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Appendix

The tight-binding extended Hückel method was used for these calculations. A list of the parameters is given in Table III. The *k* point set used for the calculation of the average properties consists of 64 *k* points and was chosen according to the method of Ramirez and Böhm.[16]

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Direct Electrochemical Synthesis of Copper and Silver Derivatives of Alkanedithiols and Crystal Structure of $[Cu_2S_2C_3H_6\text{-}1,2\cdot(C_6H_5)_2PCH_2P(C_6H_5)_2]_4\cdot 4CH_3CN$

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The electrochemical oxidation of copper or silver (=M) in acetonitrile solutions of $R(SH)_2$ ($R = 1,2\text{-}C_2H_4$, $1,2\text{-}C_3H_6$, $1,3\text{-}C_3H_6$, $1,4\text{-}C_4H_8$, $2,3\text{-}C_4H_8$, $1,5\text{-}C_5H_{10}$, $1,6\text{-}C_6H_{12}$) gives the insoluble homopolymeric M_2S_2R compounds in high yield. When $P(C_6H_5)_3$ or bis(diphenylphosphino)methane is present in the solution, the oxidation of copper yields adducts whose stoichiometry apparently depends on R. These results are discussed in terms of the possible structures involved. The compound $[Cu_2S_2C_3H_6\text{-}1,2\cdot(C_6H_5)_2PCH_2P(C_6H_5)_2]_4\cdot 4CH_3CN$ crystallizes in the triclinic centrosymmetric space group $P\bar{1}$ (No. 2) with $a = 18.483$ (7) Å, $b = 11.673$ (6) Å, $c = 17.890$ (7) Å, $\alpha = 116.57$ (3)°, $\beta = 111.35$ (3)°, $\gamma = 95.69$ (3)°, $V = 3052.08$ Å^3, and $Z = 2$. Refinement converged at $R = 0.0641$ and $R_w = 0.0657$ for those 5727 reflections with $I > 3\sigma(I)$ and $T = 20$ °C. The molecule has a core Cu_4S_4 eight-membered ring, which is capped by six-membered Cu_3S_3 and Cu_2P_2CS rings and five-membered CuS_2C_2 rings.

Introduction

In a series of papers from this laboratory, we have described the synthesis of a variety of inorganic and organometallic compounds by a direct one-step method in which a metal is electrochemically oxidized in a nonaqueous solution of a ligand or a ligand precursor. Of particular relevance to the present work are those systems in which metal thiolates were obtained in high yield by oxidation in solutions of thiols or disulfides.[1-8] This technique provides a simple, high-yield, one-step route to thiolato derivatives of both main group and transition metals. We have also shown that analogous experiments with solutions of alkanedithiols, $R(SH)_2$, give rise to MS_2R species and their adducts, for M = Zn and Cd,[9] and to some unusual low-oxidation-state species for M = In.[10] Compounds of such ligands are of current biochemical importance, but also present some challenging structural problems, especially with d^{10} ions such as copper(I),[11,12] and the interest in the structure of copper(I) compounds has also been reinforced by their use in syntheses and as catalysts for hydrogenation and similar processes. We now report the preparation of a series of copper(I) and silver(I) derivatives of various alkanedithiols and, in the case of copper, some adducts with triphenylphosphine and 1,2-bis(diphenylphosphino)methane (dppm). The structure of the tetrameric dppm adduct of $Cu_2S_2C_3H_6\text{-}1,2$ involves a novel cage involving fused five-, six-, and eight-membered rings.

Experimental Section

General Data. Copper and silver anodes were in the form of rods, 6-mm diameter (Alfa Inorganics). Acetonitrile was distilled from calcium hydride and stored over molecular sieves. All other reagents were used as supplied (Aldrich).

Metal analysis was by atomic absorption spectrophotometry, using an IL-251 instrument, and microanalysis on selected compounds was performed by Guelph Chemical Laboratories Ltd. Infrared spectra were recorded on a Nicolet 5DX interferometer, using KBr disks.

Electrochemical Procedures. The electrochemical syntheses followed the methods described in earlier papers.[1-10] The cells were set up in 100-mL tall-form beakers and were of the general form

$$Pt_{(-)}/R(SH)_2 + CH_3CN\ (+L)/M_{(+)}$$

$$M = Cu, Ag \qquad L = PPh_3,\ dppm$$

and utilized solutions whose compositions are summarized in Table I. The high applied voltage required to drive the current (Table I) in such low-conductivity media was supplied by a Coutant LQ 50/50 power supply. The surface area of the anode exposed to the solution was ca. 6 cm^2. All the preparations were done under an atmosphere of dry nitrogen, which bubbled through the solution phase and thereby provided gentle stirring throughout the electrolysis.

As the reaction proceeded, hydrogen gas was formed at the cathode. The sequence of reaction, precipitation, etc. observed at the anode in the different systems is described below. We noted that with currents higher than those recorded, the surface of the anode tended to disintegrate, causing small particles of metal to contaminate any solid product formed in the cell.

Cu- and Ag/$R(SH)_2$. In all the systems studied, the product, which was subsequently identified as $M_2S_2(CH_2)_n$, began to precipitate in the cell almost as soon as the current flowed and continued to form throughout the electrolysis. The solid was collected by filtration, washed with acetonitrile (10-15 mL) and then diethyl ether (10-15 mL), and dried in vacuo. The compounds were characterized analytically (Table II); infrared spectroscopy confirmed the presence of the dithiolate ligand and also demonstrated the absence of the ν(S-H) vibration. Yields were typically 90-95%, based on metal dissolved.

$Cu/C_2H_4(SH)_2\text{-}1,2/P(C_6H_5)_3$. The product which precipitated during electrolysis under the conditions summarized in Table I was identified analytically as $Cu_2S_2C_2H_4$, and the infrared spectrum confirmed the absence of triphenylphosphine. No change in the composition of this precipitate was detected when the final reaction mixture obtained after 1 h of electrolysis was stirred vigorously for 1 h, but when the stirring was continued for 36 h at room temperature, the final product was $Cu_2S_2C_2H_4\cdot 4P(C_6H_5)_3$, in quantitative yield.

$Cu/C_3H_6(SH)_2\text{-}1,2/P(C_6H_5)_3$. Under the conditions shown in Table I, precipitation took place within ca. 5 min of the start of the electrolysis and continued throughout the experiment. The final reaction mixture was stirred vigorously for 1 h after the end of the electrolysis, and the

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Table I. Experimental Conditions for the Electrochemical Synthesis of $M_2S_2(CH_2)_n$ Complexes and Adducts

thiol	amt,[a] mL	applied voltage,[b] V	time of electrolysis, h	amt of metal consumed, mg	electrochemical efficiency (E_f), mol/faraday	product
			Copper			
1,2-$C_2H_4(SH)_2$	1.0	15	2.1	125	1.02	$Cu_2S_2C_2H_4$
1,2-$Cu_3H_6(SH)_2$	0.5	10	1	51	1.07	$Cu_2S_2C_3H_6$
1,3-$C_3H_6(SH)_2$	0.4	15	1	49	1.04	$Cu_2S_2C_3H_6$
1,4-$C_4H_8(SH)_2$	0.5	10	0.67	34	1.08	$Cu_2S_2C_4H_8$
2,3-$C_4H_8(SH)_2$	0.3	25	1	47	1.00	$Cu_2S_2C_4H_8$
1,5-$C_5H_{10}(SH)_2$	0.5	10	1	51	1.07	$Cu_2S_2C_5H_{10}$
1,6-$C_6H_{12}(SH)_2$	0.6	10	1	50	1.06	$Cu_2S_2C_6H_{12}$
1,2-$C_2H_4(SH)_2$	1.0 + 2 g of PPh_3	10[c]	1	120	1.00	$Cu_2S_2C_2H_4$
1,2-$C_3H_6(SH)_2$	0.5 + 2 g of PPh_3	10[c]	1	120	1.00	$Cu_2S_2C_3H_6\cdot 2PPh_3$
1,4-$C_4H_8(SH)_2$	0.5 + 2 g of PPh_3	10[c]	1	120	1.00	$Cu_2S_2C_4H_8$
1,2-$C_2H_4(SH)_2$	1.0 + 2 g of dppm[d]	10[c]	2	232	0.98	$Cu_2S_2C_2H_4\cdot$2dppm
1,2-$C_3H_6(SH)_2$	0.5 + 1.5 g of dppm[d]	10[c]	2.3	269	1.01	$Cu_2S_2C_3H_6\cdot$dppm
2,3-$C_4H_8(SH)_2$	0.5 + 2 g of dppm[d]	15[c]	2.3	269	1.01	$Cu_2S_2C_4H_8\cdot$dppm
			Silver			
1,2-$C_2H_4(SH)_2$	1.0	25	1	80	1.00	$Ag_2S_2C_2H_4$
1,2-$C_3H_6(SH)_2$	0.5	20	1	84	1.05	$Ag_2S_2C_3H_6$
1,3-$C_3H_6(SH)_2$	0.5	15	1	82	1.01	$Ag_2S_2C_3H_6$
1,4-$C_4H_8(SH)_2$	0.5	20	1	82	1.01	$Ag_2S_2C_4H_8$
2,3-$C_4H_8(SH)_2$	1.0	25	1	84	1.04	$Ag_2S_2C_4H_8$
1,5-$C_5H_{10}(SH)_2$	0.4	20	1	82	1.01	$Ag_2S_2C_5H_{10}$
1,6-$C_6H_{12}(SH)_2$	0.5	25	1	82	1.02	$Ag_2S_2C_6H_{12}$

[a] Dissolved in 50 mL of CH_3CN containing ca. 100 mg of Et_4NClO_4. [b] Voltage to give an initial current of 20 mA. [c] Initial current 50 mA. [d] Dissolved in 20 mL of toluene plus 50 mL of CH_3CN.

Table II. Analytical Results for Alkanedithiol Derivatives of Copper and Silver

compd	color	% found	% calcd
M = Cu			
$M_2S_2C_2H_4$-1,2	yellow-green	57.4	58.0
$M_2S_2C_3H_6$-1,2	yellow	55.0	54.5
$M_2S_2C_3H_6$-1,3	yellow	55.0	54.5
$M_2S_2C_4H_8$-1,4	yellow-green	50.9	51.4
$M_2S_{C_4}H_8$-2,3	yellow	52.0	51.4
$M_2S_2C_5H_{10}$-1,5	yellow	48.2	48.7
$M_2S_2C_6H_{12}$-1,6	yellow	47.0	46.2
$M_2S_2C_3H_6$-1,2·2PPh_3[a]	yellow	16.7	16.8
$M_2S_2C_2H_4$-1,2·4PPh_3	yellow	9.53	10.1
$M_2S_2C_3H_6$-1,2·4PPh_3	yellow	9.45	9.92
$M_2S_2C_2H_4$-1,2·2dppm[d]	colorless	12.4	12.9
$M_2S_2C_3H_6$-1,2·dppm·CH_3CN[c]	yellow	21.3	19.3
$M_2S_2C_4H_8$-2,3·dppm[d]	yellow	20.0	20.1
M = Ag			
$M_2S_2C_2H_4$-1,2	yellow	69.3	71.0
$M_2S_2C_3H_6$-1,2	yellow	66.5	67.1
$M_2S_2C_3H_6$-1,3	orange-yellow	66.3	67.1
$M_2S_2C_4H_8$-1,4[e]	cream-yellow	63.9	64.3
$M_2S_2C_4H_8$-2,3	yellow	63.9	64.3
$M_2S_2C_4H_{10}$-1,5	yellow	60.5	61.7
$M_2S_2C_6H_{12}$-1,6	cream-yellow	58.7	59.3

[a] Calcd: C, 61.8; H, 4.76. Found: C, 61.0; H, 4.23. [b] Calcd: C, 63.2; H, 4.86. Found: C, 63.0; H, 4.51. [c] Calcd: C, 54.7; H, 4.74. Found: C, 54.1; H, 4.77. [d] Calcd: C, 55.1; H, 4.75. Found: C, 55.7; H, 5.26. [e] Calcd: C, 14.3; H, 2.4. Found: C, 14.9; H, 2.5.

product was collected, washed, and dried. This material was identified as $Cu_2S_2C_3H_6\cdot 2P(C_6H_5)_3$. In a subsequent experiment, the stirring was continued for 36 h, and in this case, the final solid product was $Cu_2S_2C_3H_6\cdot 4P(C_6H_5)_3$.

$Cu/C_4H_8(SH)_2$-1,4/$P(C_6H_5)_3$. The course of this reaction was essentially that described in the above paragraph, and the final reaction mixture was again stirred for 36 h at room temperature. The solid was collected, washed, and dried and was identified as $Cu_2S_2C_4H_8$; the infrared spectrum confirmed the absence of triphenylphosphine.

$Cu/C_2H_4(SH)_2$-1,2/dppm. A small amount of solid formed in the cell during the electrolysis; the cell and its contents were then allowed to stand at room temperature for 18 h with dry nitrogen flowing gently over the surface of the liquid phase, and during this time further quantities of solid precipitated. This material was collected, washed with acetonitrile (10–15 mL) and then diethyl ether (10–15 mL), and dried in vacuo; it was identified as $Cu_2S_2C_2H_4\cdot$2dppm (yield 85%).

Table III. Crystallographic Data for $[Cu_2S_2C_3H_6\text{-}1,2\cdot(C_6H_5)_2PCH_2P(C_6H_5)_2]_4\cdot 4CH_3CN$

chem form	$C_{112}H_{112}P_8S_8Cu_8\cdot C_8H_{12}N_4$	V, A^3	3052.08
		Z	2
fw	2634.9	ρ_c, g cm^{-3}	1.43
system, space group	triclinic, $P\bar{1}$ (No. 2)	ρ_o, g cm^{-3}	1.49
		radiation; λ, Å	Mo K_α; 0.71069
a, Å	18.483 (7)		
b, Å	11.673 (6)	T, °C	20
c, Å	17.890 (7)	abs coeff, cm^{-1}	15.79
α, deg	116.57 (3)	$R(F_o^2)$	0.0641
β, deg	111.35 (3)	$R_w(F_o^2)$	0.0657
γ, deg	95.69 (3)		

$Cu/C_3H_6(SH)_2$-1,2/dppm. A clear yellow solution formed during the electrolysis, but no precipitate was detected at this stage or on allowing the mixture to stand for 12 h under a flow of nitrogen. The solution was then stored in a refrigerator for 3–4 weeks, and during this time large well-formed crystals deposited; these were collected, washed (acetonitrile, then *n*-pentane), and dried. This product, $Cu_2S_2C_3H_6\cdot$dppm·CH_3CN, was the subject of an X-ray crystallographic study (see below). The infrared spectrum had a weak sharp band at 2248 cm^{-1}, assigned to $\nu(C{\equiv}N)$ of CH_3CN.

$Cu/C_4H_8(SH)_2$-2,3/dppm. The yellow $Cu_2S_2C_4H_8\cdot$dppm precipitated during the electrolysis and was collected and dried in the usual way.

Crystallographic Analysis. A suitable yellow crystal of $Cu_2S_2C_3H_6$-1,2·dppm·CH_3CN (**1**), dimensions 0.16 × 0.23 × 0.38 mm, was selected from the crop obtained from the preparation, sealed in a capillary tube, and mounted along its longest dimension in a Syntex $P2_1$ automated diffractometer. Data were collected at room temperature (ca. 20 °C) by the procedures described previously.[13] The intensities of three check reflections were monitored at regular intervals, and no significant change was observed during the time required for data collection. The cell parameters were measured and refined from results of 30 strong high-angle ($15 < 2\theta < 25°$) reflections. The data used in structure determination were corrected for Lorentz and polarization effects and were corrected analytically for absorption. The density was measured by the flotation method in carbon tetrachloride–benzene mixtures. Pertinent crystal and experimental data are given in Table III.

The space group $P\bar{1}$ was used, and later assumed to be correct because of the successful refinement. The structure was solved by direct methods, using the program SHELX. The copper atoms were found from the E map, and the sulfur, phosphorus, and carbon atoms from the difference Fourier syntheses. The structure was refined in blocks during the

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Table IV. Fractional Atomic Parameters and Thermal Parameters of Non-Hydrogen Atoms of $[Cu_2S_2C_3H_6\text{-}1,2\cdot(C_6H_5)_2PCH_2P(C_6H_5)_2]_4\cdot CH_3CN$ with Estimated Standard Deviations in Parentheses

atom	*x*	*y*	*z*	U_{eq},[a] Å^2 × 10^3	atom	*x*	*y*	*z*	U_{eq},[a] Å^2 × 10^3
Cu(1)	−0.271 66 (1)	−0.106 04 (2)	−0.226 79 (1)	58 (3)	C(36)	−0.491 47 (11)	−0.174 88 (18)	−0.336 05 (11)	62 (8)
Cu(2)	−0.295 12 (1)	−0.062 23 (3)	−0.060 45 (2)	77 (7)	C(41)	−0.326 88 (10)	0.133 77 (17)	−0.282 80 (12)	58 (8)
Cu(3)	−0.123 29 (1)	0.009 35 (3)	0.036 78 (2)	73 (2)	C(42)	−0.255 03 (11)	0.230 20 (18)	−0.240 58 (13)	65 (8)
Cu(4)	0.054 54 (1)	0.087 87 (2)	0.172 17 (1)	62 (4)	C(43)	−0.241 67 (13)	0.288 72 (20)	−0.289 79 (15)	94 (10)
S(1)	−0.331 51 (3)	−0.255 01 (5)	−0.196 26 (4)	74 (6)	C(44)	−0.295 40 (13)	0.257 05 (21)	−0.375 79 (16)	92 (10)
S(2)	−0.216 19 (3)	−0.124 54 (7)	0.036 92 (4)	90 (11)	C(45)	−0.371 58 (13)	0.150 88 (21)	−0.424 64 (16)	107 (11)
S(3)	−0.023 25 (3)	0.203 29 (5)	0.128 71 (3)	75 (6)	C(46)	−0.388 70 (11)	0.088 77 (19)	−0.377 34 (13)	90 (9)
S(4)	−0.135 40 (2)	−0.003 26 (5)	−0.102 12 (3)	62 (3)	C(51)	−0.445 16 (10)	0.084 17 (19)	−0.068 28 (12)	58 (8)
P(1)	−0.260 00 (3)	−0.201 93 (5)	−0.365 07 (3)	57 (4)	C(52)	−0.478 89 (12)	0.191 06 (22)	−0.049 26 (14)	90 (10)
P(2)	−0.345 00 (3)	0.038 37 (5)	−0.229 16 (3)	54 (4)	C(53)	−0.567 00 (13)	0.154 23 (23)	−0.074 85 (14)	102 (10)
P(3)	−0.333 33 (3)	0.118 16 (6)	−0.037 10 (3)	70 (5)	C(54)	−0.606 18 (13)	0.028 80 (22)	−0.111 07 (14)	90 (10)
P(4)	0.079 02 (3)	0.048 00 (5)	0.289 32 (3)	56 (3)	C(55)	−0.576 30 (14)	−0.073 47 (22)	−0.133 91 (14)	82 (9)
C(01)	−0.317 87 (9)	0.186 70 (17)	−0.107 00 (11)	66 (5)	C(56)	−0.488 69 (11)	−0.044 71 (20)	−0.110 27 (12)	70 (8)
C(02)	−0.189 76 (9)	−0.075 67 (16)	−0.364 65 (11)	63 (5)	C(61)	−0.281 29 (11)	0.269 27 (22)	0.079 17 (14)	77 (8)
C(1A)	−0.251 32 (11)	−0.327 08 (24)	−0.151 65 (14)	87 (11)	C(62)	−0.289 29 (14)	0.391 74 (26)	0.092 66 (18)	117 (10)
C(1B)	−0.239 40 (12)	−0.303 56 (26)	−0.058 74 (21)	104 (10)	C(63)	−0.245 29 (17)	0.525 49 (32)	0.197 58 (22)	164 (13)
C(1C)	−0.303 57 (17)	−0.388 29 (31)	−0.063 99 (19)	203 (11)	C(64)	−0.208 26 (15)	0.475 51 (27)	0.254 26 (19)	118 (10)
C(2A)	−0.005 32 (10)	0.225 53 (19)	0.040 03 (11)	73 (3)	C(65)	−0.196 12 (15)	0.363 54 (28)	0.239 98 (19)	128 (11)
C(2B)	0.040 89 (11)	0.374 73 (18)	0.080 29 (14)	89 (11)	C(66)	−0.235 74 (14)	0.246 01 (26)	0.148 92 (18)	100 (10)
C(2C)	−0.087 22 (9)	0.177 03 (17)	−0.047 12 (11)	68 (11)	C(71)	0.031 08 (10)	−0.122 34 (17)	0.256 82 (12)	55 (7)
C(11)	−0.225 74 (9)	−0.346 10 (16)	−0.403 16 (11)	52 (7)	C(72)	0.062 83 (11)	−0.180 69 (19)	0.308 77 (13)	68 (8)
C(12)	−0.234 95 (10)	−0.418 73 (19)	−0.495 27 (13)	67 (8)	C(73)	0.017 77 (12)	−0.311 67 (21)	0.277 74 (14)	83 (9)
C(13)	−0.208 58 (11)	−0.534 66 (19)	−0.523 97 (14)	76 (9)	C(74)	−0.055 87 (12)	−0.383 80 (21)	0.200 72 (14)	83 (9)
C(14)	−0.171 70 (11)	−0.570 06 (20)	−0.459 25 (14)	82 (9)	C(75)	−0.088 26 (14)	−0.324 32 (24)	0.151 95 (17)	99 (10)
C(15)	−0.159 95 (11)	−0.499 53 (19)	−0.368 63 (14)	76 (9)	C(76)	−0.046 08 (12)	−0.193 38 (20)	0.176 36 (14)	83 (9)
C(16)	−0.187 99 (10)	−0.387 14 (18)	−0.338 85 (14)	62 (8)	C(81)	0.046 21 (10)	0.147 64 (17)	0.375 93 (12)	58 (7)
C(21)	−0.354 73(10)	−0.255 51 (18)	−0.470 17 (11)	60 (8)	C(82)	0.011 48 (10)	0.244 95 (18)	0.365 78 (13)	79 (9)
C(22)	−0.415 87 (12)	−0.368 77 (20)	−0.498 49 (14)	80 (9)	C(83)	−0.009 28 (12)	0.331 41 (21)	0.436 86 (15)	98 (10)
C(23)	−0.492 48 (14)	−0.418 02 (23)	−0.577 41 (15)	96 (10)	C(84)	0.002 11 (12)	0.311 73 (21)	0.509 31 (15)	96 (10)
C(24)	−0.501 51 (25)	−0.355 58 (25)	−0.625 06 (17)	119 (11)	C(85)	0.039 09 (11)	0.219 98 (20)	0.523 63 (14)	92 (10)
C(25)	−0.446 24 (19)	−0.240 81 (30)	−0.599 93 (21)	160 (13)	C(86)	0.063 75 (11)	0.137 89 (13)	0.456 13 (13)	86 (9)
C(26)	−0.362 68 (14)	−0.187 50 (23)	−0.517 95 (16)	96 (10)	N(1)	0.202 46 (18)	0.013 33 (29)	0.582 02 (13)	220 (16)
C(31)	−0.456 20 (11)	−0.035 42 (18)	−0.287 68 (11)	48 (7)	N(2)	0.517 62 (34)	0.456 03 (55)	0.784 60 (41)	260 (17)
C(32)	−0.507 20 (10)	0.046 80 (17)	−0.281 34 (11)	61 (8)	C(3A)	0.192 86 (13)	0.039 15 (27)	0.643 32 (17)	194 (15)
C(33)	−0.592 96 (11)	0.006 81 (19)	−0.324 79 (12)	69 (9)	C(3B)	0.182 97 (18)	0.051 90 (29)	0.723 91 (19)	176 (14)
C(34)	−0.624 36 (11)	−0.144 32 (19)	−0.370 25 (12)	73 (9)	C(4A)	0.448 16 (29)	0.490 34 (66)	0.803 43 (47)	185 (14)
C(35)	−0.576 74 (11)	−0.230 40 (19)	−0.378 24 (13)	78 (8)	C(4B)	0.490 13 (25)	0.438 94 (44)	0.863 97 (31)	185 (14)

[a] U_{eq} for the non-hydrogen atoms is calculated from the refined anisotropic thermal parameters; $U_{eq} = {}^1/_3[\sum_i\sum_j u_{ij}a_i^*a_j^*a_ia_j]$.

least-squares analysis with Cu(1)–Cu(4), S(1)–S(4), and the carbon atoms of the 1,2-propanedithiolate dianion in one block (127 variables) and with the remaining atoms in the other block (271 variables). Hydrogen atoms were subsequently introduced in their calculated positions with a fixed C–H distance of 0.95 Å, and the final refinement was carried out with anisotropic temperature factors for the copper, phosphorus, sulfur, and carbon atoms of the propane-1,2-dithiolato dianion and dppm. Unit weights were used in the initial stages, while in the final cycles the weighting scheme was of the form $w = [\sigma(F)^2 + 0.00001F^2]^{-1}$. The refinement, minimizing the function $\sum w(|F_o| - |F_c|)^2$, converged at R = 0.0641 and R_w = 0.0657. There was evidence of disorder in the acetonitrile molecules, which could be a contributing factor to the high R values.

The computer programs and the source of scattering factors were those used in earlier work.[13,14] Fractional atomic coordinates are given in Table IV, and bond lengths and bond angles in Table V. Tables of thermal parameters, hydrogen atom coordinates, and observed and calculated structure factor amplitudes are available as supplementary material. The structure is shown in Figure 1.

Reaction with Carbon Disulfide. Following previous work,[9,15,16] which has established that many metal–thiolato compounds react with carbon disulfide, we treated a sample of $Cu_2S_2C_3H_6\text{-}1,2\cdot 2P(C_6H_5)_3$ with an excess of this solvent. The yellow compound dissolved slowly (24 h, room temperature) on stirring, and the brown solid obtained on evaporation of the solvent was collected and dried. The infrared spectrum of this product showed ν(C–S) modes at 886 and 996 cm^{-1}, absent in the parent compound, implying the presence of thioxanthate groups. The analysis of this material corresponded to the formula $Cu_2S_2C_3H_6\cdot 4(C_6H_5)_3P\cdot 3CS_2$. Anal. Calcd for $C_{78}H_{66}P_4S_8Cu_2$: Cu, 8.41; C, 62.0; H, 4.60. Found: Cu,

Table V. Interatomic Distances (Å) and Angles (deg) for $[Cu_2S_2C_3H_6\text{-}1,2\cdot(C_6H_5)_2PCH_2P(C_6H_5)_2]_4\cdot 4CH_3CN$[a]

	Distances		
Cu(1)–S(1)	2.345 (1)	Cu(4)–S(3)	2.236 (1)
Cu(4)–S(4)′	2.308 (1)	Cu(4)–P(4)	2.245 (1)
Cu(1)–S(4)	2.371 (1)	S(1)–C(1A)	1.878 (3)
mean C–P	1.831 (2)	Cu(1)···Cu(2)	2.987 (5)
mean C(0)-P	1.852 (3)	Cu(2)···Cu(3)	2.818 (3)
		Cu(3)···Cu(4)	3.026 (3)
	Mean C-C of Phenyl Rings		
C(11)–C(16)	1.400 (4)	C(51)–C(56)	1.397 (4)
C(21)–C(26)	1.395 (5)	C(61)–C(66)	1.411 (5)
C(31)–C(36)	1.399 (3)	C(71)–C(76)	1.388 (4)
C(41)–C(46)	1.400 (4)	C(81)–C(86)	1.403 (4)
	Angles		
P(1)–Cu(1)–S(1)	116.3 (2)	P(4)–Cu(4)–S(3)	116.2 (2)
P(2)–Cu(1)–S(1)	108.8 (3)	P(4)–Cu(4)–S(4)′	108.5 (3)
P(2)–Cu(1)–P(1)	108.2 (3)	Cu(2)–S(1)–Cu(1)	81.0 (2)
P(3)–Cu(2)–S(1)	129.0 (3)	Cu(3)–S(2)–Cu(2)	77.8 (4)
P(3)–Cu(2)–S(2)	134.2 (3)	Cu(4)–S(3)–Cu(3)	85.6 (3)
S(2)–Cu(2)–S(1)	96.7 (3)	S(3)–Cu(3)–S(2)	142.5 (3)
S(4)–Cu(4)–S(4)′	108.5 (3)	C(1A)–C(1B)–S(2)	118.0 (3)
C(1A)–S(1)–Cu(1)	107.4 (1)	C(1C)–C(1B)–S(2)	113.1 (3)
C(1A)–S(1)–Cu(2)	99.6 (1)	Cu(1C)–C(1A)–C(1B)	109.5 (2)
C(1B)–S(2)–Cu(2)	96.0 (1)	C(1B)–C(1A)–S(1)	108.9 (2)
C(1B)–S(2)–Cu(3)	109.3 (1)	C(2A)–C(2B)–S(3)	112.0 (2)
C(2B)–S(3)–Cu(3)	100.4 (1)	C(2B)–S(3)–Cu(3)	109.4 (2)
mean C–P–Cu	116.8 (1)	mean C–P–C	102.5 (1)
mean C(0)–P–Cu	114.8 (1)	mean C–P–C(0)	102.1 (1)

[a] The esd's on average values are calculated with the use of the "scatter formula": $\sigma = [\sum(d_i - \bar{d})^2/(N - i)]^{1/2}$. Symmetry for a primed atom: $1 - x$, $1 - y$, $1 - z$.

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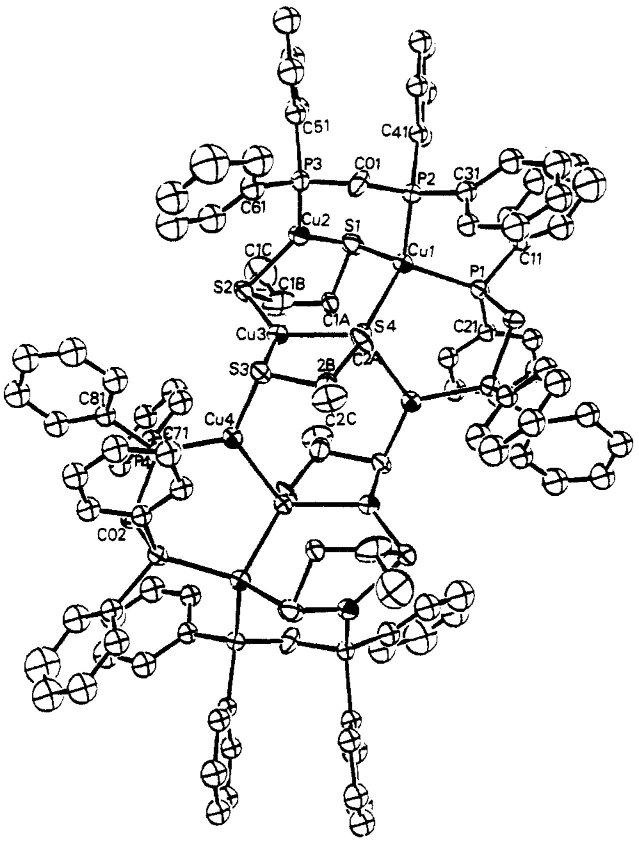

Figure 1. Molecular structure of $[Cu_2S_2C_3H_6\text{-}1,2\cdot(C_6H_5)_2PCH_2P(C_6H_5)_2]_4$ (ORTEP diagram, 30% probability ellipsoids).

8.52; C, 62.4; H, 4.60. The slow reaction to give a soluble product suggests a dismantling of the (presumed) cage structure of the starting material by attack by CS_2, but lacking X-ray results and given the complexity of another structure involving Cu–SR and Cu–S_2CSR groups,[6] the structure of this product cannot be presently identified. Qualitatively similar reactions were observed between CS_2 and $Cu_2S_2C_2H_4\cdot 4P(C_6H_5)_3$.

Results

One aim in the study of direct electrochemical synthesis in this laboratory has been to establish that it is a general, one-step, high-yield route to a wide variety of inorganic and organometallic compounds. The present work confirms this by demonstrating that in the case of copper and silver, the M_2S_2R compounds of a series of alkanedithiolates can be conveniently prepared by this simple procedure, and that a number of derivatives can also be obtained by similar methods:

$$\begin{tikzcd}
\mathrm{M}_{(+)} \arrow[r, "\mathrm{R(SH)_2}"] \arrow[rr, bend right, "\mathrm{R(SH)_2 + L}"'] & \mathrm{M_2S_2R} \arrow[r, "\mathrm{L}"] & \mathrm{M_2S_2R}\bullet n\mathrm{L}
\end{tikzcd}$$

The experimental conditions for the electrochemical synthesis are given in Table I, and the analytical data for the products in Table II. The structure of $[Cu_2S_2C_3H_6\cdot dppm]_4$ has been determined, with the results shown in Tables III–V and Figures 1 and 2. These features of the studies are discussed in detail in the sections which follow.

Discussion

Electrochemical Preparation. The reaction pathway which most simply describes the electrode processes is

$$\text{cathode:}\quad R(SH)_2 + 2e \rightarrow H_2(g) + RS_2^{2-} \qquad (1)$$

$$\text{anode:}\quad RS_2^{2-} + 2M \rightarrow M_2S_2R + 2e \qquad (2)$$

In all the systems studied, the electrochemical efficiency (E_f), defined as the number of moles of metal dissolved from the anode per faraday of charge, is close to unity (1.03 ± 0.03 for Cu and 1.03 ± 0.02 for Ag), in keeping with eqs 1 and 2. Other and more complicated series of reactions can also be written (cf. refs 9 and 10), but the above description adequately satisfies the experimental evidence in the present case. As in other systems studied, the E_f values do not change when neutral donor ligands are present in the solution phase, implying that the formation of adducts occurs subsequent to the electrochemical oxidation reaction which yields the primary M_2S_2R product. We return to this point below.

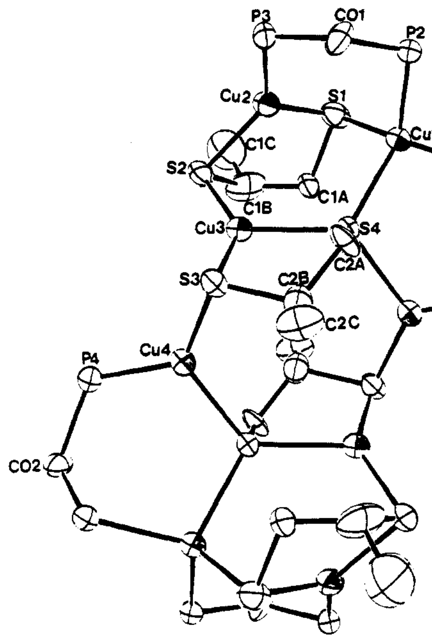

Figure 2. Core structure of $[Cu_2S_2C_3H_6\text{-}1,2\cdot(C_6H_5)_2PCH_2P(C_6H_5)_2]_4$.

Structure of $[Cu_2S_2C_3H_6\cdot dppm]_4$. The crystallographic results show clearly that the molecular structure of this compound involves a cage, reminiscent of but different from other copper(I)–thiolate cages,[10,11] and is based on a Cu_4S_4 core capped by various five- and six-membered rings involving copper atoms and the two bidentate ligands. Holm et al.[17] have rightly pointed out that there is a "formidable body of structural and related data" on thiolato derivatives of this and other metals, and the present results add to this corpus, without providing any rationale to explain why this particular combination of metal and ligands should give rise to the structure in question.

The central feature of the molecule, which has a center of inversion, is an eight-membered ring (Figure 2), Cu(3)–S(3)–Cu(4)–S(4)′–Cu(4)′–S(3)′–Cu(3)′–S(4), and this is capped by four six-membered rings, two involving Cu(3)–S(4)–Cu(1)–S(1)–Cu(2)–S(2) and its symmetry equivalent, and two incorporating one of the dppm rings, Cu(4)–P(4)–C(02)–P(1)′–Cu(1)′–S(4)′, and its equivalent. Two five-membered rings involving the bidentante dithiolate ligand are also attached to the Cu_4S_4 ring, namely Cu(3)–S(3)–C(2B)–C(2A)–S(4) and the corresponding ring on Cu(4)′. Finally, there are two six-membered rings in which dppm bridges a pair of copper atoms which are not part of the Cu_4S_4 ring, involving Cu(2)–S(1)–Cu(1)–P(2)–C(01)–P(3) and its analogue. Although this molecule shows some of the features found in the complexes of ethane-1,2-dithiolate with first-row transition elements,[15] as in the case of the M_2S_2C rings, the central eight-membered ring is apparently a new feature in this type of molecule. Given the known range of structures of these dithiolates, and those in the complexes of copper(I) with monothiolates,[11,12] it seems reasonable to avoid any generalizations about the factors that dictate the formation of any one of these fascinating structures.

The copper atoms in **1** can be identified as falling into four different categories. Cu(1) (and Cu(1)′) is four-coordinate, with the average bond angle at the metal being 110.2°, and this atom is a member of three six-membered rings, but not of the Cu_4S_4 core. The Cu–P bond distances are significantly different, but

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(17) Rao, Ch. P.; Dorfman, J. R.; Holm, R. H. *Inorg. Chem.* **1986**, *25*, 428.

the average of 2.295 Å is close to that found in two other cage structures in which dppm bridges a Cu–S–Cu[6] or Cu–P–Cu[18] system, for which the average values are 2.274 and 2.290 Å, respectively. The other copper atoms are three-coordinate. The kernel of Cu(2) (and Cu(2)′) is of the type CuPSS′ and is again distinct from the Cu_4S_4 core, and the Cu(2)–P(3) bond is significantly shorter (2.188 (1) Å) than those just discussed, which may well reflect the lower coordination number. These copper atoms are part of the fusion of two six-membered rings. The remaining metal atoms (Cu(3) and (3)′ and Cu(4) and (4)′) are in the eight-membered ring and in both cases are also part of different six-membered rings, namely Cu(3)–S(4)–Cu(1)–S(1)–Cu(2)–S(2) and Cu(4)–P(4)–C(02)–P(1)′–Cu(1)′–S(4)′.

The sulfur atoms can also be categorized in terms of their binding to copper: S(1) bridges Cu(1) and Cu(2), and S(2) links Cu(2) and Cu(3), while within the Cu_4S_4 ring, S(3) bridges Cu(3) and Cu(4), and S(4) is bonded to Cu(1), Cu(3), and Cu(4)′. Given the range of different Cu–S modes of coordination, it is not surprising that there is a wide range of Cu–S bond distances, between 2.207 (1) Å for Cu(3)–S(2) and 2.347 (1) Å for Cu(3)–S(4). There seems little to be gained by comparing these different Cu–S bonds within the molecule or in discussing them in terms of the many other Cu–S bond lengths that have been reported in the literature,[15] other than to point out that the present values are in fact compatible with these earlier results.

The geometry of the Cu_4S_4 ring does not appear to require any Cu–Cu bonding interactions, and the distances involved confirm this. The closest approach is between Cu(3) and Cu(3)′, at 2.818 (3) Å, and the cross-ring distance between Cu(4) and Cu(3)′ is 3.026 (3) Å. It has been argued elsewhere[5,19] that an approach of 2.6 Å or less implies bonding between two copper(I) atoms, and this is clearly not occurring in the present case.

The Cu_4S_4 ring is a crown conformation, not unlike that in $Cu_4(\mu\text{-}SC_5H_{11})_4\cdot 2dppm$,[6] despite the very different nature of the thiolate ligands in question. The four copper atoms lie on a plane, while the four sulfur atoms form another plane, making an angle of 38.8 (1)° with the first; viewed in another sense, the sulfur atoms S(3) and S(3)′ are 1.626 Å below the Cu_4 plane and S(4) and S(4)′ are 0.640 Å below. The comparable values in $Cu_4(\mu\text{-}SC_5H_{11})_4\cdot 2dppm$ are 1.52 and 0.42 Å, so there is some detailed similarity between the two molecules. It is not clear to what extent these conformations result from interactions within the ring, or whether they are forced upon the central ring by the mode of packing of the ligands. It is also probable that the packing in the core region of the molecule may be dictated by the conformation of the outer six-membered rings, which in turn may be the result of the phenyl groups of dppm minimizing their steric interactions. The outer six-membered rings are all in the boat conformation, and the inner rings adopt the same form insofar as this is possible given the presence of the trigonal sulfur atoms (S(1) etc.)

Finally we note that the bond distances and angles within the dppm ligand are close to those reported in other Cu^I–dppm species,[6,15] with *r*(P–C) = 1.852 Å (average) in the Cu_2SP_2C ring and P–C–P = 108.3 (3)°. The remaining C–C and C–S bond lengths and angles are in the known ranges and call for no comment here.

General Structural Considerations. The copper(I) and silver(I) M_2S_2R derivatives of alkanedithiolates all precipitate during the electrochemical synthesis and are insoluble in acetonitrile and all other organic solvents tested. Similar behavior was also found in the electrochemical synthesis of the zinc and cadmium analogues,[9] and the explanation is presumably the same in all cases, namely the formation of homopolymers by M–S–M cross-linking. Such polymerization has been demonstrated by X-ray crystallography[20] in the case of solid $PbS_2C_2H_4$. The exact details probably differ from metal to metal, and may also depend on the number of carbon atoms in the S–$(CH_2)_n$–S system, but such matters go beyond the present experimental evidence.

The stability of such polymeric structures toward complexation by the phosphorus ligands used in the present work clearly depends, inter alia, on the dithiolate ligand in question. The details in the Experimental Section demonstrate this conclusion in the case of triphenylphosphine, since adducts were obtained with $Cu_2S_2C_2H_4$ and $Cu_2S_2C_3H_6$-1,2 but not with $Cu_2S_2C_4H_8$-1,4, and this series of experiments also showed that solid $Cu_2S_2C_nH_{2n}$ (n = 2,3) reacts slowly with $P(C_6H_5)_3$ after the initial precipitation at the copper anode. With dppm, the number of bidentate ligands coordinated per Cu_2S_2 unit is 2 for $n = 2$ and is 1 for n = 3 or 4, but even between these last two cases there is a minor difference, in that one structure has CH_3CN in the lattice whereas the other does not. There are also significant differences between the adducts of $P(C_6H_5)_3$ and dppm; the former are insoluble in CH_3CN, while the latter are of varying solubility, in that the compounds of $Cu_2S_2C_2H_4$ and $Cu_2S_2C_3H_6$-1,2 are obtained by slow removal of solvent in contrast to the immediate precipitation observed with $Cu_2S_2C_4H_8$-2,3·dppm. The behavior of $Cu_2S_2C_3H_6$-1,2·dppm·CH_3CN emphasizes that this gradual crystallization depends upon slow solution reactions by which the complicated cage structure is assembled, and such processes are, not surprisingly, irreversible, since the crystalline material so obtained cannot be redissolved in acetonitrile or other common organic solvents.

Given the complexity of the structure of $[Cu_2S_2C_3H_8\cdot dppm]_4$, and of the related copper(I) thiolate and dithiolate molecules that have been reported,[11,12,15] it does not seem prudent to speculate on the controlling factors in the solution and/or solid-state chemistry which govern either the molecularity or the stereochemistry of these intriguing structures.

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Supplementary Material Available: Tables of refined anisotropic thermal parameters, final fractional coordinates and thermal parameters for hydrogen atoms, and a cell packing diagram (5 pages); a listing of observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

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