Inorganica Chimica Acta, 208 (1993) 135–143

Structural and spectroscopic features of the 'adamantane' type Cu_4S_6 core found in Cu(I) thiolates with bidentate chelate ligands

Markus Baumgartner*, Helmut Schmalle and Erich Dubler

Institute of Inorganic Chemistry, University of Zürich, Winterthurerstrasse 190, CH-8057 Zurich (Switzerland)

(Received November 30, 1992)

Abstract

Six tetranuclear Cu(I) thiolate complexes have been synthesized with the bidentate thiolate ligands dithioethane (DTE) and dithiopropane (DTP). The cell dimensions are $a=10.887(3)$, $b=12.294(6)$, $c=22.308(3)$ Å, $\alpha=96.94(2)$, $\beta=96.66(1)$, $\gamma=108.57(3)^\circ$, space group $=P\bar{1}$ and $V=2772$ Å^3 for $[(C_6H_5)_4P^+]_2[Cu_4(DTP^{2-})_3]$ (**A**); $a=11.820(6)$, $b=13.972(5)$, $c=21.371(6)$ Å, $\alpha=71.83(2)$, $\beta=77.01(3)$, $\gamma=63.61(4)^\circ$, space group $=P\bar{1}$ and $V=2988$ Å^3 for $[(C_6H_5)_4P^+]_2[Cu_4(DTP^{2-})_3]\cdot 3MeOH$ (**B**); $a=9.779(3)$, $b=9.779(4)$, $c=17.694(6)$ Å, $\alpha=90.0$, $\beta=90.0$, $\gamma=120.0^\circ$, space group $=P6_3$ and $V=1465$ Å^3 for $[(CH_3)_4N^+]_2[Cu_4(DTP^{2-})_3]\cdot MeOH$ (**C**); $a=15.835(3)$, $b=20.413(4)$, $c=9.866(1)$ Å, $\alpha=90.0$, $\beta=91.05(1)$, $\gamma=90.0^\circ$, space group $=P2_1/n$ and $V=3188$ Å^3 for $[(C_2H_5)_4N^+]_2[Cu_4(DTE^{2-})_3]$ (**D**); $a=9.939(5)$, $b=9.939(8)$, $c=34.201(7)$ Å, $\alpha=90.0$, $\beta=90.0$, $\gamma=90.0^\circ$, tetragonal, $V=3378$ Å^3 for $[C_6H_5CH_2N^+(CH_3)_3]_2[Cu_4(DTE^{2-})_3]$ (**E**) and $a=10.899(2)$, $b=10.879(2)$, $c=18.604(3)$ Å, $\alpha=90.0$, $\beta=90.0$, $\gamma=120.0^\circ$, hexagonal, $V=1913$ Å^3 for $[(C_2H_5)_4N^+]_2[Cu_4(DTP^{2-})_3]\cdot MeOH$ (**F**). The structures were refined to R/R_w values (%) of 6.75/5.63, 4.60/5.70, 6.56/7.42 and 5.59/5.35 for **A–D**, respectively. All compounds exhibit an anionic 'adamantane' type Cu_4S_6 cluster unit. Within two of the structures, inserted solvent molecules are linked with the Cu–S core by S···H–O hydrogen bonds. Crystallization of the anionic $[Cu_4(RS^-)_6]^{2-}$ or $[Cu_4(^-SRS^-)_3]^{2-}$ units together with bulky ammonium cations yields white or pale yellow compounds, whereas yellow, orange or deep red crystals are formed using the $(C_6H_5)_4P^+$ cation as the counterion. A review of IR data of different $[Cu_4(RS^-)_6]^{2-}$ or $[Cu_4(^-SRS^-)_3]^{2-}$ is given.

Introduction

The polynuclear aggregates obtained in reactions of copper(I) with sulfur-containing ligands display a wide variety in composition and structure. Among these clusters, Cu–S core units of different stoichiometries have been structurally characterized: Cu_3S_6 [1], Cu_4S_6 [2–10], Cu_5S_6 [11–13], Cu_5S_7 [3, 5, 14, 15], Cu_7S_9 [16, 17], Cu_8S_8 [18], Cu_8S_{12} [19–22] and $Cu_{12}S_{12}$ [23, 24]. In addition, two polymeric chain structures are known: $(Cu_7(C_2H_5S^-)_8)_\infty$ [2] and $(Cu(CH_3S^-))_\infty$ [3].

We are interested in crystallizing metal-rich Cu(I) thiolates as model compounds of Cu(I) thioneines. Metallothioneines (MT) are believed to play a role in the metabolism and detoxification of a number of essential and non-essential trace metals in animals and plants, mainly of the metals zinc, cadmium, mercury and copper [25]. They are characterized by an unusually high cysteinate content of the peptide and a characteristic metal-to-cysteinate ratio. In the case of pure Cu(I) MTs, cluster core types of the stoichiometries Cu_6S_9 and Cu_8S_{12} have been suggested [26, 27]. A copper-to-sulfur ratio of 2:3 seems to be typical for Cu(I)–MTs as well as for synthetic polynuclear Cu(I) complexes with mono- or bidentate thiolates [28, 29]. In addition, compounds with higher copper percentages have also been isolated. The MT with the highest metal content is a fungal MT found in *Neurospora crassa* with a Cu(I)-to-cysteinate ratio of 6:7 [30].

The most favoured Cu_4S_6 'adamantane' type can be obtained either with mono- (RS^-) or bidentate ligands ($^-SRS^-$). Bidentate 1,1-dithiolate ligands ($R(S^-)_2$) are thereby excluded because the small intraligand S–S distances (S–S 'bite' distances ~3.0 Å) cannot span the edges of the S_6 octahedron of a Cu_4S_6 core; thus a Cu_8S_{12} 'cubane' cluster is formed [31].

In this context, we report here the synthesis and structure of compounds exhibiting a Cu_4S_6 'adamantane' type cluster with bidentate ligands ($^-SRS^-$). Structural properties are discussed in detail, spectroscopic features (UV–Vis and IR) only qualitatively.

---

*Author to whom correspondence should be addressed.

0020-1693/93/$6.00

TABLE 1. Crystal data and structure determination parameters for: $[(Ph)_4P^+]_2[Cu_4(DTP^{2-})_3]$ (**A**), $[(Ph)_4P^+]_2[Cu_4(DTP^{2-})_3]\cdot 3MeOH$ (**B**), $[(CH_3)_4N^+]_2[Cu_4(DTP^{2-})_3]\cdot MeOH$ (**C**), $[(C_2H_5)_4N^+]_2[Cu_4(DTE^{2-})_3]$ (**D**), $[C_6H_5CH_2N^+(CH_3)_3]_2[Cu_4(DTE^{2-})_3]$ (**E**) and $[(C_2H_5)_4N^+]_2[Cu_4(DTP^{2-})_3]\cdot MeOH$ (**F**)

	A	**B**	**C**	**D**	**E**	**F**
Chemical formula	$C_{57}H_{58}Cu_4P_2S_6$	$C_{60}H_{70}Cu_4O_3P_2S_6$	$C_{18}H_{46}Cu_4N_2OS_6$	$C_{22}H_{52}Cu_4N_2S_6$	$C_{26}H_{44}Cu_4N_2S_6$	$C_{26}H_{62}Cu_4ON_2S_6$
Formula weight	1250.2	1346.2	752.5	790.5	831.2	865.3
Colour	red	orange	white	white	white	white
a (Å)	10.887(3)	11.820(6)	9.779(3)	15.835(3)	9.939(5)	10.899(2)
b (Å)	12.294(6)	13.972(5)	9.779(4)	20.413(4)	9.939(8)	10.879(2)
c (Å)	22.308(3)	21.371(6)	17.694(6)	9.866(1)	34.201(7)	18.604(3)
α (°)	96.94(2)	71.83(2)	90.0	90.0	90.0	90.0
β (°)	96.66(1)	77.01(3)	90.0	91.05(1)	90.0	90.0
γ (°)	108.57(3)	63.61(4)	120.0	90.0	90.0	120.0
V (Å^3)	2772	2988	1465	3188	3378	1913
Space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P6_3$ (No. 173)	$P2_1/n$ (No. 14)	tetragonal	hexagonal
Z	2	2	2	4	4	2
T (°C)	22	-95.5 ± 2.0	22	22		
D_{calc} (g/cm^3)	1.498	1.497	1.706	1.648		
μ(Mo Kα) (cm^{-1})	17.55	16.34	31.93	29.34		
Data measured (incl. stds.)	12610	12175	11539	10183		
Observed data ($I \geqslant 3\sigma(I)$)	3209	9556	1274	5151		
$R(F_o)$	0.0675	0.0460	0.0656	0.0559		
$R_w(F_o)$	0.0563	0.0570	0.0742	0.0535		
Weight k/p	1.9641/0.0	2.2497/0.00005	1 (unit weight)	3.2289/0.0		

Experimental

Materials and methods

Dithiopropane (DTP), dithioethane (DTE), $(CH_3)_4NCl$, $(C_6H_5)_4PBr$, $C_6H_5CH_2N(CH_3)_3Cl$, $(C_2H_5)_4NBr$, Cu_2O and a solution of $(C_2H_5)_4NOH$ in MeOH (25%) were purchased from Fluka AG, Buchs/Switzerland and used without further purification. The 1 M solution of NaOMe was obtained by adding 23.0 g (1 mol) sodium to 1000 ml methanol, stirred on a ice bath. The syntheses were performed in a Schlenk-type apparatus in nitrogen atmosphere.

Cu content and solvent molecules were determined by thermogravimetry (TG). These data in the temperature range 30–700 °C were recorded in a flowing N_2 atmosphere, with use of heating rates of 10°/min and sample weights of 4–15 mg on a Perkin-Elmer TGS-2 thermobalance. The final product of this degradation was in all cases synthetic Chalcocit $Cu_{1.96}S$ (ASTM No 29-578 [32], identified by X-ray powder diffraction performed on a Guinier type camera with a Johansson monochromator (Cu Kα_1 radiation)). For details of this thermal decomposition see refs. 5 and 33. C, H and S analyses were performed by H. Frohofer, Institute of Organic Chemistry, University of Zürich.

Preparation of $[(C_6H_5)_4P^+]_2[Cu_4(DTP^{2-})_3]$ *(A)*

970 mg (8.96 mmol) DTP were added to a solution of 2.1 g (5.01 mmol) $(C_6H_5)_4PBr$ in 20 ml of ethylene glycol and 10 ml 1 M NaOMe/MeOH. After addition of 450 mg (3.14 mmol) Cu_2O, the solution was kept at 55 °C for 1 h until it became clear yellow. Slow evaporation at room temperature yielded dark red bulky crystals. *Anal.* Calc. for $C_{57}H_{58}Cu_4P_2S_6$: C, 54.71; H, 4.64; Cu, 20.27; S, 15.39. Found: C, 54.10; H, 4.37; Cu, 20.31 (TG analysis); S, 15.21%.

Preparation of $[(C_6H_5)_4P^+]_2[Cu_4(DTP^{2-})_3]\cdot 3MeOH$ *(B)*

970 mg (8.96 mmol) DTP were added to a solution of 4.2 g (10.01 mmol) $(C_6H_5)_4PBr$ in 20 ml of MeOH and 10 ml 1 M NaOMe/MeOH. After addition of 440 mg (3.08 mmol) Cu_2O, the solution was kept at 60 °C for 3 h until it became dark yellow. Crystallization at 5 °C yielded a microcrystalline sample. Recrystallization in the mother solution at −28 °C yielded bulky orange crystals. *Anal.* Calc. for $C_{57}H_{58}Cu_4P_2S_6\cdot 3MeOH$: C, 53.47; H, 5.20; Cu, 18.87; MeOH, 7.13. Found: C, 52.80; H, 5.17; Cu, 19.01 (TG analysis); MeOH, 7.10% (TG analysis).

Preparation of $[(CH_3)_4N^+]_2[Cu_4(DTP^{2-})_3]\cdot MeOH$ *(C)*

1.93 g (17.82 mmol) DTP were added to a solution of 3.01 g (36.45 mmol) $(CH_3)_4NCl$ in 80 ml MeOH, 16 ml 1 M NaOMe/MeOH and 10 ml CH_3CN. This reaction mixture was heated up to 45 °C and then 850 mg (5.94 mmol) Cu_2O were added. The mixture was

TABLE 2. Positional parameters (only Cu, S and C atoms of the Cu(I) thiolates and O, C and H atoms of the solvent molecules) of $[(Ph)_4P^+]_2[Cu_4(DTP^{2-})_3]$ (**A**), $[(Ph)_4P^+]_2[Cu_4(DTP^{2-})_3]\cdot 3MeOH$ (**B**), $[(CH_3)_4N^+]_2[Cu_4(DTP^{2-})_3]\cdot MeOH$ (**C**) and $[(C_2H_5)_4N^+]_2[Cu_4(DTE^{2-})_3]$ (**D**)

Atom	*x/a*	*y/b*	*z/c*	U_{eq}/U_{iso}[a] (Å^2)	Atom	*x/a*	*y/b*	*z/c*	U_{eq}/U_{iso}[a] (Å^2)
A					**B**				
Cu(1)	0.8529(2)	0.6748(1)	0.79591(9)	0.0597(6)	Cu(1)	0.05593(5)	0.36263(4)	0.32460(2)	0.03110(9)
Cu(2)	0.9549(1)	0.4941(1)	0.77388(9)	0.0488(5)	Cu(2)	0.28914(5)	0.32694(4)	0.26135(3)	0.03740(9)
Cu(3)	0.8072(1)	0.5393(1)	0.68299(9)	0.0555(6)	Cu(3)	0.12571(5)	0.28355(4)	0.21472(2)	0.03060(8)
Cu(4)	0.6961(1)	0.4508(1)	0.78043(9)	0.0561(6)	Cu(4)	0.08142(5)	0.49213(4)	0.20105(2)	0.03220(9)
S(1)	1.0644(4)	0.6841(4)	0.8178(1)	0.055(1)	S(1)	0.2381(1)	0.29200(9)	0.37335(5)	0.0360(2)
S(2)	0.8124(5)	0.7275(4)	0.7024(1)	0.078(2)	S(2)	−0.0116(1)	0.24758(8)	0.30354(5)	0.0323(2)
S(3)	0.6963(4)	0.6002(4)	0.8526(1)	0.076(2)	S(3)	−0.05460(9)	0.54737(8)	0.28959(5)	0.0297(2)
S(4)	0.9758(4)	0.4763(3)	0.6727(1)	0.055(1)	S(4)	0.3363(1)	0.18041(9)	0.22222(5)	0.0313(2)
S(5)	0.8268(4)	0.3558(3)	0.8176(1)	0.064(1)	S(5)	0.2683(1)	0.49676(9)	0.20239(5)	0.0418(2)
S(6)	0.6019(4)	0.4158(4)	0.6821(1)	0.066(1)	S(6)	0.0225(1)	0.42941(9)	0.13525(5)	0.0348(2)
C(1)	1.150(2)	0.744(1)	0.7566(8)	0.074(6)	C(1)	0.2823(4)	0.1432(3)	0.3993(2)	0.039(1)
C(2)	0.643(2)	0.715(2)	0.6821(8)	0.125(9)	C(2)	−0.1714(4)	0.3343(4)	0.2762(2)	0.047(1)
C(3)	0.768(2)	0.571(2)	0.9251(7)	0.110(8)	C(3)	0.0184(4)	0.6090(3)	0.3234(2)	0.050(1)
C(4)	1.126(2)	0.593(1)	0.6650(7)	0.064(5)	C(4)	0.3533(4)	0.0654(3)	0.2955(2)	0.0408(9)
C(5)	0.866(2)	0.401(2)	0.9012(6)	0.080(7)	C(5)	0.2412(4)	0.5720(5)	0.2643(2)	0.079(2)
C(6)	0.498(2)	0.507(2)	0.668(1)	0.15(1)	C(6)	−0.1463(4)	0.4628(3)	0.1607(2)	0.046(1)
C(7)	1.212(2)	0.666(2)	0.7236(8)	0.085(7)	C(7)	0.1072(4)	0.6568(3)	0.2769(2)	0.048(1)
C(8)	0.538(3)	0.624(3)	0.701(1)	0.21(2)	C(8)	−0.1836(4)	0.3693(3)	0.2026(2)	0.041(1)
C(9)	0.880(2)	0.531(2)	0.9260(7)	0.107(9)	C(9)	0.3905(4)	0.0727(3)	0.3569(2)	0.038(1)
D					O(L1)	0.6368(3)	0.1309(2)	0.1959(1)	0.0633(9)
Cu(1)	0.25209(6)	0.22471(5)	0.1992(1)	0.0455(2)	C(L1)	0.6572(5)	0.1896(4)	0.2309(2)	0.080(1)
Cu(2)	0.18526(6)	0.14393(5)	0.39597(9)	0.0412(2)	O(L2)	0.5094(3)	0.5464(3)	0.1381(1)	0.075(1)
Cu(3)	0.30468(6)	0.10043(5)	0.2232(1)	0.0463(2)	C(L2)	0.5633(4)	0.4872(4)	0.0887(2)	0.058(1)
Cu(4)	0.14364(6)	0.12499(5)	0.14026(9)	0.0408(2)	O(L3)	0.0589(3)	−0.0104(2)	0.3497(1)	0.0573(8)
S(1)	0.2569(1)	0.2404(1)	0.4318(2)	0.0556(6)	C(L3)	0.0818(4)	−0.0393(4)	0.4158(2)	0.0581(1)
S(2)	0.3748(1)	0.1857(1)	0.1162(2)	0.0534(6)	H(L4)	0.5600	0.1294	0.2031	0.03
S(3)	0.1231(1)	0.2364(1)	0.0967(2)	0.0494(5)	H(L8)	0.4375	0.5203	0.1613	0.03
S(4)	0.2977(1)	0.0775(1)	0.4437(2)	0.0526(5)	H(L12)	0.0286	0.0745	0.3306	0.03
S(5)	0.0560(1)	0.1213(1)	0.3170(1)	0.0427(5)	**C**				
S(6)	0.2372(1)	0.0654(1)	0.0287(2)	0.0467(5)	Cu(1)	0.1606(2)	0.6418(2)	0.0000	0.0437(2)
C(1)	0.3612(5)	0.2045(5)	0.4767(9)	0.073(3)	Cu(2)	0.3333	0.6667	−0.1257(2)	0.0377(4)
C(2)	0.3581(5)	0.1569(5)	−0.0562(8)	0.072(3)	S(1)	0.2997(4)	0.8830(4)	0.0568(2)	0.0477(5)
C(3)	0.0572(4)	0.2545(3)	0.2439(8)	0.048(2)	S(2)	0.1060(3)	0.6759(3)	−0.1218(2)	0.0406(5)
C(4)	0.3585(5)	0.1395(4)	0.5363(8)	0.066(3)	C(1)	0.241(2)	0.999(2)	−0.003(1)	0.053(2)
C(5)	0.0015(5)	0.1996(4)	0.2862(9)	0.050(2)	C(2)	0.281(2)	1.005(2)	−0.0859(8)	0.045(2)
C(6)	0.2746(5)	0.1262(4)	−0.0889(7)	0.060(2)	C(3)	0.161(1)	0.885(1)	−0.1356(9)	0.043(2)
					O(L)	0.03(1)	0.874(9)	0.182(5)	0.15(2)
					C(L)	0.0000	0.0000	0.177(2)	0.108(9)

[a] $U_{eq}=\frac{1}{3}\Sigma_i\Sigma_j U_{ij}a^*_i a^*_j a_i a_j$.

kept for 45 min at 50 °C until it was a clear pale yellow solution. White hexagonal platelets crystallized within 1 week in the refrigerator. *Anal.* Calc. for $C_{17}H_{42}Cu_4N_2S_6\cdot MeOH$: C, 28.70; H, 6.11; Cu, 33.77; N, 3.72; MeOH, 4.25. Found: C, 28.57; H, 5.88; Cu, 34.05 (TG analysis); N, 3.42; MeOH, 4.27% (TG analysis).

Preparation of $[(C_2H_5)_4N^+]_2[Cu_4(DTE^{2-})_3]$ *(D)*

1.2 g (12.74 mmol) DTE were added to a mixture of 30 ml MeOH, 10 ml 25% $(C_2H_5)_4NOH$/MeOH and 10 ml CH_3CN. This solution was heated up to 50 °C and then 550 mg (3.84 mmol) Cu_2O were added. Slow evaporation at room temperature yielded transparent, white multifaced crystals. *Anal.* Calc. for $C_{22}H_{52}Cu_4N_2S_6$: C, 33.40; H, 6.58; Cu, 32.16; N, 3.54. Found: C, 33.42; H, 6.75; Cu, 32.21 (TG analysis); N, 3.21%.

Preparation of $[C_6H_5CH_2N(CH_3)_3{}^+]_2[Cu_4(DTE^{2-})_3]$ *(E)*

1.05 g (11.15 mmol) DTE were dissolved in a mixture of 20 ml C_3H_7OH, 10 ml 1 M NaOMe/MeOH, 10 ml glycerol and 1.10 g (5.92 mmol) $C_6H_5CH_2(CH_3)_3NCl$. This solution was heated up to 45 °C and then 450 mg (3.12 mmol) Cu_2O were added. Within 4 days, white tetragonal platelets crystallized. *Anal.* Calc. for

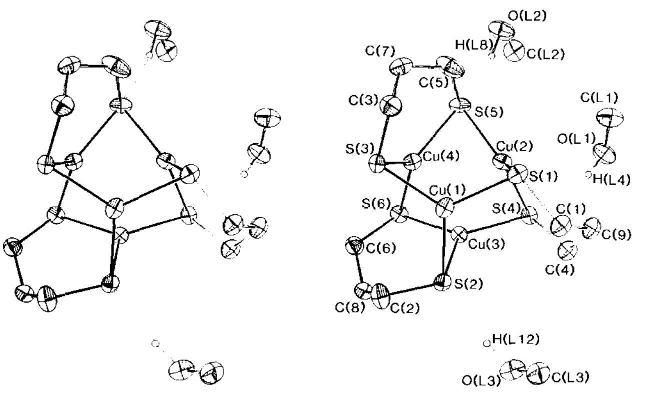


Fig. 1. Stereoview of the adamantane type $[Cu_4(DTP^{2-})_3]^{2-}$ cluster anion found in $[(C_6H_5)_4P^+]_2[Cu_4(DTP^{2-})_3]\cdot 3MeOH$ with numbering scheme and vibrational ellipsoids at the 50% probability level. The three MeOH solvent molecules are linked to the Cu–S core by S···H–O hydrogen bonds.

$C_{26}H_{44}Cu_4N_2S_6$: C, 37.57; H, 5.33; Cu, 30.57; N, 3.37. Found: C, 37.60; H, 4.89; Cu, 31.64 (TG analysis); N, 3.42%.

Preparation of $[(C_2H_5)_4N^+]_2[Cu_4(DTP^{2-})_3]\cdot MeOH$ *(F)*

1.93 g (17.82 mmol) DTP were added to a solution of 8.6 g (40.9 mmol) $(C_2H_5)_4NBr$ in 80 ml of MeOH, 10 ml CH_3CN and 16 ml 1 M NaOMe/MeOH. After addition of 850 mg (5.94 mmol) Cu_2O, the solution was kept at 50 °C for 45 min until it became pale yellow. Crystallization at 5 °C yielded after many weeks white hexagonal platelets. *Anal.* Calc. for $C_{25}H_{58}Cu_4N_2S_6\cdot MeOH$: C, 36.08; H, 7.22; N, 3.23; Cu, 29.37; MeOH, 3.70. Found: C, 35.83; H, 7.08; N, 3.51; Cu, 29.10 (TG analysis); MeOH, 3.29% (TG analysis).

Crystallographic studies

Symmetry, preliminary cell parameters and space groups of the investigated complexes were established by precession and Weissenberg photography. Final lattice parameters and crystal orientations were obtained from least-squares refinement of the θ values of 25 reflections on an Enraf-Nonius CAD-4 diffractometer. Crystal parameters are summarized in Table 1.

Intensity data were collected by using graphite-monochromated Mo Kα radiation. Eight standard reflections chosen in different regions of the reciprocal space were monitored periodically and showed no significant changes during data collection for **C**. The intensity data of the other compounds had to be corrected for a total loss in intensity of −3.34% (**A**), −4.21% (**D**) and −1.10% (**B**). The intensities were reduced to F_o after applying corrections for Lorentz and polarization effects. Numerical absorption corrections based on indexed and carefully measured crystal faces were carried out for all compounds.

The structures of **A–D** were solved using the Patterson interpretation routine in SHELX-86 [34] and by conventional Fourier techniques and were refined with full-matrix least-squares methods including anisotropic displacement factors for copper, sulfur, phosphorus or nitrogen, oxygen and carbon. Anomal dispersion corrections were applied for all atoms. Hydrogen atoms were included in the refinement with calculated (**A**, **C** and **D**) or observed (**B**) positional parameters. The weighting scheme used was either $w=1$ (unit weight) or $w=k/(\sigma^2(F)+pF^2)$; for k and p values see Table 1. The phenyl rings in structures **A** and **B** were not treated as rigid groups and refined with free varying anisotropic displacement parameters. In the refinement of **D**, all CH_2 groups of one of the two crystallographically independent $(C_2H_5)_4N^+$ cations were located on two split positions A and B. The distribution ratio of 2:1 was determined experimentally by equalizing the isotropic displacement factors.

Calculations were performed with the programs SHELX-86 [34] and SHELX-76 [35] on an IBM 3033 and an NAS AS/XL V60 computer of the University of Zurich. Data collection details and results of the

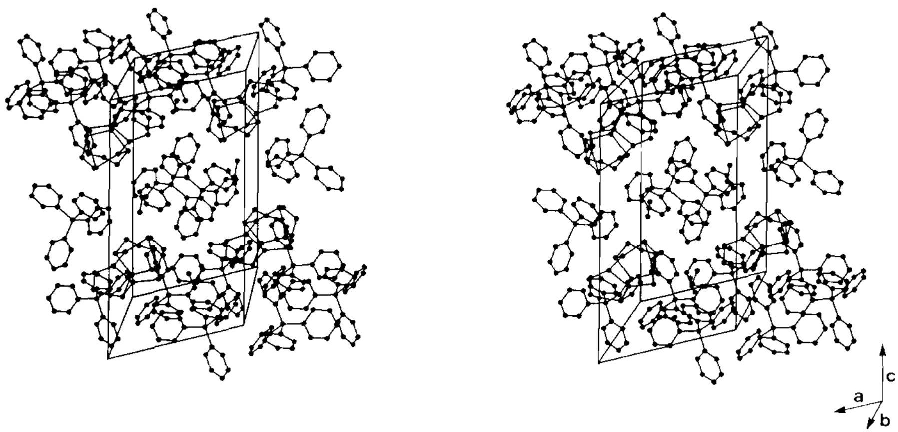


Fig. 2. Stereoview of the unit cell of $[(C_6H_5)_4P^+]_2[Cu_4(DTP^{2-})_3]\cdot 3MeOH$.

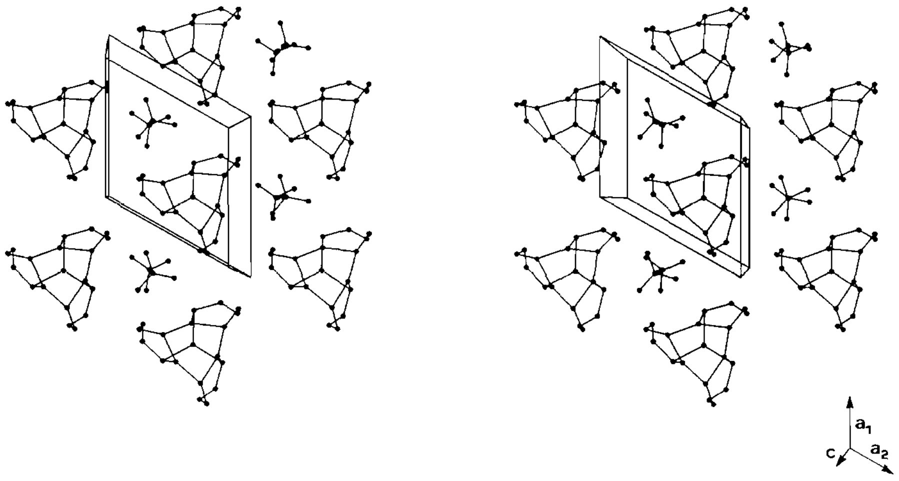


Fig. 3. Stereoview of the unit cell of $[(CH_3)_4N^+]_2[Cu_4(DTP^{2-})_3] \cdot MeOH$ perpendicular to (110). The MeOH solvent molecules are omitted for clarity.

refinements are summarized in Table 1. Positional parameters are given in Table 2. Bond distances and angles were calculated by the program ORFFE [36], stereoplots were generated by the program ORTEP [37] and by the plot routine in SHELXTL PLUS [38].

Infrared spectroscopy

Solid state IR spectra in the range 800–190 cm^{-1} were obtained on a Perkin-Elmer spectrophotometer type 983. Spectra were run on Nujol mulls between CsI or polyethylene plates; FT-IR spectra (500–20 cm^{-1}) were run by BIO-RAD Laboratories GmbH (D-8000 Munich).

Results and discussion

Description of the structures

All the compounds are built up of bulky cations separating the anionic copper(I) thiolate cluster units. The refinements of the cations $(C_6H_5)_4P^+$, $(C_2H_5)_4N^+$ and $(CH_3)_4N^+$ show no unexpected geometries. See also 'Supplementary material'.

The Cu_4S_6 entity found in structures **A**–**D** is named the 'adamantane'-type cluster unit due to the special arrangement of the copper and sulfur atoms (see Figs. 1–3): the four copper atoms form a tetrahedron with doubly-bridging thiolate ligands across each of the six edges of this tetrahedron. Each copper atom has approximately trigonal planar CuS_3 coordination. The Cu_4S_6 core can also be described as an octahedron of sulfur atoms with copper atoms lying at the midpoints of four faces of this octahedron. Thus a hexa-(μ-organothiolato)–tetra-cuprate(I) cage dianion is formed. With bidentate ligands, one sulfur atom of each chelate bridges across an edge of the base of the 'trigonal copper(I) pyramid' and the other links between a basal and the apical copper (Cu(1)). The three chelates form a 'propeller' about the Cu_4S_6 core. Only the cluster found in compound **C** exhibits exactly the overall symmetry C_3 expected from the Cu–S framework; all other Cu_4S_6 entities structurally characterized so far only approximate to C_3 symmetry; they are asymmetric due to the inversion of the S–C vector leading to different asymmetric configuration isomers [11]. In Fig. 1, the $[Cu_4(DTP^{2-})_3]$ anion found in **B** is presented as a representative of this adamantane cluster unit.

Using an alternative description of the structures of **A**–**D**, the CuS_3 group is regarded as a rigid triangle with the copper atoms located a little above or below the S_3 plane. The geometry of these triangles is determined by a set of three S–Cu–S angles which range from 94.2(1) to 142.3(1)° with a mean value of 119.9° and by three Cu–S distances ranging from 2.224(2) to 2.317(2) Å with a mean value of 2.274 Å. The large ranges are a consequence of the dominant influence of the S–S 'bite' distances of the different chelating thiolates used on the geometry (see discussion below). The deviation of the Cu atoms from the corresponding S_3 plane ranges from 0.050 to 0.106 Å. With this point of view, the Cu_4S_6 entity is built up by four CuS_3 groups, each triangle being linked by corner-sharing to the three other triangles. All copper atoms are systematically displaced from the plane through the three S atoms in a direction away from the centroid of the cage.

Selected bond lengths and interbond angles of the Cu–S framework found in **A**–**D** are given in Table 3.

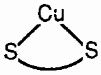
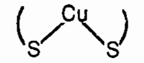
Till now crystal structures of copper(I) thiolates are known with three bidentate thiolates of the type $(S–R–S)^{2-}$, all exhibiting the Cu_4S_6 core: $(o\text{-}(SCH_2)_2C_6H_4)^{2-}$ (XYL [9]), $(SCH_2CH_2S)^{2-}$ (DTE [6,

TABLE 3. Summarized bond distances (Å), deviations (Å) of the Cu atoms from the S_3 planes and angles (°) in $[(Ph)_4P^+]_2[Cu_4(DTP^{2-})_3]$ (**A**), $[(Ph)_4P^+]_2[Cu_4(DTP^{2-})_3]\cdot 3MeOH$ (**B**), $[(CH_3)_4N^+]_2[Cu_4(DTP^{2-})_3]\cdot MeOH$ (**C**) and $[(C_2H_5)_4N^+]_2[Cu_4(DTE^{2-})_3]$ (**D**)

	A	B	C[a]	D
Cu(1)–Cu(2)	2.800(4)	2.683(1)	Cu(1)–Cu(2): 2.729(3)	2.772(1)
Cu(1)–Cu(3)	2.745(3)	2.712(1)		2.679(1)
Cu(1)–Cu(4)	2.694(3)	2.736(1)		2.719(1)
Cu(2)–Cu(3)	2.662(3)	2.716(1)	Cu(1)–Cu(1′): 2.739(3)	2.718(1)
Cu(2)–Cu(4)	2.721(3)	2.747(1)		2.624(1)
Cu(3)–Cu(4)	2.778(3)	2.652(1)		2.710(1)
Cu(1)–S(1)	2.260(5)	2.274(1)	Cu(1)–S(1): 2.284(4)	2.317(2)
Cu(1)–S(2)	2.293(5)	2.275(2)		2.267(2)
Cu(1)–S(3)	2.266(5)	2.273(1)		2.274(2)
Cu(2)–S(1)	2.290(4)	2.284(1)	Cu(1)–S(1′): 2.258(5)	2.296(2)
Cu(2)–S(4)	2.285(5)	2.246(1)		2.280(2)
Cu(2)–S(5)	2.234(5)	2.244(1)		2.226(2)
Cu(3)–S(2)	2.284(6)	2.288(1)	Cu(1)–S(2): 2.285(4)	2.328(2)
Cu(3)–S(4)	2.232(6)	2.268(1)		2.230(2)
Cu(3)–S(6)	2.263(5)	2.256(1)		2.294(2)
Cu(4)–S(3)	2.291(5)	2.281(1)	Cu(2)–S(2): 2.271(4)	2.336(2)
Cu(4)–S(5)	2.257(6)	2.245(2)		2.250(2)
Cu(4)–S(6)	2.241(5)	2.232(2)		2.224(2)
S(1)–C(1)	1.836(20)	1.830(5)	S(1)–C(1): 1.839(19)	1.854(10)
S(2)–C(2)	1.796(25)	1.844(5)		1.815(9)
S(3)–C(3)	1.839(20)	1.826(7)		1.842(8)
S(4)–C(4)	1.841(15)	1.833(4)	S(2)–C(2): 1.853(13)	1.824(9)
S(5)–C(5)	1.840(16)	1.827(8)		1.839(9)
S(6)–C(6)	1.857(30)	1.827(5)		1.806(8)
Cu(1) [1,2,3]	0.091	0.048	Cu(1) [1,2,1′]: 0.069	0.106
Cu(2) [1,4,5]	0.093	0.080		0.079
Cu(3) [2,4,6]	0.050	0.053	Cu(2) [2,2′,2″]: 0.078	0.097
Cu(4) [3,5,6]	0.089	0.071		0.072
S(1)–Cu(1)–S(2)	110.9(2)	119.9(1)	S(1)–Cu(1)–S(2): 109.0(1)	113.2(1)
S(1)–Cu(1)–S(3)	124.3(2)	121.4(1)		116.0(1)
S(2)–Cu(1)–S(3)	124.4(2)	118.6(1)		130.2(1)
S(1)–Cu(2)–S(4)	107.7(2)	111.7(1)	S(1)–Cu(1)–S(1′): 122.4(2)	95.5(1)
S(1)–Cu(2)–S(5)	126.6(2)	120.6(1)		132.9(1)
S(4)–Cu(2)–S(5)	125.3(2)	127.3(1)		131.2(1)
S(2)–Cu(3)–S(4)	127.6(2)	117.6(1)	S(1′)–Cu(1)–S(2): 128.2(1)	129.2(1)
S(2)–Cu(3)–S(6)	110.1(2)	111.5(1)		94.2(1)
S(4)–Cu(3)–S(6)	122.1(2)	130.7(1)		136.1(1)
S(3)–Cu(4)–S(5)	111.1(2)	110.1(1)	S(2)–Cu(2)–S(2′): 119.9(1)	95.1(1)
S(3)–Cu(4)–S(6)	125.3(2)	119.1(1)		122.2(1)
S(5)–Cu(4)–S(6)	123.2(2)	130.5(1)		142.3(1)
Cu(1)–S(1)–Cu(2)	76.0(1)	72.1(1)	Cu(1)–S(1)–Cu(1″): 74.2(2)	73.9(1)
Cu(1)–S(2)–Cu(3)	73.7(2)	72.9(1)		71.3(1)
Cu(1)–S(3)–Cu(4)	72.5(2)	73.9(1)		72.3(1)
Cu(2)–S(4)–Cu(3)	72.2(2)	74.0(1)	Cu(1)–S(2)–Cu(2): 73.6(2)	74.1(1)
Cu(2)–S(5)–Cu(4)	74.6(2)	75.5(1)		71.8(1)
Cu(3)–S(6)–Cu(4)	76.1(1)	72.5(1)		73.7(1)
Cu(1)–S(1)–C(1)	107.8(7)	105.1(2)	Cu(1)–S(1)–C(1): 100.1(5)	101.2(3)
Cu(2)–S(1)–C(1)	102.5(5)	104.4(1)		97.7(3)
Cu(1)–S(2)–C(2)	111.9(7)	106.1(2)		109.9(3)
Cu(3)–S(2)–C(2)	103.0(7)	105.3(1)	Cu(1″)–S(1)–C(1): 112.2(6)	96.9(3)
Cu(1)–S(3)–C(3)	111.2(7)	104.9(1)		100.8(2)
Cu(4)–S(3)–C(3)	104.5(8)	105.5(1)		97.4(3)
Cu(2)–S(4)–C(4)	107.7(5)	105.4(2)	Cu(1)–S(2)–C(3): 109.0(5)	95.4(3)
Cu(3)–S(4)–C(4)	113.0(7)	107.6(1)		107.9(3)
Cu(2)–S(5)–C(5)	108.9(6)	104.7(2)		107.6(3)
Cu(4)–S(5)–C(5)	107.7(8)	105.7(2)	Cu(2)–S(2)–C(3): 107.0(4)	97.9(3)
Cu(3)–S(6)–C(6)	103.1(7)	105.6(1)		99.8(3)
Cu(4)–S(6)–C(6)	111.8(7)	104.8(2)		99.9(3)

[a] Symmetry operators: ′ $-y, x-y, z$; ″ $-x+y, -x, z$.

TABLE 4. Comparison of the S---S 'bite' distance (Å) and the two angles α(S–Cu–S) (°) and α′(S–Cu–S) (°) found in Cu(I) thiolates with bidentate chelate ligands

Ligand[a]	'Bite' distance (Å) 	α(S–Cu–S) (°) 	α′(S–Cu–S) (°) 	Cu–S cluster	Reference
DTE	3.384–3.403	94.2–95.5	113.2–142.3	$[Cu_4(DTE^{2-})_3]^{2-}$	6, 13, this work
	3.378–3.391	95.7–96.0	123.9–140.1	$[Cu_3(DTE^{2-})_3]^{2-}$	1
DTP	3.694–3.757	107.7–111.7	110.9–130.7	$[Cu_4(DTP^{2-})_3]^{2-}$	13, this work
XYL	3.861–3.905	117.1–118.7	111.1–128.1	$[Cu_4(XYL^{2-})_3]^{2-}$	9
DTS	3.904–3.938		111.4–118.6	$[Cu_8(DTS^{2-})_6]^{4-}$	21
MNT	3.077–3.088		116.7–120.5	$[Cu_8(MNT^{2-})_6]^{4-}$	22
DED	3.042–3.044		116.1–122.4	$[Cu_8(DED^{2-})_6]^{4-}$	21
RS/RSCS$_2$	3.033		111.7–130.0	$[Cu_8(RSCS_2^-)_4(RS^-)_4]$	19, 20

[a] Abbreviations: DTE, 1,2-dithioethane; DTP, 1,3-dithiopropane; XYL, *o*-xylene-α,α′-dithiolate; DTS, 1,2-dithiosquarate ($C_4O_2(S^-)_2$); MNT, 1,1-dicyanoethylene-2,2-dithiolate; DED, 1,1-dicarboethoxyethylene-2,2-dithiolate; RS/RSCS$_2$, R = 2-methyl-2-butane.

TABLE 5. Bonding characteristics (Å, °) of S···H–O hydrogen bonds in the two Cu(I) thiolate clusters **B** and **C**, compared with literature data (**I–VII**)

	B		**C**		**I**	**II**	**III**	**IV**	**V**	**VI**	**VII**
S···O	S(2)···O(L3)	3.185(3)	S(1)···O(L)	3.40(9)	3.01(2)	3.21(4)	3.170(7)	3.03(1)		3.298(4)	3.30
	S(4)···O(L1)	3.252(4)			3.17(2)	3.15(4)					3.13
	S(5)···O(L2)	3.145(4)			3.35(2)						3.40
S···H	S(2)···H(L12)	2.154(1)				2.09(1)	2.28(1)		2.259	2.367(4)	2.52
	S(4)···H(L4)	2.385(1)							2.297		2.38
	S(5)···H(L8)	2.120(1)									2.59
M–S···O	Cu(1)–S(2)···O(L3)	134.9(1)	Cu(1)–S(1)···O(L)	102.0(12)	103.6(6)	128.2(7)	156.5(2)	132.7(3)			
	Cu(2)–S(4)···O(L1)	92.1(1)	Cu(1′)–S(1)···O(L)	162.5(17)	105.8(5)	134.5(6)	114.4(2)	137.5(4)			
	Cu(2)–S(5)···O(L2)	120.5(1)			111.8(6)	129.2(5)					
	Cu(3)–S(2)···O(L3)	109.7(1)			124.0(5)	136.7(7)					
	Cu(3)–S(4)···O(L1)	156.0(1)			92.3(6)						
	Cu(4)–S(5)···O(L2)	154.6(1)			104.3(6)						
					104.3(6)						
					123.2(5)						
S···O–C	S(2)···O(L3)–C(L3)	104.4(3)	S(1)···O(L)–C(L)	115.8(39)	112.4(12)	99.8(30)	102.9(6)	104.1(8)			
	S(4)···O(L1)–C(L1)	107.4(3)			97.7(10)	115.2(3)					
	S(5)···O(L2)–C(L2)	104.3(4)			112.5(12)						
					98.8(11)						
S···H–O	S(2)···H(L12)–O(L3)	169.3(3)				157.4(2)	142.4(8)		171.3	163.0(3)	143.2
	S(4)···H(L4)–O(L1)	163.2(3)							168.8		142.8
	S(5)···H(L8)–O(L2)	169.7(2)									145.2

Compounds: $[(C_6H_5)_4P^+]_2[Cu_4(DTP^{2-})_3]\cdot 3MeOH$ (**B**), $[(CH_3)_4N^+]_2[Cu_4(DTP^{2-})_3]\cdot MeOH$ (**C**), $[(C_6H_5)_4P^+]_2[Cu_5(CH_3S^-)_7]\cdot C_2H_6O_2$ (**I**) [3], $[(C_3H_7)_4N^+]_2[Cu_4(CH_3S^-)_6]\cdot CH_4O$ (**II**) [3], $[(C_6H_5)_4P^+]_2[Cu_4(C_2H_5S^-)_6]\cdot 0.5C_2H_6O_2$ (**III**) [2], *catena*(μ-C_6H_5S)[(μ-$C_6H_5S)_6Zn_4(CH_3OH)C_6H_5S$] (**IV**) [41], $Na_2[VO(SCH_2CH_2S)_2]\cdot 4EtOH$ (**V**) [43], $BaS_2O_3\cdot H_2O$ (**VI**) [42], $Na_2S_2O_3\cdot 5H_2O$ (**VII**) [44].

this work]) and $(SCH_2CH_2CH_2S)^{2-}$ (DTP [this work]). In addition, with DTE a Cu_3S_3 core was obtained [1]. Thus, the different S–S 'bite' distances of these chelate ligands do not favour different core types, but they have a great influence on the bonding angles around the copper and the sulfur atoms. A comparison of the Cu–S–C angles found in different compounds with the Cu_4S_6 entity shows a decrease of the mean values from monodentate thiolates (109.3°) to DTP (106.8°) and to DTE (101.3°) [13]. A stronger effect is observed on the S–Cu–S angles. Table 4 summarizes a comparison of the two different S–Cu–S angles (α: intraligand angle, α′: interligand angle) with the S–S 'bite' distances.

Within two of the structures under investigation, the inserted solvent molecules are linked by hydrogen bonds of the type S···H–O to the Cu–S cage. The observed S···H distances in the range 2.120(1)–2.385(1) Å are significantly shorter than the sum of van der Waals radii of S and H (3.05 Å) [39]. No significant influence of these hydrogen bonds on the binding properties

TABLE 6. IR data for copper(I) thiolates exhibiting a Cu_4S_6 cage unit

A	C	D	E	III	VIII	IX	X	XI
348(w, sh)	352(m)			368(s)			347(w)	350(s)
316(m)		322(s)	322(s)		326(m)			333(m)
	283(s)	290(m)		288(s)	280(w, sh)	288(s)	298(w)	
273(s)			269(s)		271(w)		275(w, sh)	273(s)
248(w)	249(s)	259(m)	249(s)	240(m)	247(m)		241(m)	248(s)
		248(s)						
226(w)		230(m)	223(m)	223(w, sh)	225(m)		223(w)	230(m)
		218(m)						
204(w)	212(s)	203(m)		201(m)	208(w, sh)	216(m)	210(w, sh)	203(w, sh)
			200(s)		199(m)	190(w)	196(m)	
182(w)	180(m)	180(w)	181(w)		185(w)		191(m)	
		175(m)	172(w)				180(w)	
	147(w)	148(m)	146(m)					166(s)
	135(m)		132(m)					
	112(m)					112(m)		120(m)
	106(m)	106(s)	109(m)					103(s)
			98(m)			94(m)		
	62(s)	65(s)	72(s)			78(m)		75(m)
		58(s)						

Compounds: $[(C_6H_5)_4P^+]_2[Cu_4(DTP^{2-})_3]$ (**A**), $[(CH_3)_4N^+]_2[Cu_4(DTP^{2-})_3]\cdot MeOH$ (**C**), $[(C_2H_5)_4N^+]_2[Cu_4(DTE^{2-})_3]$ (**D**), $[C_6H_5CH_2(CH_3)_3N^+]_2[Cu_4(DTE^{2-})_3]$ (**E**), $[(C_6H_5)_4P^+]_2[Cu_4(C_2H_5S^-)_6]\cdot 0.5C_2H_6O_2$ (**III**) [2], $[(C_6H_5)_4P^+]_2[Cu_4(DTE^{2-})_3]$ (**VIII**) [6, 13], $[(CH_3)_4N^+]_2[Cu_4(CH_3S^-)_6]$ (**IX**) [10, 46], $[(C_6H_5)_4P^+]_2[Cu_4(C_6H_5S^-)_6]\cdot CH_3COCH_3$ (**X**) [5, 7], $[(CH_3)_4N^+]_2[Cu_4(C_6H_5S^-)_6]$ (**XI**) [8, 10]. Abbreviations: s, strong; m, medium; w, weak; sh, shoulder.

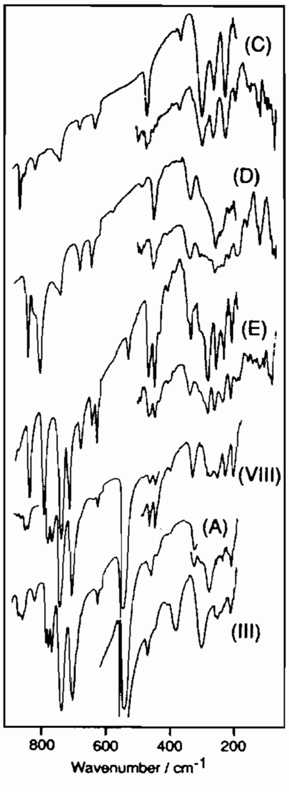


Fig. 4. IR spectra of different compounds with a Cu_4S_6 unit: $[(C_6H_5)_4P^+]_2[Cu_4(DTP^{2-})_3]$ (**A**), $[(CH_3)_4N^+]_2[Cu_4(DTP^{2-})_3]\cdot MeOH$ (**C**), $[(C_2H_5)_4N^+]_2[Cu_4(DTE^{2-})_3]$ (**D**), $[C_6H_5CH_2N^+(CH_3)_3]_2[Cu_4(DTE^{2-})_3]$ (**E**), $[(C_6H_5)_4P^+]_2[Cu_4(C_2H_5S^-)_6]\cdot 0.5C_2H_6O_2$ (**III**) [2], $[(C_6H_5)_4P^+]_2[Cu_4(DTE^{2-})_3$ (**VIII**) [6, 13]. For experimental details see text.

around the sulfur atoms is observed. Hydrogen bonding characteristics of some compounds describing this bond type are reviewed in Table 5. Such bonds could be important considering hydrogen bonding contacts in biological systems.

Spectroscopic properties and characterization

Cu(I) thiolates are intrinsically colorless. By crystallization of the anionic Cu_4S_6 unit with different $R_3(R')N^+$ cations ($R=R'=CH_3$, C_2H_5, C_3H_7; $R=CH_3$, $R'=CH_2C_6H_5$) colorless crystals are formed; using $(C_6H_5)_4P^+$ as counterion, however, intensively colored yellow to deep red crystals were obtained. An analogous phenomenon has been observed with the monomeric $[Cu(C_6H_5S^-)_3]^{2-}$ species [7, 40]. Therefore, we conclude that the yellow to red colour of the compounds is not a property of the cluster system, e.g. induced by Cu–Cu interactions, but is dependent on the type of counterion.

The color of the $(C_6H_5)_4P^+$ compounds is as follows: $[Cu_4(C_6H_5S^-)_6]^{2-}$ is yellow, $[Cu_4(DTP)_3]^{2-}$ is orange–red and $[Cu_4(DTE)_3]^{2-}$ as well as $[Cu_4(C_2H_5S^-)_6]^{2-}$ are red. Thus, less space filling ligands favour a stronger bathochromic effect on the absorption maximum of copper(I) thiolates. However, our results so far do not establish unequivocally the explanation given in ref. 40 or any other.

The IR spectra of the compounds are dominated by peaks from the coordinating ligands and the counterion. The vibrations of the cluster core are expected to appear in the range below 400 cm^{-1} [45]. However, the rather low intensities of these bands provided only limited information about structure and symmetry of the Cu–S core (see Fig. 4). A list of IR data of different $[Cu_4(RS^-)_6]^{2-}$ compounds is given in Table 6, including some data from the literature [46].

Supplementary material

Supplementary material including tables of observed and calculated structure factors and of anisotropic thermal parameters may be obtained on request from author M.B.; in addition it can be ordered from the Fachinformationszentrum Karlsruhe, W-7514 Eggenstein-Leopoldshafen 2, Germany. Please quote reference no. CSD-56798, the names of authors and the title of the paper.

Acknowledgements

We thank Professor H. R. Oswald for standing support of this project. Research grants from the Swiss National Science Foundation (No. 21-27924.89) are gratefully acknowledged.

References

1 Ch. P. Rao, J. R. Dorfman and R. H. Holm, *Inorg. Chem., 25* (1986) 428.
2 M. Baumgartner, H. Schmalle and E. Dubler, *Polyhedron, 9* (1990) 1155.
3 M. Baumgartner, H. Schmalle and Ch. Baerlocher, *Solid State Chem.,* (1993) in press.
4 I. G. Dance, M. L. Scudder and L. J. Fitzpatrick, *Inorg. Chem., 24* (1985) 2547.
5 M. Baumgartner, W. Bensch, P. Hug and E. Dubler, *Inorg. Chim. Acta, 136* (1987) 139.
6 G. Henkel, B. Krebs, P. Betz, H. Fietz and K. Saatkamp, *Angew. Chem., 100* (1988) 1373; *Angew. Chem., Int. Ed. Engl., 27* (1988) 1326.
7 D. Coucouvanis, C. N. Murphy and S. K. Kanodia, *Inorg. Chem., 19* (1980) 2993.
8 I. G. Dance and J. C. Calabrese, *Inorg. Chim. Acta, 19* (1976) 141.
9 J. R. Nicholson, I. L. Abrahams, W. Clegg and C. D. Garner, *Inorg. Chem., 24* (1985) 1092.
10 I. G. Dance, G. A. Bowmaker, G. R. Clark and J. K. Seadon, *Polyhedron, 2* (1983) 1031.
11 G. A. Bowmaker, G. R. Clark, J. K. Seadon and I. G. Dance, *Polyhedron, 3* (1984) 535.
12 I. G. Dance, *J. Chem. Soc., Chem. Commun.,* (1976) 68.
13 M. Baumgartner, *Ph.D. Thesis,* University of Zürich, Switzerland, 1990.
14 I. G. Dance, *Aust. J. Chem., 31* (1978) 2195.
15 I. G. Dance, *J. Chem. Soc., Chem. Commun.,* (1976) 103.
16 G. Henkel, P. Betz and B. Krebs, *Proc. Int. Conf. Coord. Chem., 24* (1986) 737 (Chemika Chronika New Series, Special Issue, Aug. 1986).
17 M. Baumgartner, E. Dubler and H. Schmalle, *J. Inorg. Biochem.,* to be published.
18 Q. Yang, K. Tang, H. Liao, Y. Han, Z. Chen and Y. Tang, *J. Chem. Soc., Chem. Commun.,* (1987) 1076.
19 R. K. Chadha, R. Kumar and D. G. Tuck, *J. Chem. Soc., Chem. Commun.,* (1986) 188.
20 R. K. Chadha, R. Kumar and D. G. Tuck, *Polyhedron, 7* (1988) 1121.
21 F. J. Hollander and D. Coucouvanis, *J. Am. Chem. Soc., 99* (1977) 6268.
22 L. E. McCandlish, E. C. Bissell, D. Coucouvanis, J. P. Fackler and K. Knox, *J. Am. Chem. Soc., 90* (1968) 7357.
23 E. Block, M. Gernon, Hyunkyu Kang, Shuncheng Liu and J. Zubieta, *J. Chem. Soc., Chem. Commun.,* (1988) 1031.
24 E. Block, M. Gernon, Hyunkyu Kang, G. Ofori-Okai and J. Zubieta, *Inorg. Chem., 28* (1989) 1263.
25 J. H. R. Kägi and Y. Kojima, *Abstr., 2nd Int. Meet. Metallothionein, Zurich, Switzerland, 1985,* p. 25.
26 K. B. Nielson, C. L. Atkin and D. R. Winge, *J. Biol. Chem., 260* (1985) 5342.
27 G. N. George, J. Byrd and D. R. Winge, *J. Biol. Chem., 263* (1988) 8199.
28 F. J. Hollander and D. Coucouvanis, *J. Am. Chem. Soc., 96* (1974) 5646.
29 J. Byrd, R. M. Berger, D. R. McMillin, C. F. Wright, D. Hamer and D. R. Winge, *J. Biol. Chem., 263* (1988) 6688.
30 M. Beltramini and K. Lerch, *Environ. Health Perspect., 65* (1986) 21, and refs. therein.
31 D. Coucouvanis, D. Swenson, N. C. Baenziger, R. Pedelty, M. L. Caffery and S. Kanodia, *Inorg. Chem., 28* (1989) 2829.
32 *JCPDS, Powder Diffraction File,* Swarthmore, PA, USA.
33 E. Dubler and M. Baumgartner, *Solid State Ionics, 43* (1990) 193.
34 G. M. Sheldrick, *SHELXS-86,* in G. M. Sheldrick, C. Krüger and R. Goddard (eds.), *Crystallographic Computing,* Oxford University Press, Oxford, UK, 1985, p. 175.
35 G. M. Sheldrick, *SHELX-76,* program for crystal structure determination, University of Cambridge, Cambridge, UK, 1976.
36 W. R. Busing, K. O. Martin, H. A. Levy, G. M. Brown, C. K. Johnson and W. A. Thiessen, *ORFFE3,* a Fortran function and error program, Oak Ridge National Laboratory, TN, 1971.
37 C. K. Johnson, *ORTEPII, Rep. ORNL-5138,* Oak Ridge National Laboratory, TN, 1976.
38 *SHELXTL PLUS,* Siemens Analytical X-Ray Instruments, 1989.
39 L. Pauling, *The Nature of the Chemical Bond,* Cornell University Press, Ithaca, NY, 3rd edn., 1960, p. 260.
40 C. D. Garner, J. R. Nicholson and W. Clegg, *Inorg. Chem., 23* (1984) 2148.
41 I. G. Dance, *J. Am. Chem. Soc., 102* (1980) 3445.
42 J. K. Money, J. C. Huffman and G. Christou, *Inorg. Chem., 24* (1985) 3297.
43 L.-J. M. Manojlovic, *Nature (London), 224* (1969) 686.
44 V. M. Padmanabhan, V. S. Yadava, Q. Q. Navarro, A. Garcia, L. Karsono, I-H. Suh and L. S. Chien, *Acta Crystallogr., Sect. B, 27* (1971) 253.
45 A. J. Canty, R. Kishimoto, G. B. Deacon and G. J. Farquharson, *Inorg. Chim. Acta, 20* (1976) 161.
46 G. A. Bowmaker and L.-Ch. Tan, *Aust. J. Chem., 32* (1979) 1443.