge was already predicted on the basis of a simple orbital description.[7] In the localized nonorthogonal magnetic orbital scheme already reported,[28,29] the unpaired electron of each copper(II) ion is described by a d_{xy} magnetic orbital (**10**), and their in-phase and out-of-phase combinations give rise to the singly occupied molecular orbitals b_u and b_g, sketched in **11**.

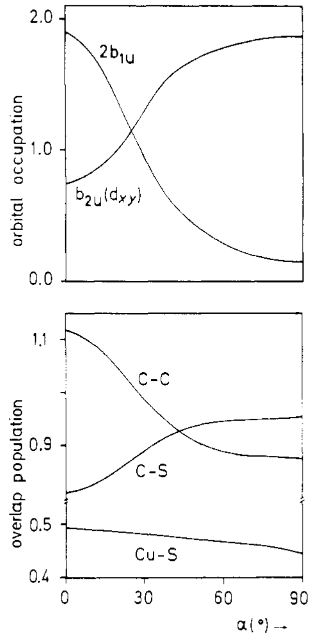
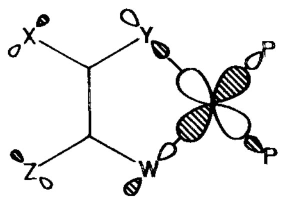


Figure 6. Changes in fragment orbital occupations (top) with rotation angle α (defined as in Figure 4) for $[H_2Cu(\mu\text{-}C_2S_4)CuH_2]^{2-}$, showing the gradual conversion of $C_2S_4^{4-}$ ($\alpha = 0°$) to $C_2S_4^{2-}$ ($\alpha = 90°$) and of Cu(I) ($\alpha = 0°$) to Cu(II) ($\alpha = 90°$) and changes in overlap populations with α (bottom).

Table IV. Correlation between the Degree of Tetrahedral Distortion (α) and Bond Strengths in the Bridging ett Ligand

		C–C		C–S		
compd	α, deg	d_{CC}, Å	ov pop	d_{CS}, Å	ov pop	ref
A $[(\mu\text{-}C_2S_4)Pt_2(PEt_3)_2Cl_2]$	3.0	1.34	1.244	1.75	0.805	23
B $[(\mu\text{-}C_2S_4)Cu_2(C_3OS_4)_2]^{2-}$	28.3	1.47	1.189	1.67	0.836	this work
C $[(\mu\text{-}C_2S_4)Cu_2(PPh_3)_4]$	49.4	1.53	1.068	1.67	0.900	6



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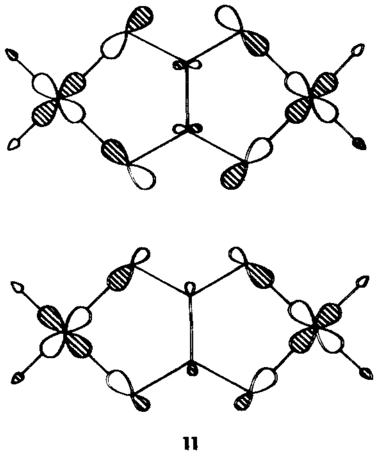

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[28] Kahn, O. *Inorg. Chim. Acta* **1982**, *62*, 3.

[29] Girerd, J. J.; Journeaux, Y.; Kahn, O. *Phys. Lett.* **1981**, *82*, 534.

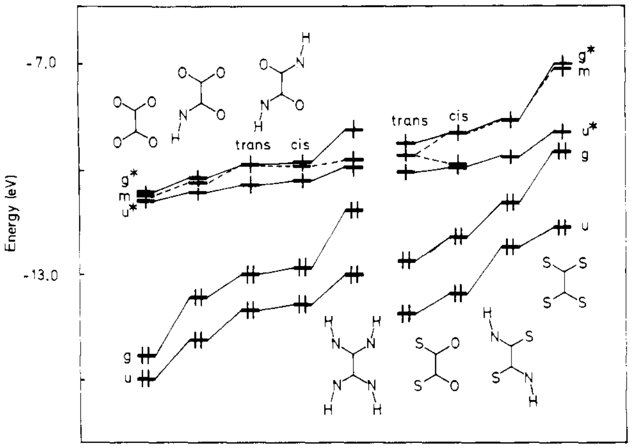

Figure 7. Schematic representation of the energies calculated from extended Hückel calculations on different systems, varying bridging atoms (X, Y, W, Z = O, N, S). The lower two orbitals (u and g) are molecular orbitals of bridging ligands, g* and u* are the singly occupied molecular orbitals, and m (bound with dashed line) is the magnetic orbital of the mononuclear complex.

In a first approximation, when ferromagnetic contributions can be neglected, J is expressed as

$$J \propto \Delta S \propto \Delta^2 \propto S^2$$

where S is the overlap integral between the magnetic orbitals **10** and Δ is the energy gap between the singly occupied molecular orbitals **11**. The larger Δ is, the larger $|J|$ is.

In order to properly describe Δ, extended Hückel calculations were carried out on a more realistic model with the geometry obtained from the crystallographic data and sulfur atoms as peripheral ligands.[30] The calculated gap between the b_u and b_g orbitals is 1.7 eV, which compares well with the one obtained from previous calculations with an approximate geometry,[7] 1.9 eV. We reproduce in Figure 7 the results of ref 7 for some bisbidentate-bridged binuclear complexes. The figure displays the evolution of the energy of (1) the molecular orbital of the bridging ligand, L, symmetry adapted to overlap with the symmetric and antisymmetric combinations of d_{xy} metallic orbitals of the Cu(II) ions (noted respectively as g and u; this notation is adapted only to centrosymmetrical complexes); (2) the magnetic orbitals of the mononuclear complexes (noted m), and (3) the molecular orbitals of the binuclear complexes, which are singly occupied in the triplet state (noted as g* and u* in the upper part of the diagram).

Two factors explain the large Δ gap between the singly occupied MO in our compound and others in Figure 7, and therefore the large value of $|J|$: (1) the σ through-space interaction between the sulfur atoms in each CS_2 group, which is the largest in the whole series; (2) the increase in energy of the ligand's molecular orbitals relative to the copper d orbitals, which favors a larger metal–bridge interaction.

The distortion from planar geometry, analyzed in the structural discussion, appears to have a small influence upon the magnetic properties. The important point seems to be the planarity of the CuC_2S_4Cu unit allowing a good interaction between the magnetic orbitals through the bridge.

Finally, we want to point out another interesting feature in the C_2S_4 bridge, related to the properties of the HOMO: the energy of the HOMO of C_2S_4 is high, close to that of the Cu(II) d orbitals; i.e., we are very close to a situation where the bridge can reduce the Cu(II) ion to a Cu(I) state by an intramolecular redox process. Indeed, in our case, this does not happen, since UV–visible spectroscopy identifies the Cu ions as Cu(II) ones, but with such electron-rich molecules and large metal–ligand overlap, we are near the limit where the through-bridge exchange interaction becomes an electron-transfer process from the bridge to the metallic species. In such case, C_2S_4 would become a neutral species and cleavage of the carbon–carbon bond would result,[22] thereby producing carbon disulfide.

Conclusions

We present the synthesis, structure, magnetic properties, and MO analysis of the first Cu(II) binuclear complex with a C_2S_4 bridge. We show that the deviation from the planarity found in the binuclear complex can be explained as a second-order Jahn–Teller distortion and that the degree of distortion of the copper coordination sphere is correlated with the carbon–carbon bond strength of the bridging C_2S_4 ligand.

As for the magnetic properties, we propose a lower limit of $|J|$ of $|J| > 800$ cm^{-1}. This value is the largest one in a series of bisbidentate bridges: oxalato, oxamido, dithiooxamido, tetrathiooxalato. It can be understood in the light of a simple orbital model: the overlap between the p sulfur orbitals engaged in the singly occupied molecular orbitals of the complex and the spin delocalization on the C_2S_4 bridge, favored by the closeness in energy of the HOMO ligand orbitals and the metallic d_{xy} orbital, are the two important parameters that explain the phenomenon.

Our example shows the interest of sulfur-rich ligands not only to synthesize conducting and superconducting systems, but also to obtain molecular polynuclear complexes with large antiferromagnetic interactions.

Acknowledgment. Financial assistance from the CIRIT (Generalitat de Catalunya) and from the CAICYT (Grant No. 0855/84 for the experimental part and No. 0657/81 for the computational part) are acknowledged.

Appendix: Computational Details

All the calculations were of extended Hückel type[31] with a modified Wolfsberg–Helmholtz formula.[32] The parameters used for S and Cu were taken from ref 22 and 33, respectively. Bond angles of 120° and bond distances of 1.47 (C–C) and 1.70 Å (C–S) were used for the C_2S_4 bridge. The Cu–S and Cu–H distances employed were 2.26 and 1.80 Å, respectively. The final calculation used for the discussion of the magnetic properties was carried out on $[S_2Cu(C_2S_4)CuS_2]$ with the experimental structure.

Registry No. 3, 64394-45-2; $(AsPh_4)_2[Cu_2(\mu\text{-}C_2S_4)(C_3OS_4)_2]$, 104469-50-3; $(AsPh_4)_2[Cu(C_3OS_4)_2]$, 104469-48-9; $[H_2Cu(\mu\text{-}C_2S_4)CuH_2]^{2-}$, 110528-79-5; H_2dmit, 78906-81-7.

Supplementary Material Available: A packing diagram for the molecule and listings of anisotropic thermal parameters, hydrogen atom coordinates, hydrogen bond distances, and hydrogen bond angles (5 pages); a listing of observed and calculated structure factors (16 pages). Ordering information is given on any current masthead page.

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(30) The slightly different set of EH parameters used in a previous paper (see ref 7) was used for this particular calculation, in order to keep the results comparable with those previously reported for different bridging ligands.

(31) Hoffmann, R.; Lipscomb, W. N. *J. Chem. Phys.* **1962**, *36*, 2179; **1962**, *37*, 2872. Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397.

(32) Ammeter, J.; Bürgi, H. B.; Thibeault, J.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 3686.

(33) Hay, P. J.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1975**, *97*, 4884.