Thermal Degradation of Copper(I) Thiolate Clusters and the Crystal Structure of Solvent-free $(Ph_4P)_2[Cu_4(SPh)_6]$

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Abstract

Copper(I) thiolate clusters of the type $(Ph_4P)_2[Cu_4(SPh)_6]$ or $((CH_3)_4N)_2[Cu_x(SPh)_y]$ with or without solvent molecules and with x:y = 4:6 or 5:7 have been crystallized from different solvents. Their thermal degradation behavior was characterized by thermogravimetry and simultaneous mass spectrometry of the evolved molecules. The solvent-containing complexes lose the solvent in a first decomposition step between 100 and 160 °C. The subsequent degradation is dependent on the cation only, not on the Cu(I)–S core type and finally leads to $Cu_{1.96}S$. In the course of this decomposition intermediate products with the stoichiometry $Cu_x(SPh)_x$ are formed.

The crystal structure of solvent-free $(Ph_4P)_2[Cu_4(SPh)_6]$ (a = 23.290(9), b = 13.008(4), c = 25.622(6) Å, β = 107.31(3)°, Z = 4, space group $P2_1/a$) has been solved and refined to R = 6.9% for 2982 observed reflections. The structure consists of adamantan-type $[Cu_4S_6]^{2-}$ clusters and Ph_4P^+ cations. The mean Cu–Cu distance within the cluster is 2.744 Å, Cu–S distances range from 2.252 to 2.315 Å.

Crystals of $((CH_3)_4N)_2[Cu_5(SPh)_7]$ have been shown by thermal analysis to contain one solvent molecule per formula unit. The crystal structure of this solvent-containing complex (a = 12.244(10), b = 20.058(11), c = 11.506(5) Å, α = 103.59(5), β = 90.04(5), γ = 82.98(6)°, Z = 2, space group $P\bar{1}$, R = 6.1% including 3409 observed reflections) exhibits $[Cu_5(SPh_7)]^{2-}$ clusters and $(CH_3)_4N^+$ cations and shows no significant deviations from data given in the literature for the 'solvent-free' complex.

Introduction

Synthetic transition metal complexes of sulfur-containing ligands are of much current interest, especially in view of their significance as model compounds for iron-, molybdenum-, copper-, cadmium- or zinc-proteins. Mononuclear copper thiolate as well as thioether coordination has been established for example in the 'blue' copper(II) proteins plastocyanin [1] and azurin [2]; polynuclear copper(I) thiolate coordination without additional ligands occurs in the copper(I) thioneins. A cuban-type Cu_4S_8 core has been proposed for yeast copper(I) thionein, which exhibits a copper-to-sulfur ratio of 1:2 [3], whereas a single Cu_6S_7 core is suggested for the *Neurospora crassa* copper thionein [4].

In polynuclear copper–sulfur model compounds aryl thiolates are usually used as ligands, for example thiophenol. We have tried to prepare modified clusters of such copper–thiophenolate compounds by partial thermal decomposition. During the preparation of these clusters to be used as starting materials, some interesting features were observed. X-ray investigations revealed different lattice parameters as a function of the preparation conditions for 'identical' compounds. This observation is in agreement with a statement of Dilworth, who reported that a careful control of reaction conditions is necessary to produce a particular Cu(I)– or Ag(I)–thiolate cluster [5]. Dance *et al.* have described the specific solvent compositions and reaction conditions to be used to achieve the crystallization of clusters with a distinct stoichiometry [6, 7]. In addition we have observed that different solvent molecules can be inserted in the crystal lattice of a given compound, leading to an increase of the cell volume. The solvent molecules were identified by simultaneous thermogravimetry and mass spectrometry. In this paper we report the preparation, thermoanalytical and structural characterization of Cu(I)–thiophenolate clusters with Cu:S ratios of 4:6 and 5:7, with $(CH_3)_4N^+$ or Ph_4P^+ as cations and with different solvent molecules inserted.

With the knowledge of the preferably inserted solvent molecules, we were able to crystallize solvent-free $(Ph_4P)_2[Cu_4(SPh)_6]$. The crystal structure of a compound with this composition and the cell dimensions a = 26.93(5), b = 14.121(7), c = 23.57(5) Å, β = 119.41(2)°, V = 7808 Å^3 and space group $P2_1/c$ was reported in 1980 by Coucouvanis [8]. As a consequence of considerable refinement difficulties and

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low resolution of the data, no positional parameters for the atoms as well as no detailed bond distances and angles were given in this publication. Our data, however, show that crystals with cell parameters very close to those given above contain one solvent molecule per formula unit, whereas the solvent-free compound exhibits a different cell with $a = 23.290(9)$, $b = 13.008(4)$, $c = 25.622(6)$ Å, $\beta = 107.31(3)^\circ$, $V = 7411$ Å^3 and space group $P2_1/a$. Therefore we have solved and refined the structure of this solvent-free $(Ph_4P)_2[Cu_4(SPh)_6]$.

In addition, we have redetermined the crystal structure of $((CH_3)_4N)_2[Cu_5(SPh)_7]$·solvent. Cell parameters of this complex are $a = 12.244(10)$, $b = 20.058(11)$, $c = 11.506(5)$ Å, $\alpha = 103.59(5)$, $\beta = 90.04(5)$, $\gamma = 82.98(6)^\circ$, $V = 2724$ Å^3 and space group $P\bar{1}$. The structure of a complex with nearly identical cell parameters ($a = 12.250(1)$, $b = 20.151(4)$, $c = 11.531(2)$ Å, $\alpha = 103.50(1)$, $\beta = 90.01(1)$, $\gamma = 83.20(1)^\circ$, $V = 2747$ Å^3, space group $P\bar{1}$) has been solved by Dance *et al.* [7], but was described as solvent-free $((CH_3)_4N)_2[Cu_5(SPh)_7]$. According to our thermogravimetric data, however, the stoichiometry should be given as $((CH_3)_4N)_2[Cu_5(SPh)_7]$·solvent.

Experimental

Preparation

Copper was used either in the form of its acetonitrile complex $[Cu(I)(CH_3CN)_4]BF_4$, which was prepared as described in ref. 9, or in the form of $Cu(II)(NO_3)_2 \cdot 3H_2O$. Thiophenol, piperidine and $(Ph)_4PCl$ were purchased from Fluka AG, Buchs/Switzerland and used without further purification. The syntheses were performed in a Schlenk-type apparatus in a nitrogen atmosphere.

$(Ph_4P)_2[Cu_4(SPh)_6]$

A solution of 0.35 g (1.1 mmol) $[Cu(CH_3CN)_4]BF_4$ in 15 ml acetone was added slowly to a solution of 0.55 g (5 mmol) thiophenol, 0.43 g (5 mmol) piperidine and 1.2 g (3 mmol) Ph_4PCl in 120 ml absolute ethanol. This reaction mixture was refluxed for 10 min. Crystallization at room temperature was finished within 10 h. To obtain the pure product, it was necessary to separate manually the orange prisms of $(Ph_4P)_2[Cu_4(SPh)_6]$ from the white needles of Ph_4PBF_4. *Anal.* Calc. for $C_{84}H_{70}Cu_4P_2S_6$: C, 63.54; H, 4.41. Found: C, 63.83; H, 4.70%.

$(Ph_4P)_2[Cu_4(SPh)_6]$·acetone

To a solution of 0.55 g (5 mmol) thiophenol and 0.43 g (5 mmol) piperidine in 50 ml ethanol, 0.35 g (1.1 mmol) $[Cu(CH_3CN)_4]BF_4$ in 20 ml acetone was added. Slow addition of 1.2 g (3 mmol) $(Ph)_4PCl$ in 30 ml ethanol yielded a yellow precipitate. This was collected by filtration and then redissolved in 40 ml acetone. Slow evaporation at room temperature yielded yellow hexagonal platelets. *Anal.* Calc. for $C_{87}H_{76}Cu_4OP_2S_6$: C, 63.48; H, 4.68; S, 11.70. Found: C, 63.39; H, 4.77; S, 11.41%.

$(Ph_4P)_2[Cu_4(SPh)_6]$·0.5acetone·0.5propanol

Addition of 0.35 g (1.1 mmol) $[Cu(CH_3CN)_4]BF_4$ in 20 ml acetone to 0.55 g (5 mmol) thiophenol and 0.43 g (5 mmol) piperidine in 50 ml propanol resulted in a yellow solution. While heating this solution, 1.2 g (3 mmol) $(Ph)_4PCl$ in 20 ml propanol and 10 ml acetone was added and the mixture was refluxed until all the precipitate was redissolved. Bright yellow, very thin platelets crystallized within 3 h at room temperature. *Anal.* Calc. for $C_{87}H_{77}Cu_4OP_2S_6$: C, 63.47; H, 4.68; S, 11.70. Found: C, 63.70; H, 4.82; S, 11.50%.

$((CH_3)_4N)_2[Cu_4(SPh)_6]$ and
$((CH_3)_4N)_2[Cu_4(SPh)_6]$·acetonitrile

2 g (18.2 mmol) thiophenol, 1.7 g (16.8 mmol) triethylamine and 1.5 g (13.7 mmol) $(CH_3)_4NCl$ were dissolved in a mixture of 10 ml ethanol, 60 ml propanol, 8 ml methanol and 25 ml acetonitrile. 0.8 g (3.3 mmol) $Cu(NO_3)_2 \cdot 3H_2O$ in 15 ml ethanol was added to this solution. The reaction mixture, a pale yellow solution, was then allowed to stand at room temperature. Crystallization yielded a mixture of white bulky needles of the solvent-free species and of pale yellow blocks of $((CH_3)_4N)_2[Cu_4SPh)_6]$·acetonitrile. The crystals were separated manually. *Anal.* Calc. for solvent-free $C_{44}H_{54}Cu_4N_2S_6$: C, 49.98; H, 5.11; N, 2.70. Found: C, 50.38; H, 5.25; N, 2.91%.

$((CH_3)_4N)_2[Cu_5(SPh)_7]$·solvent

2 g (18.2 mmol) thiophenol, 1.7 g (16.8 mmol) triethylamine and 1.5 g (13.7 mmol) tetramethylammonium chloride were dissolved in 50 ml ethanol plus 8 ml methanol. Slow addition of 1.0 g (4.14 mmol) $Cu(NO_3)_2 \cdot 3H_2O$, dissolved in 20 ml ethanol, yielded a yellow precipitate. This was collected by filtration and redissolved in 80 ml propanol, 20 ml ethanol and 20 ml acetone. Yellow brickstone-like crystals of $((CH_3)_4N)_2[Cu_5(SPh)_7]$ with, according to thermoanalytical and mass spectrometric data, different solvents inserted (ethanol, propanol, acetone) grew within 20 h at room temperature. *Anal.* Calc. for $C_{50}H_{59}Cu_5N_2S_7 \cdot \frac{1}{3}$acetone$\cdot \frac{1}{3}$propanol$\cdot \frac{1}{3}$ethanol: C, 49.13; H, 5.14; N, 2.18; S, 17.49. Found: C, 49.13; H, 5.09; N, 1.96; S, 17.21%.

Thermal Analysis

The thermal degradation of the compounds was registered by thermogravimetry on a Perkin-Elmer thermogravimetric system TGS-2. Evolved gas analyses were performed simultaneously with a Balzers QMG-511 quadrupole mass spectrometer coupled to the thermobalance. To avoid oxidation, all experiments were carried out in an inert nitrogen atmosphere. The final temperature of the experiments and the heating rates were kept invariant at 600 °C and 10°/min, respectively.

X-ray Crystallography

Lattice parameters for all crystals investigated were obtained from least-squares refinements of respective 25 reflections in the range $14 < 2\theta < 26°$ (Mo Kα) on a Enraf-Nonius CAD-4 diffractometer. The space groups were established by single crystal Weissenberg photographs. A list of crystallographic data is given in Table I.

A single crystal of $(Ph_4P)_2[Cu_4(SPh)_6]$ with approximate dimensions $0.2 \times 0.27 \times 0.09$ mm was mounted on the diffractometer. The lattice parameters were obtained from the least-squares refinement of 23 reflections in the range $14.5 < 2\theta < 24.5°$. With $Z = 4$ formula units per cell the calculated density is in good agreement with the value determined by the flotation method using $CHCl_3–CH_2I_2$ mixtures at 295 K. Monoclinic symmetry was established by single crystal Weissenberg photographs and confirmed by powder X-ray diffraction data. The extinction conditions are in accordance with the centrosymmetric space group $P2_1/a$. Intensity data were collected up to $2\theta = 46°$ with the $\omega–2\theta$ scan mode using graphite monochromated Mo Kα radiation ($\lambda = 0.7107$ Å; h: 0 to 25, k: 0 to 14, l: −28 to 28). The maximum measuring time per reflection was 70 s. The orientation was checked by six control reflections remeasured every 300 data. Three intensity control reflections measured at regular intervals gave no indication of significant decay (≤3%). The intensities were reduced to F_o by applying corrections for Lorentz and polarisation effects. Absorption effects were neglected ($\mu = 13.2$ cm^{-1}). Out of a total of 11 722 reflections measured (including standards) 6664 unique data remained after averaging equivalent reflections. 2982 data with $I > 3\sigma(I)$ were used for the structure determination. The structure was solved using the Patterson interpretation routine in SHELXS-84 [10] and by conventional Fourier techniques and was refined with full-matrix least-squares methods including anisotropic temperature factors for copper, sulfur and phosphorous. Anomalous dispersion corrections were applied for all atoms. The hydrogen atoms were not included in the refinement. All phenyl-rings were refined as rigid bodies with free varying isotropic temperature factors for the carbon atoms. The refinements (including a correction for isotropic secondary extinction, $g = 6 \times 10^{-9}$) converged to values of R and wR of 0.069 and 0.080, respectively, based on F. The weighting scheme used was $w = k/(\sigma^2(F) + 0.00144\ F^2)$; k finally refined to 1.7. The last difference Fourier map showed maximum and minimum

TABLE I. Lattice Parameters of Copper(I) Thiophenolate Clusters

Compound	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	V (Å^3)	Z	Space group
$(Ph_4P)_2[Cu_4(SPh)_6]$	23.290(9)	13.008(4)	25.622(6)	90.0	107.31(3)	90.0	7411	4	$P2_1/a$
$(Ph_4P)_2[Cu_4(SPh)_6]$·acetone	26.880(9)	14.033(7)	23.612(4)	90.0	119.35(3)	90.0	7727	4	$P2_1/c$
$(Ph_4P)_2[Cu_4(SPh)_6]$·0.5acetone·0.5propanol	26.256(8)	14.040(5)	23.755(5)	90.0	118.06(2)	90.0	7763	4	$P2_1/c$
$((CH_3)_4N)_2[Cu_4(SPh)_6]$[a]	19.037(15)	15.384(9)	17.480(16)	90.0	104.04(8)	90.0	4966	4	$P2_1/a$
$((CH_3)_4N)_2[Cu_5(SPh)_7]$·ethanol·propanol·acetone	12.244(10)	20.058(11)	11.506(5)	103.59(5)	90.04(5)	82.98(6)	2724	2	$P\bar{1}$

[a] Data given by Dance *et al.* [6] are $a = 23.733(3)$, $b = 12.428(2)$, $c = 35.853(4)$ Å, $\beta = 106.84(2)°$, $V = 10121$ Å^3, $Z = 8$, space group = $P2_1/c$ for $((CH_3)_4N)_2[Cu_4(SPh)_6]$ and $a = 19.125(2)$, $b = 15.433(1)$, $c = 17.500(2)$ Å, $\beta = 103.73(1)°$, $V = 5018$ Å^3, $Z = 4$, space group = $P2_1/a$ for $((CH_3)_4N)_2[Cu_4(SPh)_6]$·ethanol.

TABLE II. Positional Coordinates and Thermal Parameters of Solvent-free $(Ph_4P)_2[Cu_4(SPh)_6]$ [a]

Atom	x	y	z	U_{eq}
Cu(1)	0.0230(1)	0.2443(2)	0.2349(1)	0.0572
Cu(2)	0.5158(1)	0.9412(2)	0.7937(1)	0.0564
Cu(3)	0.9171(1)	0.5949(2)	0.7029(1)	0.0587
Cu(4)	0.4100(1)	0.8815(2)	0.8064(1)	0.0635
S(1)	0.4344(3)	0.7128(4)	0.8324(2)	0.0611
S(2)	0.4397(2)	0.7477(4)	0.6722(2)	0.0571
S(3)	0.4863(3)	1.0328(4)	0.7136(2)	0.0603
S(4)	0.5740(3)	0.8065(4)	0.7861(2)	0.0560
S(5)	0.4861(3)	0.9654(4)	0.8692(2)	0.0643
S(6)	0.3332(2)	0.9075(4)	0.7293(2)	0.0587
P(1)	0.6713(2)	0.3357(4)	0.8981(2)	0.0443
P(2)	0.8540(2)	0.0430(4)	0.4690(2)	0.0471
C(11)	0.3712(5)	0.6299(9)	0.8118(5)	0.0494
C(12)	0.3819(5)	0.5242(9)	0.8142(5)	0.0644
C(13)	0.3337(5)	0.4556(9)	0.8020(5)	0.0804
C(14)	0.2748(5)	0.4926(9)	0.7873(5)	0.0779
C(15)	0.2642(5)	0.5983(9)	0.7848(5)	0.0612
C(16)	0.3124(5)	0.6669(9)	0.7971(5)	0.0543
C(21)	0.3715(6)	0.6757(11)	0.6505(4)	0.0402
C(22)	0.3647(6)	0.5908(11)	0.6814(4)	0.0713
C(23)	0.3134(6)	0.5295(11)	0.6639(4)	0.0875
C(24)	0.2689(6)	0.5531(11)	0.6154(4)	0.0773
C(25)	0.2757(6)	0.6381(11)	0.5845(4)	0.0830
C(26)	0.3270(6)	0.6993(11)	0.6021(4)	0.0744
C(31)	0.5345(4)	1.0041(10)	0.6728(5)	0.0382
C(32)	0.5103(4)	0.9636(10)	0.6204(5)	0.0551
C(33)	0.5474(4)	0.9455(10)	0.5876(5)	0.0570
C(34)	0.6087(4)	0.9678(10)	0.6071(5)	0.0646
C(35)	0.6329(4)	1.0082(10)	0.6595(5)	0.0696
C(36)	0.5957(4)	1.0264(10)	0.6923(5)	0.0613
C(41)	0.6181(5)	0.7596(9)	0.8503(4)	0.0364
C(42)	0.6752(5)	0.7226(9)	0.8530(4)	0.0407
C(43)	0.7129(5)	0.6852(9)	0.9023(4)	0.0483
C(44)	0.6937(5)	0.6847(9)	0.9489(4)	0.0607
C(45)	0.6366(5)	0.7216(9)	0.9462(4)	0.0606
C(46)	0.5989(5)	0.7591(9)	0.8969(4)	0.0551
C(51)	0.4757(7)	1.0972(13)	0.8796(4)	0.0618
C(52)	0.4571(7)	1.2726(13)	0.8481(4)	0.1263
C(53)	0.4651(7)	1.3052(13)	0.9017(4)	0.1056
C(54)	0.4785(7)	1.2338(13)	0.9442(4)	0.0864
C(55)	0.4837(7)	1.1298(13)	0.9332(4)	0.0838
C(56)	0.4624(7)	1.1686(13)	0.8371(4)	0.0752
C(61)	0.3007(6)	1.0338(9)	0.7225(5)	0.0529
C(62)	0.2135(6)	1.1393(9)	0.7162(5)	0.0690
C(63)	0.2453(6)	1.2262(9)	0.7089(5)	0.0822
C(64)	0.3048(6)	1.2170(9)	0.7084(5)	0.0989
C(65)	0.3325(6)	1.1207(9)	0.7151(5)	0.0747
C(66)	0.2412(6)	1.0430(9)	0.7230(5)	0.0624
C(111)	0.7598(5)	0.9025(10)	0.0918(3)	0.0410
C(112)	0.6827(5)	0.9707(10)	0.1276(3)	0.0775
C(113)	0.6489(5)	0.9993(10)	0.0749(3)	0.0558
C(114)	0.6706(5)	0.9795(10)	0.0307(3)	0.0667
C(115)	0.7261(5)	0.9311(10)	0.0391(3)	0.0501
C(116)	0.7382(5)	0.9223(10)	0.1360(3)	0.0646
C(121)	0.8134(4)	0.7015(10)	0.1011(5)	0.0474
C(122)	0.8499(4)	0.5269(10)	0.1056(5)	0.0639
C(123)	0.7923(4)	0.4903(10)	0.1012(5)	0.0677
C(124)	0.7453(4)	0.5594(10)	0.0968(5)	0.0578
C(125)	0.7558(4)	0.6649(10)	0.0968(5)	0.0554
C(126)	0.8604(4)	0.6325(10)	0.1055(5)	0.0602
C(131)	0.8619(6)	0.8645(8)	0.0484(6)	0.0474
C(132)	0.8501(6)	0.7990(8)	0.0033(6)	0.0758
C(133)	0.8726(6)	0.8219(8)	−0.0401(6)	0.0820
C(134)	0.9069(6)	0.9104(8)	−0.0384(6)	0.0719
C(135)	0.9187(6)	0.9760(8)	0.0066(6)	0.0817
C(136)	0.8962(6)	0.9530(8)	0.0500(6)	0.0666
C(141)	0.8789(6)	0.8727(9)	0.1670(5)	0.0393
C(142)	0.8871(6)	0.9772(9)	0.1793(5)	0.0633
C(143)	0.9253(6)	1.0083(9)	0.2299(5)	0.0738
C(144)	0.9553(6)	0.9350(9)	0.2680(5)	0.0910
C(145)	0.9471(6)	0.8306(9)	0.2556(5)	0.0858
C(146)	0.9089(6)	0.7995(9)	0.2051(5)	0.0630
C(211)	0.8892(5)	0.1177(8)	0.5279(5)	0.0399
C(212)	0.8867(5)	0.0885(8)	0.5796(5)	0.0514
C(213)	0.9115(5)	0.1518(8)	0.6246(5)	0.0563
C(214)	0.9388(5)	0.2443(8)	0.6180(5)	0.0755
C(215)	0.9414(5)	0.2734(8)	0.5663(5)	0.0729
C(216)	0.9165(5)	0.2101(8)	0.5213(5)	0.0721
C(221)	0.7772(8)	0.0273(10)	0.4661(5)	0.0496
C(222)	0.7422(8)	−0.0462(10)	0.4312(5)	0.0840
C(223)	0.6815(8)	−0.0569(10)	0.4272(5)	0.1179
C(224)	0.6557(8)	0.0059(10)	0.4582(5)	0.1133
C(225)	0.6906(8)	0.0795(10)	0.4932(5)	0.1008
C(226)	0.7514(8)	0.0902(10)	0.4971(5)	0.0728
C(231)	0.8571(5)	0.1070(9)	0.4093(5)	0.0480
C(232)	0.9112(5)	0.1095(9)	0.3964(5)	0.0532
C(233)	0.9161(5)	0.1687(9)	0.3525(5)	0.0753
C(234)	0.8669(5)	0.2253(9)	0.3215(5)	0.0724
C(235)	0.8128(5)	0.2227(9)	0.3344(5)	0.0781
C(236)	0.8079(5)	0.1636(9)	0.3783(5)	0.0476
C(241)	0.8881(5)	−0.0815(9)	0.4718(4)	0.0529
C(242)	0.9182(5)	−0.1281(9)	0.5214(4)	0.0460
C(243)	0.9399(5)	−0.2282(9)	0.5222(4)	0.0605
C(244)	0.9316(5)	−0.2817(9)	0.4733(4)	0.0756
C(245)	0.9015(5)	−0.2351(9)	0.4237(4)	0.0809
C(246)	0.8798(5)	−0.1350(9)	0.4229(4)	0.0719

[a] The standard deviation in the last significant digits is given in parentheses. The equivalent temperature factor U_{eq} ($Å^2$) is defined as one third of the trace of the orthogonalized U tensor.

peaks of 0.65 $e^-/Å^3$ and −0.41 $e^-/Å^3$. The calculations were performed with the programs SHELXS-84 [10] and SHELX-76 [11] on an IBM 3033 computer of the University of Zurich. Final positional atomic coordinates as well as isotropic thermal parameters for $(Ph_4P)_2[Cu_4(SPh)_6]$ are listed in Table II. Selected bond distances and angles are given in Table III. See also 'Supplementary Material'.

Single crystal diffraction data of $((CH_3)_4)_2[Cu_5(SPh)_7]$·solvent were collected on the diffractometer following the procedures given for $(Ph_4P)_2[Cu_4(SPh)_6]$. Crystal data: $Z = 2$, $D_{calc} = 1.57$ g cm^{-3},

TABLE III. Bond Distances (Å) and Angles (°) in Solvent-free $(Ph_4P)_2[Cu_4(SPh)_6]$

Cu(1)–S(1)	2.267(7)	S(1)–C(11)	1.773(11)
Cu(1)–S(2)	2.278(5)	S(2)–C(21)	1.785(16)
Cu(1)–S(4)	2.310(6)	S(3)–C(31)	1.784(14)
Cu(2)–S(3)	2.295(6)	S(4)–C(41)	1.767(13)
Cu(2)–S(4)	2.260(6)	S(5)–C(51)	1.763(18)
Cu(2)–S(5)	2.262(7)	S(6)–C(61)	1.795(15)
Cu(3)–S(2)	2.308(6)		
Cu(3)–S(3)	2.272(6)	P(1)–C(111)	1.773(15)
Cu(3)–S(6)	2.252(7)	P(1)–C(121)	1.781(15)
Cu(4)–S(1)	2.315(6)	P(1)–C(131)	1.803(19)
Cu(4)–S(5)	2.286(6)	P(1)–C(141)	1.795(13)
Cu(4)–S(6)	2.261(5)		
		P(2)–C(211)	1.777(14)
Cu(1)–Cu(2)	2.743(4)	P(2)–C(221)	1.779(19)
Cu(1)–Cu(3)	2.746(4)	P(2)–C(231)	1.764(15)
Cu(1)–Cu(4)	2.778(4)	P(2)–C(241)	1.796(14)
Cu(2)–Cu(3)	2.780(4)		
Cu(2)–Cu(4)	2.693(4)		
Cu(3)–Cu(4)	2.723(4)		
Cu(2)–Cu(1)–Cu(3)	60.9(1)	Cu(1)–Cu(3)–Cu(2)	59.5(1)
Cu(2)–Cu(1)–Cu(4)	58.4(1)	Cu(1)–Cu(3)–Cu(4)	61.1(1)
Cu(3)–Cu(1)–Cu(4)	59.1(1)	Cu(2)–Cu(3)–Cu(4)	58.6(1)
Cu(1)–Cu(2)–Cu(3)	59.6(1)	Cu(1)–Cu(4)–Cu(2)	60.1(1)
Cu(1)–Cu(2)–Cu(4)	61.5(1)	Cu(1)–Cu(4)–Cu(3)	59.9(1)
Cu(3)–Cu(2)–Cu(4)	59.7(1)	Cu(2)–Cu(4)–Cu(3)	61.8(1)
Cu(1)–S(1)–Cu(4)	74.7(2)	Cu(2)–S(4)–Cu(1)	73.8(2)
Cu(1)–S(2)–Cu(3)	73.5(2)	Cu(2)–S(5)–Cu(4)	72.6(2)
Cu(3)–S(3)–Cu(2)	75.0(2)	Cu(3)–S(6)–Cu(4)	74.3(2)
S(1)–Cu(1)–S(2)	133.0(2)	S(2)–Cu(3)–S(3)	117.6(2)
S(1)–Cu(1)–S(4)	120.4(2)	S(2)–Cu(3)–S(6)	115.0(2)
S(2)–Cu(1)–S(4)	106.1(2)	S(3)–Cu(3)–S(6)	126.9(2)
S(3)–Cu(2)–S(4)	110.7(2)	S(1)–Cu(4)–S(5)	100.6(2)
S(3)–Cu(2)–S(5)	127.4(2)	S(1)–Cu(4)–S(6)	117.1(2)
S(4)–Cu(2)–S(5)	121.7(2)	S(5)–Cu(4)–S(6)	142.2(2)
Cu(1)–S(1)–C(11)	113.3(5)	Cu(3)–S(2)–C(21)	107.4(6)
Cu(1)–S(2)–C(21)	109.9(4)	Cu(3)–S(3)–C(31)	108.9(5)
Cu(1)–S(4)–C(41)	110.7(5)	Cu(3)–S(6)–C(61)	111.2(7)
Cu(2)–S(3)–C(31)	110.1(5)	Cu(4)–S(1)–C(11)	112.3(5)
Cu(2)–S(4)–C(41)	112.7(5)	Cu(4)–S(5)–C(51)	117.3(5)
Cu(2)–S(5)–C(51)	110.8(6)	Cu(4)–S(6)–C(61)	115.1(5)
C(111)–P(1)–C(121)	108.0(8)	C(211)–P(2)–C(221)	107.6(7)
C(111)–P(1)–C(131)	111.2(7)	C(211)–P(2)–C(231)	110.6(6)
C(111)–P(1)–C(141)	108.4(7)	C(211)–P(2)–C(241)	111.8(8)
C(121)–P(1)–C(131)	109.0(8)	C(221)–P(2)–C(231)	108.6(7)
C(121)–P(1)–C(141)	110.3(8)	C(221)–P(2)–C(241)	109.0(7)
C(131)–P(1)–C(141)	110.0(9)	C(231)–P(2)–C(241)	109.1(6)

triclinic, space group $P\bar{1}$, crystal dimensions 0.25 × 0.38 × 0.13 mm. Intensity data were collected up to $2\theta = 40°$ (h: −11 to 11, k: −11 to 11, l: 0 to 19). Out of a total of 5414 reflections measured (including standards) 3409 observed reflections with $I > 3\sigma(I)$ remained after averaging equivalent reflections. The structure was solved using the Patterson interpretation routine in SHELXS-84 [10] and Fourier techniques and was refined with full-matrix least-squares methods including anisotropic temperature factors for copper, sulfur, nitrogen and the carbon atoms of the $(CH_3)_4N$-groups. The phenyl-rings were refined as rigid bodies with free varying isotropic temperature factors for the carbon atoms, and the carbon hydrogen bond distance was kept invariant at 1.08 Å. The refinement converged to values of R and wR of 6.1 and 8.7, respectively, based on F.

Since most of the resulting structural parameters for $((CH_3)_4N)_2[Cu_5(SPh)_7]$·solvent do not differ significantly from those given for $((CH_3)_4N)_2[Cu_5(SPh)_7]$ by Dance [7], no atomic positions are listed in this paper.

The last difference Fourier map showed maximum and minimum peaks of 1.41 $e^-/Å^3$ and -0.73 $e^-/Å^3$, which were not located near the copper or the sulfur atoms or any other atomic positions. Several of the highest peaks were separated by about 1.40 Å from each other, suggesting the occurrence of – possibly disordered – solvent molecules. Attempts to refine these peaks as partially localized solvent molecules, however, were not successful. Thus, although the occurrence of solvent molecules in $((CH_3)_4N)_2[Cu_5(SPh)_7]$·solvent is evidenced by thermal analytical measurements, we were not able to localize these molecules unequivocally within the structure.

Results and Discussion

Thermal Analytical Results

Thermogravimetric investigations allow a characterization referring to the stoichiometry of the compounds investigated and to possible decomposition mechanisms. For all different clusters the final product of degradation was $Cu_{1.96}S$, as identified by X-ray powder diffraction (Guinier-IV camera, Cu Kα1 radiation). The patterns were in agreement with those reported in ref. 12 for a synthetic Chalcocite.

All compounds, except the solvent free samples, exhibit a first decomposition step in the range of 100 to 160 °C. Within this temperature range, the inserted solvent molecules are evolved. Identification of these solvents was performed by mass spectrometry. While heating up the compound, we continuously registered the characteristic mass peaks for each solvent. These *m/e* values are 58 and 43 for acetone, 41 for acetonitrile, 45 and 31 for ethanol and 59 and 31 for propanol. The investigation of crystals of $(Ph_4P)_2[Cu_4(SPh)_6]$ grown from a solvent mixture revealed, that in this tetraphenylphosphonium salt, three of the four solvents used were inserted, *i.e.* propanol, acetone and acetonitrile, but not ethanol. In contrast, in the tetramethylammonium salts $((CH_3)_4N)_2[Cu_5(SPh)_7]$ or $((CH_3)_4N)_2[Cu_4(SPh)_6]$, all four solvents investigated can be inserted into the crystal lattice. As calculated from the corresponding weight losses, the insertion of solvent molecules seems to be stoichiometric.

The subsequent decomposition of the solvent-free species is dependent on the cation only, not on the Cu(I)–S core type. If the cation is Ph_4P^+, the thermal decomposition is a one step reaction leading to the final product $Cu_{1.96}S$. Figure 1 shows the decrease in weight during the thermal degradation reaction of the Ph_4P-compounds and the appertaining course of the detected mass peaks. The only detectable mass peaks for this step were 78 and 45. The *m/e* peak of 78 is consistent with a C_6H_6-fragment, while the weak *m/e* peak of 45 corresponds to SCH-fragments.

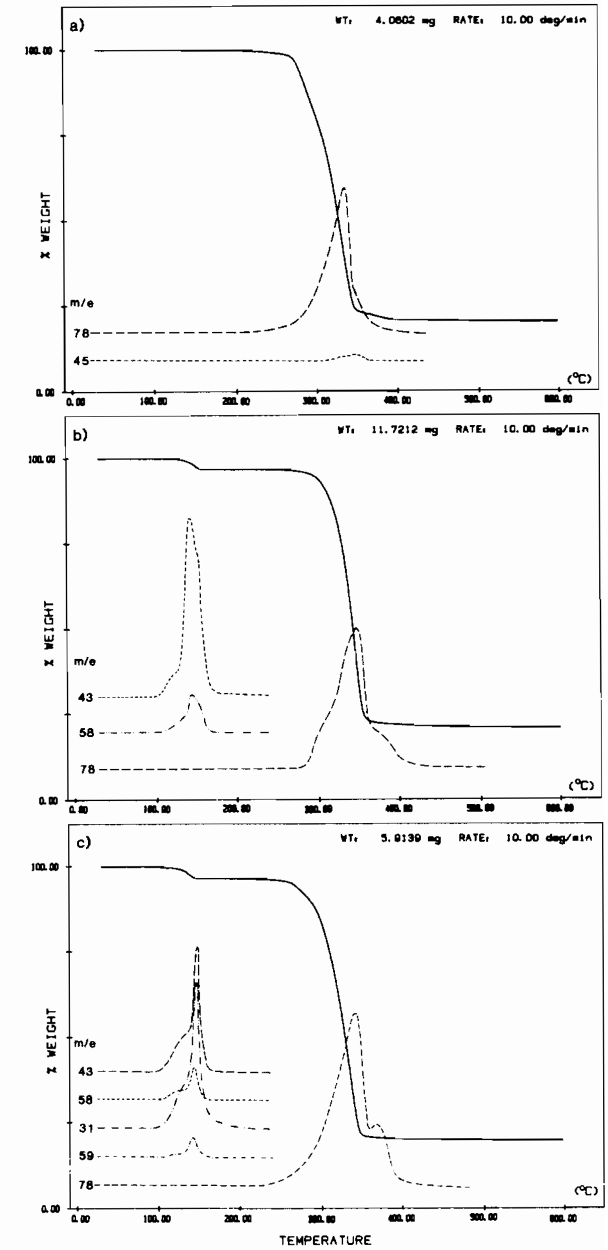

Fig. 1. Thermal degradation of $(Ph_4P)_2[Cu_4(SPh)_6]$ complexes: (a) $(Ph_4P)_2[Cu_4(SPh)_6]$, (b) $(Ph_4P)_2[Cu_4(SPh)_6]$·acetone, (c) $(Ph_4P)_2[Cu_4(SPh)_6]$·0.5acetone·0.5propanol.

In contrast to the behaviour described above, the degradation of the solvent-free species occurs in two steps in the complexes with $(CH_3)_4N^+$ as cation. This is shown in Fig. 2. We explain the first step (step 2a) with the simultaneous loss of two $(CH_3)_4N^+$ groups and two thiophenolates. Thus, the stoichiometry of the intermediate product is $Cu_x(SPh)_x$. This decom-

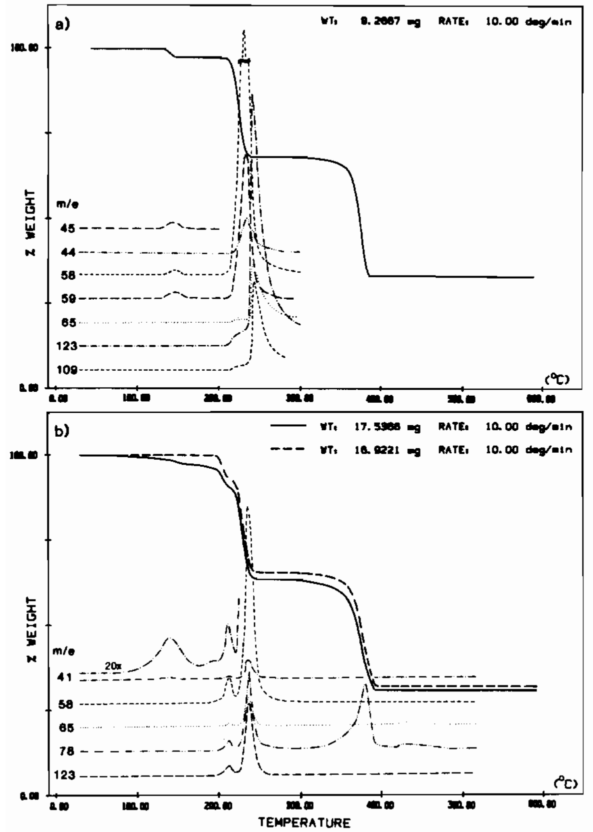

Fig. 2. Thermal degradation of (a) $(Me_4N)_2[Cu_5(SPh)_7]\cdot$ solvent, (b) $(Me_4N)_2[Cu_4(SPh)_6]$ (– – –) and $(Me_4N)_2$-$[Cu_4(SPh)_6]\cdot CH_3CN$ (——).

position mechanism is in agreement with mass spectrometry data. The following mass peaks were observed: 41, 44, 58, 59, 65, 78, 109, 123. These *m/e* values can be explained assuming dealkylation reactions of $(CH_3)_4N^+$ with thiophenolate as described by Hesse [13]. A possible fragmentation mechanism is displayed in Fig. 3. For step 2b only fragments with *m/e* 78 (C_6H_6) are observed.

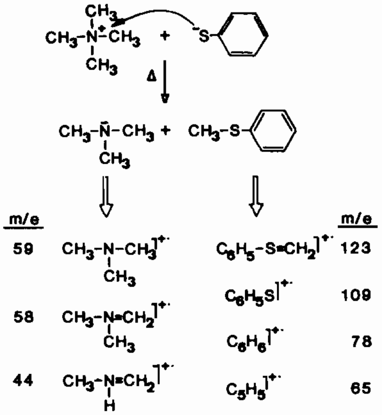

Fig. 3. Possible fragmentation mechanism leading to the detected *m/e* peaks in the thermal degradation of the tetramethylammonium salts.

Calculated and observed weight losses of the degradative reactions described above are summarized in Table IV.

The Structure of Solvent-free $(Ph_4P)_2[Cu_4(SPh)_6]$

The structure is built up by Cu_4S_6 adamantane-type cluster units, separated by the bulky cations, as shown in Fig. 4. Figure 5 displays the $[Cu_4(SPh)_6]^{2-}$ anion. The structure of this cluster anion can be considered as a tetrahedron of copper atoms inscribed in a distorted octahedron of sulfur atoms. It contains copper(I) in a distorted trigonal planar coordination by three μ_2-sulfur atoms. This structure of the Cu_4S_6 core is similar to that of the $[Cu_4I_6]^{2-}$ anion [14]. Thus, the principle structural features of the solvent-free complex are as described by Coucouvanis for the solvent containing complex [8]. The Cu–Cu distances range from 2.693(4) to 2.780(4) Å with a mean Cu–Cu distance of 2.744 Å. This value is about 8% longer than in cubic-close-packed copper metal (Cu–Cu 2.55 Å). The Cu–S bond distances range

TABLE IV. Observed and Calculated (in Parentheses) Weight Losses (%) from Thermogravimetric Analysis of Cu(I)–thiolate Clusters

	Step 1 desolvation	Step 2a formation of $Cu_x(SPh)_x$	Step 2b formation of $Cu_{1.96}S$
$(Ph_4P)_2[Cu_4(SPh)_6]$			79.78 (79.86)
$(Ph_4P)_2[Cu_4(SPh)_6]\cdot$acetone	3.31 (3.53)		76.79 (77.04)
$(Ph_4P)_2[Cu_4(SPh)_6]\cdot$ 0.5acetone·0.5propanol	3.65 (3.59)		76.39 (76.99)
$((CH_3)_4N)_2[Cu_4(SPh)_6]$		34.79 (34.67)	33.53 (35.13)
$((CH_3)_4N)_2[Cu_4(SPh)_6]\cdot$acetonitrile	4.81 (4.17)	32.14 (33.21)	34.04 (33.63)
$((CH_3)_4N)_2[Cu_5(SPh)_7]\cdot$ ethanol/propanol/acetone	2.64 (4.10)	29.29 (28.57)	36.07 (36.17)

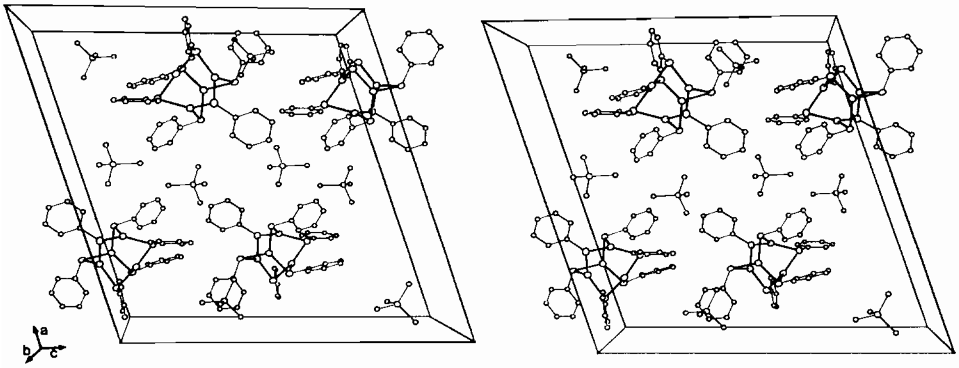

Fig. 4. Stereoview of the crystal structure of solvent-free $(Ph_4P)_2[Cu_4(SPh)_6]$. The Ph_4P^+ cations are given as their corresponding $(C_1-)_4P$ units only.

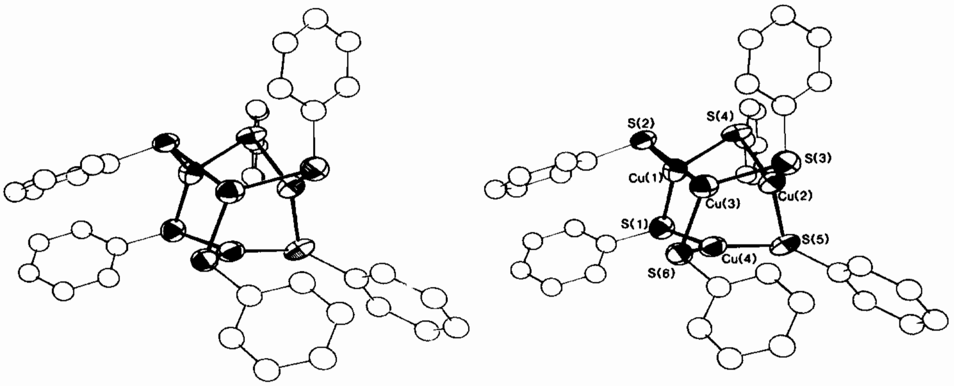

Fig. 5. Stereoview of the adamantan-type $[Cu_4(SPh)_6]^{2-}$ cluster anions in solvent-free $(Ph_4P)_2[Cu_4(SPh)_6]$.

from 2.251(7) to 2.315(6) Å with a mean distance of 2.281 Å and compare well with corresponding distances in other copper(I)–thiolate clusters. The Cu–Cu–Cu angles range from 58.4(1) to 61.8(1)° and the angles for Cu–S–Cu are found to be between 72.6(2) and 75.0(2)°. S–Cu–S angles vary from 100.6(2) to 142.2(2)°, with an accumulation between 115 and 128°. Structural data of Cu(I)–S polyhedra in pure Cu(I) thiolate clusters without additional coordinating ligands are summarized in Table V.

The geometry as well as the bond distances and angles of the $(Ph_4P)^+$ cations show no unusual features. The P–C distances range from 1.764(15) to 1.803(19) Å and the mean P–C bond length is 1.784 Å. The C–P–C angles gave no indication for a strong distortion of the tetrahedral environment about the P atoms.

The Structure of $((CH_3)_4N)_2[Cu_5(SPh)_7]\cdot$*solvent*

The structural features given by Dance [7] for the compound considered to be free from solvent molecules could be confirmed. The structure contains isolated $[Cu_5(SPh)_7]^{2-}$ clusters with four copper atoms exhibiting approximate trigonal planar coordination and the fifth copper atom exhibiting almost linear digonal coordination. Cu–S distances range from 2.169(4) to 2.334(4) Å, the mean distances are 2.269 Å for the 12 Cu–S bonds forming a trigonal coordination and 2.173 Å for the two digonal bonds. The shortest copper-to-copper distance within the cluster is 2.649(2) Å. None of these values differs significantly from the data given by Dance [7] for the 'solvent-free' complex.

Supplementary Material

Supplementary material including tables of observed and calculated structure factors and of anisotropic thermal parameters may be obtained on request from one of the authors (E.D.).

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TABLE V. Structural Data of Cu–S Polyhedra in Copper(I) Thiolate Clusters. Pure Cu_xS_y Clusters only Without Additional Coordinating Ligands are Included[a]

Compound	Cu_x-geometry	Cu–Cu (Å)	S ligands	Cu–S (Å)	Reference
Trimeric					
$(Me_3NCH_2Ph)_2NaCu_3(EDT)_3$	trig. planar	2.75–2.85	3 × μ_2, 3 × term.	2.21–2.31	15
$(Et_4N)_3Cu_3S_{18}$	trig. planar		3 × μ_2, 3 × term.	2.20(mean)	16
Tetrameric					
$(Ph_4P)_2Cu_4(SPh)_6$	tetrahedron	2.69–2.77	6 × μ_2	2.24–2.34	[b]
$(Me_4N)_2Cu_4(SPh)_6$	tetrahedron	2.68–2.81	6 × μ_2	2.25–2.35	6
$(Me_4N)_2Cu_4(SPh)_6 \cdot EtOH$	tetrahedron	2.64–2.85	6 × μ_2	2.25–2.35	6
$(Me_4N)_2Cu_4(SMe)_6$	tetrahedron	2.67–2.79	6 × μ_2	2.25–2.32	6
$(Ph_4P)_2Cu_4(S_2$-*o*-xyl$)_3$	tetrahedron	2.70–2.74	6 × μ_2	2.24–2.30	17
$[(IDD)_3Cu_4](CuCl_2) \cdot CCl_4$	tetrahedron	2.76–2.82	6 × μ_2	2.26–2.28	18
Pentameric					
'$(Me_4N)_2Cu_5(SPh)_7$'[c]	[d]	⩾2.65	7 × μ_2	2.16–2.33	[b], 7
$(Et_4N)Cu_5(S$-t-Bu$)_6$	trig. bipyr.	⩾2.69	6 × μ_2	2.14–2.29	19
$(Et_3NH)Cu_5(S$-t-Bu$)_6$	trig. bipyr.	⩾2.72	6 × μ_2	2.15–2.37	19
Octameric					
$(Ph_4P)_4Cu_8(DTS)_6 \cdot CH_3CN$	cube	⩾2.79	12 × μ_2	2.23–2.27	20
$(Bu_4N)_4Cu_8(DED)_6$	cube	⩾2.76	12 × μ_2	2.24–2.27	20
$(Ph(CH_3)_3N)_4Cu_8$(i-MNT$)_6$	cube	⩾2.78	12 × μ_2	2.24–2.27	21

[a] Abbreviation of ligand names and symbols: EDT = ethane-1,2-dithiolate; SPh = thiophenolate; S_2-*o*-xyl = *o*-xylene-α-α'-dithiolate; IDD = imidotetraphenyldithiodiphosphinate; DTS = 1,2-dithiosquarate; DED = 1,1-dicarboethoxyethylene-2,2-dithiolate; i-MNT = 1,1-dicyanoethylene-2,2-dithiolate; term. = terminal, non-bridging ligand atom. [b] This work. [c] Shown to be $(Me_4N)_2[Cu_5(SPh)_7] \cdot$solvent by the thermoanalytical data given in this paper. [d] Cu_4-tetrahedron plus fifth Cu over one elongated edge.

References

1 P. M. Colman, H. C. Freeman, J. M. Guss, M. Murata, V. A. Norris, J. A. M. Ramshaw and M. P. Venkatappa, *Nature (London), 272,* 319 (1978).

2 E. T. Adman, R. E. Stenkamp, L. C. Sieker and L. H. Jensen, *J. Mol. Biol., 123,* 35 (1978).

3 M. Linss, M. G. Weller and U. Weser, *Inorg. Chim. Acta, 80,* 201 (1983).

4 K. Münger and K. Lerch, *2nd Int. Meeting on Metallothionein,* Zurich, Switzerland, 1985, Abstr. Book, p. 18.

5 J. R. Dilworth, in A. Müller and B. Krebs (eds.), 'Sulfur', Elsevier, Amsterdam, 1984, p. 141.

6 I. G. Dance, G. A. Bowmaker, G. R. Clark and J. K. Seadon, *Polyhedron,* 1031 (1983).

7 I. G. Dance, *Aust. J. Chem., 31,* 2195 (1978).

8 D. Coucouvanis, C. N. Murphy and S. K. Kanodia, *Inorg. Chem., 19,* 2993 (1980).

9 H. Meerwein, V. Hederich and K. Wunderlich, *Ber. Dtsch. Pharm. Ges., 63,* 548 (1958).

10 G. M. Sheldrick, 'SHELXS84', program for crystal structure determination, Univ. Cambridge, 1984.

11 G. M. Sheldrick, 'SHELX76', program for crystal structure determination, Univ. Cambridge, 1976.

12 JCPDS, Powder Diffraction File, Card No. 29-578, Swarthmore, Pa, U.S.A.

13 M. Hesse, *Fortschr. Chem. Forsch., 8,* 608 (1967).

14 G. A. Bowmaker, G. R. Clark and D. K. P. Yuen, *J. Chem. Soc., Dalton Trans.,* 2329 (1976).

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

16 A. Müller and U. Schimanski, *Inorg. Chim. Acta, 77,* L187 (1983).

17 J. R. Nicholson, I. L. Abrahams, W. Clegg and C. D. Garner, *Inorg. Chem., 24,* 1092 (1985).

18 C. P. Huber, M. L. Post and O. Siiman, *Acta Crystallogr., Sect. B, 34,* 2629 (1978).

19 G. A. Bowmaker, G. R. Clark, J. K. Seadon and I. G. Dance, *Polyhedron, 3,* 535 (1984).

20 F. J. Hollander and D. Coucouvanis, *J. Am. Chem. Soc., 99,* 6268 (1977).

21 L. E. McCandlish, E. C. Bissell, D. Coucouvanis, J. P. Fackler and K. Knox, *J. Am. Chem. Soc., 90,* 7357 (1968).