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Copper Thiolate Cluster Compounds. X-ray Structure and Properties of Pentathallium(I) μ_8-Chloro-dodecakis(α-mercaptoisobutyrato)octacuprate(I)hexacuprate(II) Hydrate, $Tl_5[Cu^{II}_6Cu^{I}_8(SC(CH_3)_2COO)_{12}Cl]{\cdot}{\sim}12H_2O$

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Crystalline derivatives of a Cu^I,Cu^{II} cluster complex of α-mercaptoisobutyric acid (H_2MIBA) were obtained with $Co(NH_3)_6^{3+}$ and Tl^+ as counterions. The structure of the Tl^+ derivative was determined by X-ray diffraction. The compound $Tl_5[Cu^{II}_6Cu^{I}_8(SC(CH_3)_2COO)_{12}Cl]{\cdot}nH_2O$ crystallizes in the space group $C2/c$ with $a = 18.339$ (2) Å, $b = 21.114$ (2) Å, $c = 24.858$ (3) Å, $\beta = 101.77$ (2)°, $V = 9423$ (2) Å^3, $d_m = 2.52$ (1) g cm^{-3}, and $d_x = 2.52$ g cm^{-3} for $n = 12$ and $Z = 4$. The intensities of 5771 independent reflections were measured by counter methods by using Mo Kα radiation ($\theta_{max} = 22°$). The structure was solved by direct phasing and refined by full-matrix least-squares methods. The final residual for 3908 reflections with $I > \sigma(I)$ and $(\sin\theta)/\lambda > 0.09$ Å^{-1} was 0.19. The structure consists of ordered cluster anions interlinked by Tl–O bonds. The Tl^+ ions and the water molecules in the structure are disordered. The $[Cu_{14}(MIBA)_{12}Cl]^{5-}$ clusters consist of a chloride ion at the center of a cube of eight Cu^I atoms, which is inscribed into an icosahedron of 12 sulfur atoms. The sulfur atoms form bridges between two Cu^I atoms and one Cu^{II} atom. The six Cu^{II} atoms in the structure form an octahedron in such an orientation that there is a Cu^{II} atom centered above each of the six faces of the Cu^I_8 cube. The Cu^I atoms are trigonally coordinated by three sulfur atoms. The Cu^{II} atoms are bound to two sulfur and two oxygen atoms of cis-bidentate-chelating H_2MIBA ligands. The structural and spectral parameters of the Cu–MIBA complex are compared with those of other copper thiolate complexes. The strong absorption in the visible spectra of the Cu–MIBA complex (485 nm, ϵ 21 000 mol^{-1} dm^3 cm^{-1}) and related compounds has previously been assigned to a S → $Cu^{II}(d_{x^2-y^2})$ charge-transfer transition. An alternative assignment to a S(3p) → Cu^I(4s,4p) transition is discussed.

Introduction

The reaction between Cu^{II} and thiols often leads to the formation of intensely colored reddish brown or purple products. Klotz et al.[1] first described this phenomenon for a number of thiol ligands and characterized them as mixed-valence Cu^I,Cu^{II} complexes. Structural investigations of these complexes were hampered for many years by instability, irreproducible analytical results, and lack of crystals.

All thiols which are able to form such colored complexes contain, apart from the thiol group, one or more potentially metal-binding substituents (e.g., COO^- or NH_2 groups) in a position suitable for the formation of a five-membered chelate ring.[2] When the carbon atom adjacent to the sulfur atom has two alkyl substituents, the colored Cu complex tends to be exceptionally stable.[3] The presence of halide ions is essential for the formation of this class of exceptionally stable colored complexes. Examples of such ligands are (i) penicillamine[3–7] (H_2Pen[8]), (ii) β,β-dimethylcysteamine[9] (HDMC[8]), and (iii) α-mercaptoisobutyric acid[5,6] (H_2MIBA[8]). The copper complexes with D-penicillamine and β,β-dimethylcysteamine have been crystallized and their structures have been solved.[7,9] The complex ions are mixed-valence cluster anions of composition $[Cu^{II}_6Cu^{I}_8L_{12}Cl]^z$, where z = 5− for L = D-penicillamine and z = 7 + for L = β,β-dimethylcysteamine. It has been postulated[7] that the copper–mercaptoisobutyric acid complex is a similar mixed-valence cluster $[Cu^{II}_6Cu^{I}_8(MIBA)_{12}Cl]^{5-}$, with cis-bidentate $Cu^{II}S_2O_2$ coordination instead of the $Cu^{II}S_2N_2$ coordination found in the H_2Pen and HDMC compounds. This hypothesis is proved to be correct by the present work.

Experimental Section

Materials. Mercaptoisobutyric acid was prepared as described by Biilmann.[10] All other reagents and solvents were of reagent grade quality.

Preparations. The crude sodium salt of the complex was prepared by adding a solution of H_2MIBA (80 mg, 0.67 mmol) in 15 mL of 0.2 M sodium acetate buffer to a solution of $CuCl_2{\cdot}2H_2O$ (85 mg, 0.5 mmol) in 2 mL of water. The dark brown solution thus obtained was treated with 35 mL of alcohol and 125 mL of ether. A dark brown oily layer separated out. The almost colorless supernatant was removed and discarded. Addition of 15 mL of alcohol to the brown residue resulted in the precipitation of a brown-black solid product. This

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Table I. Crystal and Analytical Data for MIBA Complexes

	derivative	
	Tl^+	$Co(NH_3)_6{}^{3+}$
crystal system	monoclinic	triclinic
a, Å	18.339 (2)	14.8
b, Å	21.114 (2)	22.0
c, Å	24.858 (3)	31.0
α, deg	90	110.2
β, deg	101.77 (2)	113.7
γ, deg	90	120.1
V, Å^3	9423 (2)	5777
space group	*C*2/*c*	*P*1 or $P\bar{1}$
vol of asymm unit, Å^3	1178	5777 or 2888
density, g cm^{-3}	2.52 (1)	
% Cu	26.6	31.9
% counterion	27.2	4.0
Cu/counterion (exptl)	0.32	0.14
Cu/counterion (theoret)	5/14 = 0.36	5/42 = 0.12

precipitate was filtered off and washed with alcohol and ether (yield 40 mg).

Crystals of $Tl_5[Cu^{II}{}_6Cu^I{}_8(MIBA)_{12}Cl]\cdot nH_2O$. The sodium salt of the complex prepared as described above was dissolved in water (10 mg in 0.2 mL). This solution was mixed with a solution of $TlNO_3$ (10 mg in 0.1 mL of water) in a small test tube (diameter 7 mm). A layer of alcohol was introduced above this solution with a Pasteur pipet. After about 5 h small crystals had grown on the wall of the test tube.

Crystals of $[Co(NH_3)_6]_5[Cu^{II}{}_6Cu^I{}_8(MIBA)_{12}Cl]\cdot xH_2O$. The sodium salt of the complex (2 mg) prepared as described above was dissolved in water (0.1 mL). A layer of water (0.5 mL) was placed above this solution in a small test tube (diameter 7 mm). An aqueous solution of $Co(NH_3)_6Cl_3$ (2 mg in 0.1 mL) was added to the aqueous upper layer. After 24 h small purple needles of the compound had grown on the wall of the test tube.

Physical Measurements. Metal analyses were carried out with a Varian Techtron AA6 atomic absorption spectrophotometer.

Crystal Data, Diffraction Measurements, and Solution of the Structure. The crystals were sealed in capillary tubes to reduce deterioration. The crystal data were collected on a Nonius CAD4/F computer-controlled four-circle diffractometer with Ni-filtered Cu Kα radiation. The crystal data shown in Table I were obtained by automatic indexing and a limited fast data collection. The Tl^+ salt of the Cu–MIBA complex was preferred to the $Co(NH_3)_6{}^{3+}$ salt for structure analyis because it has the smaller asymmetric unit. Accurate cell dimensions for this complex were calculated by least-squares refinement of the 2θ values of 11 automatically centered reflections ($16° < \theta < 35°$). The density was determined by flotation of superficially dried crystals in a $CHCl_3/CHBr_3$ mixture. The formula weight of $Tl_5Cu_{14}(MIBA)_{12}Cl\cdot nH_2O$ is 3364.75 + 18.015*n*. For $n = 12$ the formula weight is 3580.93, and the calculated density of 2.52 g cm^{-3} agrees well with the measured value of 2.52 (1) g cm^{-3}. The systematic absences *hkl* ($h + k = 2n + 1$) and *h*0*l* ($l = 2n + 1$) indicated that the space group was either *Cc* or *C*2/*c*. For reasons of laboratory organization an initial set of data ($\theta < 40°$) was measured with Ni-filtered Cu Kα radiation. The Wilson plot statistics based on these data favored a centrosymmetric structure. The space group was therefore assumed to be *C*2/*c* which was confirmed by the solution of the structure.

The structure was solved by the direct-methods program MULTAN.[11] For 150 |*E*|'s greater than 2.0, the set of phases with the highest combined figure of merit was used to calculate an *E* map. The positions of the Cl atom, the Cu atoms, and three partly populated Tl sites were found. The other atoms of the cluster anion were found in a series of Fourier and structure factor calculations, but only four partly populated Tl sites and no water molecules could be located. Obviously the Tl atoms and water molecules are disordered as in the Cu–Pen complex.[7] The disorder explains the low resolution of the reflection data (1.2 Å).

The quality of the data was inadequate for refinement of the structure. Possible reasons for the poor quality of the data were strong absorption by the crystal (μ(Cu Kα) = 227 cm^{-1}),[12] by the glass capillary, and possibly by droplets of $TlNO_3$-containing mother liquor. Absorption corrections could not compensate for the differences in the intensities of equivalent reflections.

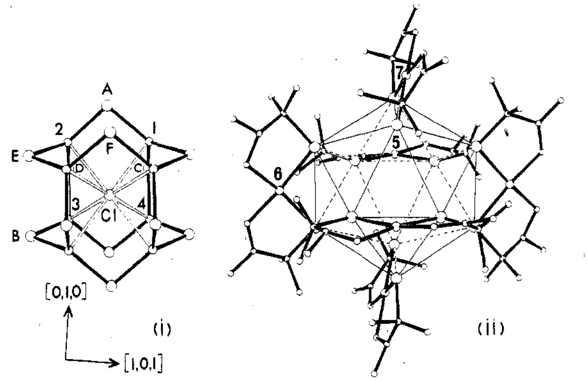


Figure 1. Structure of the $[Cu^{II}{}_6Cu^I{}_8(MIBA)_{12}Cl]^{5-}$ cluster. (i) The central $Cu^I{}_8Cl$ cube in an icosahedron of 12 sulfur atoms. (ii) The same icosahedron of sulfur atoms with the rest of the ligands chelating the Cu^{II} atoms. The lines connecting the sulfur atoms do not represent bonds. Capital letters represent sulfur atoms; numerical labels represent Cu atoms. Both codes are described in the text.

For the refinement of the structure a new set of data was collected with graphite-monochromated Mo Kα radiation (μ(Mo Kα) = 121 cm^{-1}).[12] A crystal of approximately 0.2-mm thickness in all directions was used. This thickness represents the optimum crystal size for the given absorption coefficient. Profile analysis of a suitable reflection led to the selection of the ω–($^1/_3$)2θ scan mode, an ω scan angle of (1.00 + 0.35 tan θ)°, and a horizontal aperture of (1.20 + 0.35 tan θ) mm. The scan speeds were determined by a required precision of $\sigma(I) < 0.01I$ with a maximum scan time of 100 s per reflection. The intensity *I* and its standard deviation $\sigma(I)$ were calculated as described previously.[7] Intensity and orientation controls were carried out as earlier reported.[7] No decomposition was detected. The intensities of 5771 independent reflections were measured ($\theta < 22°$). Lorentz and polarization corrections were applied in the usual way. Absorption correction by the analytical method of Coppens et al.[11] was not possible, since the crystal faces of the small and irregular crystal (sealed in a capillary) could not be accurately measured and indexed. Absorption corrections were therefore made by an empirical method based on the measurement of the intensity of a suitable reflection at different azimuthal positions.[11] Scattering factor curves for Tl, Cu, S, O, C, and Cl were taken from ref 13. The Tl, Cu, S, and Cl atoms were treated as anomalous scatterers.

The positional parameters and isotropic temperature factors of all atoms in the cluster anion and the occupancy and position of each of the partly occupied Tl sites were refined. The water molecules were disordered and could not be located. The isotropic temperature factors for the Tl atoms were kept fixed at $B = 3.5$ Å^2 (cf. ref 7). Refinement was achieved by full-matrix least-squares methods by using 3908 observed ($I > \sigma(I)$) reflections for which $(\sin\theta)/\lambda > 0.09$ Å^{-1}. Data at lower resolution were strongly affected by the disorder in the structure (cf. ref 7). The function minimized was $\sum w(|F_o| - k|F_c|)^2$. Three weighting schemes were tested: (i) unit weighting, (ii) statistical weighting, and (iii) $\sigma = \sigma_{stat} + 10^{-3}F_o$, where σ_{stat} is based on counting statistics. Scheme i tends to attribute too much importance to the weaker high-angle reflections, whereas scheme ii does the same for the stronger low-angle data. Scheme iii gives a greater weight to the reflections of intermediate intensity. In the present work schemes ii and iii led to fading of the light atoms and the refinements did not converge to give a realistic structure. Refinement using unit weights led to the most realistic values for bond lengths and angles in the structure and was therefore used. The final residual R^{14} was 0.19. The final atomic parameters are listed in Table II.

Description of the Structure

The Cluster Anions. The geometry of the $[Cu_{14}(MIBA)_{12}Cl]^{5-}$ cluster closely resembles the geometries of the penicillamine[7] and β,β-dimethylcysteamine[9] complexes, except for the coordination of the Cu^{II} atoms. The structure of the copper–penicillamine complex has been described[7] in terms of regular $Cu^I{}_8$, $Cu^{II}{}_6$, and S_{12} polyhedra centered around a chloride ion. The structure of the Cu–MIBA complex is shown in Figure 1.

Table II. Positional[a] and Thermal Parameters[b] for $Tl_5[Cu^{II}_6Cu^{I}_8(MIBA)_{12}Cl]\cdot nH_2O$

atom	10^4x	10^4y	10^4z	10^3U_{iso}	atom	10^4x	10^4y	10^4z	10^3U_{iso}
Cu(1)	3480 (4)	3578 (3)	5049 (3)	55 (2)	Cu(5)	3511 (4)	3174 (3)	3525 (3)	55 (2)
Cu(2)	1810 (4)	3460 (3)	4211 (3)	59 (2)	Cu(6)	99 (4)	2270 (3)	3948 (3)	50 (2)
Cu(3)	2200 (4)	1972 (3)	3896 (3)	55 (2)	Cu(7)	2142 (4)	4565 (3)	5548 (3)	48 (2)
Cu(4)	3895 (4)	2085 (3)	4735 (3)	55 (2)	Cl	5000	2500	2500	47 (5)

atom	10^4x	10^4y	10^4z	10^3U_{iso}	occupancy	atom	10^4x	10^4y	10^4z	10^3U_{iso}	occupancy
Tl(1)	2034 (2)	1906 (2)	1286 (1)	44	0.526 (6)	Tl(3)	5000	4134 (6)	2500	44	0.099 (3)
Tl(2)	2788 (2)	3880 (2)	1313 (2)	44	0.506 (6)	Tl(4)	4390 (8)	2710 (6)	2261 (6)	44	0.141 (5)

atom	10^3x	10^3y	10^3z	10^2U_{iso}	10^3x	10^3y	10^3z	10^2U_{iso}	10^3x	10^3y	10^3z	10^2U_{iso}
	ligand A				ligand B				ligand C			
S	244 (1)	420 (1)	477 (1)	5.1 (4)	108 (1)	162 (1)	404 (1)	4.0 (3)	402 (1)	309 (1)	442 (1)	5.3 (4)
C(1)	261 (5)	548 (4)	476 (3)	9 (3)	−20 (3)	109 (2)	349 (2)	5 (1)	506 (6)	338 (5)	390 (5)	14 (4)
C(2)	254 (4)	498 (3)	447 (3)	7 (2)	62 (3)	97 (2)	363 (2)	5 (1)	496 (3)	330 (2)	439 (2)	4 (1)
C(3)	339 (4)	495 (4)	426 (3)	9 (2)	86 (5)	35 (4)	401 (4)	13 (3)	535 (6)	285 (5)	447 (4)	16 (4)
C(4)	209 (4)	508 (3)	404 (3)	9 (2)	87 (5)	90 (4)	304 (3)	11 (3)	508 (5)	396 (5)	456 (4)	12 (3)
O(1)	246 (2)	539 (2)	534 (2)	6 (1)	−48 (2)	160 (2)	360 (2)	7 (1)	453 (3)	345 (2)	346 (2)	11 (2)
O(2)	286 (3)	600 (3)	476 (2)	10 (2)	−62 (3)	62 (3)	328 (2)	10 (1)	550 (5)	376 (4)	369 (3)	19 (3)
	ligand D				ligand E				ligand F			
S	233 (1)	296 (1)	356 (1)	4.4 (3)	69 (1)	313 (1)	435 (1)	5.0 (4)	177 (1)	363 (1)	584 (1)	5.3 (4)
C(1)	251 (4)	302 (3)	257 (3)	6 (2)	−68 (5)	329 (4)	416 (3)	11 (2)	181 (3)	455 (3)	659 (2)	6 (2)
C(2)	192 (3)	311 (3)	284 (2)	6 (2)	−9 (3)	370 (2)	419 (2)	5 (1)	143 (3)	396 (2)	645 (2)	4 (1)
C(3)	128 (3)	264 (3)	268 (2)	6 (2)	−5 (3)	416 (2)	464 (2)	7 (2)	54 (3)	408 (3)	616 (2)	7 (2)
C(4)	168 (3)	381 (3)	278 (2)	6 (2)	−8 (4)	403 (3)	361 (3)	9 (2)	154 (4)	346 (4)	690 (3)	9 (2)
O(1)	315 (2)	311 (2)	275 (2)	6 (2)	−80 (2)	271 (2)	395 (2)	7 (1)	203 (2)	491 (2)	626 (2)	6 (1)
O(2)	230 (3)	288 (2)	202 (2)	9 (1)	−133 (4)	352 (3)	415 (3)	16 (3)	190 (2)	472 (2)	712 (2)	9 (1)

[a] Atomic labels are explained in the text and in Figure 1. [b] The temperature factors are $\exp[-8\pi^2U[(\sin\theta)/\lambda]^2]$. Estimated standard deviations are shown in parentheses.

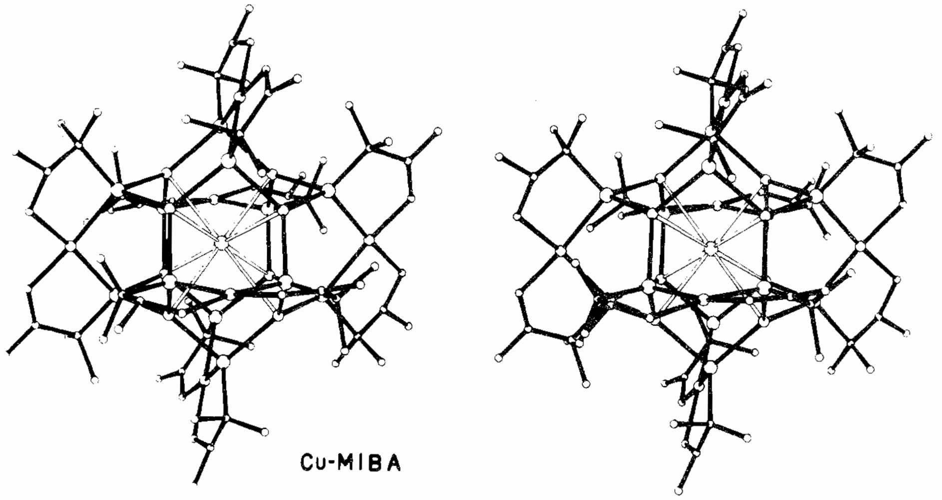
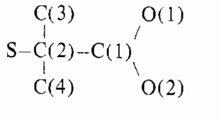


Figure 2. Stereodrawing of $[Cu^{II}_6Cu^{I}_8(MIBA)_{12}Cl]^{5-}$. The orientation is the same as in Figure 1.

In the tables and figures each crystallographically independent ligand is given a letter code (A–F). The atomic numbering in the ligands is



$$\begin{array}{lcll} \mathrm{C(3)} & & & \mathrm{O(1)} \\ | & & / & \\ \mathrm{S{-}C(2)} & - & \mathrm{C(1)} & \\ | & & \backslash & \\ \mathrm{C(4)} & & & \mathrm{O(2)} \end{array}$$

where O(1) is the oxygen atom bound to Cu^{II}.

Inspection of Figure 1 and comparison with ref 7 should be self-explanatory. A stereodrawing of the whole cluster is shown in Figure 2. The geometry of the complex is highly symmetric. The arrangement of a cube inscribed into an icosahedron which fits inside an octahedron is similar to Kepler's constructions with the five regular Euclidean solids.[15]

The S_{12} icosahedron fits inside the Cu^{II}_6 octahedron in such a way that each Cu^I-filled trigonal icosahedral face is approximately coplanar with a face of the Cu^{II}_6 octahedron (Figure 3). These planar $Cu^{II}_3S_3Cu^I$ arrangements contain the most likely pathways for Cu^{II}–Cu^{II} exchange interactions.

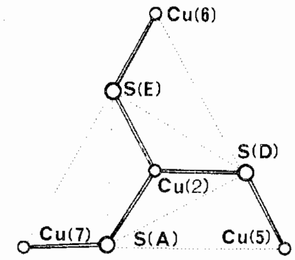


Figure 3. One of the eight $Cu^{II}_3SCu^I$ planes in the complex ion, looking along the Cu(2)–Cl bond: (---) outline of a face of the Cu^{II}_6 octahedron; (-- --) outline of a face of the S_{12} icosahedron.

The shortest nonbonded contacts with each of the Cu^I atoms are formed by three methyl substituents of three different H_2MIBA ligands. These methyl groups protect the Cu^I atoms

Table III. Bond Lengths[a] (Å) and Angles (deg) for the Copper Coordination Sites in the $[Cu^{II}_6Cu^{I}_8(MIBA)_{12}Cl]^{5-}$ Ion

Cu^I Atoms

Bond Lengths

Cu(1)–Cl	2.89 (7)	Cu(2)–Cl	2.92 (7)	Cu(3)–Cl	2.91 (7)	Cu(4)–Cl	2.90 (7)
Cu(1)–S(A)	2.30 (2)	Cu(2)–S(A)	2.26 (2)	Cu(3)–S(B)	2.28 (1)	Cu(4)–S(C)	2.29 (2)
Cu(1)–S(B^i)	2.28 (1)	Cu(2)–S(D)	2.28 (1)	Cu(3)–S(D)	2.28 (1)	Cu(4)–S(E^i)	2.29 (2)
Cu(1)–S(C)	2.27 (2)	Cu(2)–S(E)	2.26 (2)	Cu(3)–S(F^i)	2.26 (2)	Cu(4)–S(F^i)	2.26 (2)

Bond Angles

S(A)–Cu(1)–S(B^i)	120.4 (5)	S(A)–Cu(2)–S(D)	121.4 (6)	S(B)–Cu(3)–S(D)	121.4 (5)	S(C)–Cu(4)–S(E^i)	119.3 (6)
S(A)–Cu(1)–S(C)	120.2 (6)	S(A)–Cu(2)–S(E)	119.1 (6)	S(B)–Cu(3)–S(F^i)	119.9 (6)	S(C)–Cu(4)–S(F^i)	118.5 (6)
S(B^i)–Cu(1)–S(C)	119.3 (6)	S(D)–Cu(2)–S(E)	119.3 (6)	S(D)–Cu(3)–S(F^i)	118.5 (6)	S(E^i)–Cu(4)–S(F^i)	121.7 (6)

Cu^{II} Atoms

Bond Lengths

Cu(5)–S(C)	2.23 (2)	Cu(6)–S(B)	2.24 (1)	Cu(7)–S(A)	2.25 (2)
Cu(5)–O(1C)	1.99 (5)	Cu(6)–O(1B)	1.87 (4)	Cu(7)–O(1A)	1.95 (4)
Cu(5)–S(D)	2.24 (1)	Cu(6)–S(E)	2.25 (2)	Cu(7)–S(F)	2.26 (2)
Cu(5)–O(1D)	1.90 (4)	Cu(6)–O(1E)	1.89 (4)	Cu(7)–O(1F)	1.96 (4)

Bond Angles

S(C)–Cu(5)–O(1C)	84 (2)	S(B)–Cu(6)–O(1B)	87 (1)	S(A)–Cu(7)–O(1A)	86 (1)
S(C)–Cu(5)–S(D)	98.8 (6)	S(B)–Cu(6)–S(E)	98.5 (5)	S(A)–Cu(7)–S(F)	97.3 (6)
O(1C)–Cu(5)–O(1D)	94 (2)	O(1B)–Cu(6)–O(1E)	87 (2)	O(A1)–Cu(7)–O(1F)	90 (2)
S(D)–Cu(5)–O(1D)	84 (1)	S(E)–Cu(6)–O(1E)	87 (1)	S(F)–Cu(7)–O(1F)	86 (1)

[a] Estimated standard deviations in parentheses. The superscript i indicates the symmetry operation $^1/_2 - x$, $^1/_2 - y$, $1 - z$.

Table IV. Geometrical Data for the Cu^I_8, Cu^{II}_6, and S_{12} Polyhedra in $Tl_5[Cu^{II}_6Cu^I_8(MIBA)_{12}Cl]\cdot{\sim}12H_2O$

		av	range
Cu^I_8 cube	Cu–Cu (edge), Å	3.35 (2)	3.33 (1)–3.38 (1)
	Cu–Cu–Cu (angle), deg	90.0 (6)	89.1 (2)–91.3 (2)
Cu^{II}_6 octahedron	Cu–Cu (edge), Å	6.6 (2)	6.29 (1)–6.87 (1)
S_{12} icosahedron	S–S (Cu^{II} bridged), Å	3.39 (1)	3.38 (2)–3.40 (2)
	S–S (other), Å	3.94 (3)	3.89 (2)–3.97 (2)

against chemical attack by reagents in the surrounding medium.[7]

Selected bond lengths and angles are given in Table III. Some relevant geometrical data for the Cu^I, Cu^{II}, and S polyhedra are listed in Table IV.

Packing of the Unit Cell. Interionic Interactions. The structure consists of ordered cluster anions surrounded by disordered water molecules and Tl^+ ions. Although the elemental analyses (Table I) clearly indicate the presence of five Tl^+ counterions per cluster, the four partly populated Tl^+ positions account for only 0.51 of the total amount of thallium in the structure.

There are four symmetry-related clusters on inversion centers in each unit cell (Figure 4). There can be no direct intercluster hydrogen bonds, because the clusters have no hydrogen atoms which are suitable for hydrogen bonding. Those Tl^+ positions which have been identified lie close to two or more oxygen atoms of carboxylate groups. Bonding interactions between clusters are therefore formed by electrostatic interactions with bridging Tl^+ ions and possibly by hydrogen bonds to bridging water molecules. The Tl–O sites are shown in Figure 4. It is likely that additional coordination sites around the Tl^+ ions are filled by water molecules. The shortest contact between different clusters is O(2D)···O(1E) = 3.3 (1) Å. These two oxygen atoms are bound to the same Tl^+ ion (Figure 4). All other contact distances between clusters are longer than 3.5 (1) Å.

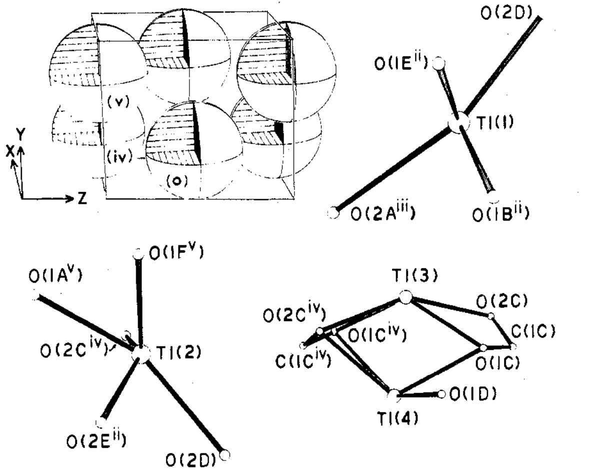


Figure 4. Packing of the $[Cu_{14}(MIBA)_{12}Cl]^{5-}$ clusters in the unit cell and the coordination of the partly populated Tl^+ sites in the same orientation. The superscripts indicate the following symmetry operations: (none) x, y, z; (ii) $-x, y, ^1/_2 - z$; (iii) $^1/_2 - x, -^1/_2 - y, ^1/_2 - z$; (iv) $1 - x, y, ^1/_2 - z$; (v) $x, 1 - y, -^1/_2 - z$. The clusters are represented by spheres with 6-Å radii. The cluster labeled (o) contains the atoms for which coordinates are listed in Table II. The clusters labeled (iv) and (v) contain the atoms related to these by symmetry operations iv and v. The presence of H_2O molecules in the coordination spheres around the Tl^+ ions cannot be excluded. Only oxygen atoms within 3.5 Å from the thallium atoms are shown.

Discussion

Comparison with Related Structures. The properties of the Cu–MIBA cluster are closely related to those of the Cu–Pen cluster.[7] Both compounds have the same $[Cu_{14}(L)_{12}Cl]^{5-}$ composition and form crystalline derivatives with Ti^+ and $Co(NH_3)_6^{3+}$ counterions. However, the packing of the ions in the crystalline Tl^+ is much denser in the Cu–MIBA complex than in the Cu–Pen complex (2355 and 4108 Å^3 per cluster anion respectively). Consequently the crystalline Cu–Pen complex contains more water molecules per complex ion (~ 55) and has a lower density (1.89 (2) g cm^{-3}).[7] The unit cell of the Cu–MIBA complex resembles more closely that of the Cu–DMC complex.[9] The H_2MIBA and HDMC complexes crystallize in the same space groups (*C*2/*c*) and have similar unit cell dimensions. The structural dimensions of the Pen and MIBA clusters are equal within the limits of precision, except for the coordination of the Cu^{II} atoms. In ref 7 the dimensions of the Cu–Pen complex are compared with those of structurally related thiolate complexes. The instability of Cu^I,Cu^{II} clusters formed with ligands lacking substituents on the carbon atom adjacent to the sulfur atom indicates the

Table V. Spectral Data for Cluster Complexes Containing a $Cu^{I}_{8}S_{12}$ Core

compd[a]	color	λ_{max}, nm	ϵ, mol^{-1} dm^3 cm^{-1}	medium	ref
$Na_5[Cu^{II}_6Cu^{I}_8(D\text{-}Pen)_{12}Cl]$	purple	518	25 500	H_2O	7
$[Cu^{II}_6Cu^{I}_8(DMC)_{12}Cl]_2(SO_4)_7$	purple	518	20 400	H_2O	9
$Na_5[Cu^{II}_6Cu^{I}_8(MIBA)_{12}Cl]$	brown-red	485	21 000	H_2O	5[b]
$(Pr_4N)_4[Cu^{I}_8(i\text{-}MNT)_6]$	orange-red	403	23 000	EtOH	19
		395		acetone	19
		510	strong	solid[c]	19
$(Bu_4N)_4[Cu^{I}_8(DED)_6]$	orange				20
$(Ph_4P)_4[Cu^{I}_8(DTS)_6]$	dark red				20

[a] For explanation of abbreviations see footnote 8. [b] ϵ calculated from the published value per Cu (1500) in ref 5. [c] Reflectance spectrum.

importance of the methyl substituents for the stability of H_2Pen, H_2MIBA, and HDMC complexes. It is interesting to note that also in all known crystals of copper(I) thiolates[16-18] the carbon atoms adjacent to sulfur are bound to at least two other carbon atoms.

Visible Spectrum. The intense absorption band in the visible spectra of cluster compounds containing the $Cu^{II}_6Cu^{I}_8S_{12}Cl$ core has been assigned[9] to a $S \rightarrow Cu^{II}$ charge-transfer transition. An alternative assignment can be made. The ligand field of the donor atoms around Cu^{II} in the Cu–Pen complex (S_2N_2 coordination) is stronger than in the MIBA complex (S_2O_2 coordination). If the intense absorption is of $S \rightarrow Cu^{II}$ charge-transfer origin, it would—on the basis of a ligand field model—be expected at a shorter wavelength in the Cu–Pen complex because the energy level of its half-filled $Cu^{II}(d_{x^2-y^2})$ acceptor orbital will be higher than in the MIBA complex. However, the absorption in the Cu–Pen complex is found at much longer wavelength (Table V). Moreover a similar absorption band with a comparable molar extinction coefficient has been reported for the orange-red Cu^{I} complex $[Cu^{I}_8(i\text{-}MNT)_6]^{4-}$ which also contains a Cu^{I}_8 cube inscribed into an S_{12} icosahedron[19] (Table V). This complex contains no chloride and, more importantly, no copper(II). Related $Cu^{I}_8S_{12}$-containing clusters have similar colors[20] (Table V). A self-consistent charge and configuration molecular orbital calculation[19] indicates that the intense band at 400–500 nm in $[Cu^{I}_8(i\text{-}MNT)_6]^{4-}$ arises from a $S(3p) \rightarrow Cu^{I}(4s,4p)$ charge-transfer transition. Assignment of the intense absorptions at 485 and 518 nm in the Cu–MIBA and Cu–Pen complexes, respectively, to $S \rightarrow Cu^{I}$ charge transfer seems to be a reasonable alternative. The difference in wavelength of this absorption for the Pen and MIBA complexes must then be caused by more subtle inductive effects from the different coordination geometries around Cu^{II} on the sulfur orbitals. A definite assignment of the absorption in the visible spectra of these complexes will have to wait until more detailed molecular orbital calculations are carried out.

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Registry No. $Tl_5[Cu^{II}_6Cu^{I}_8(MIBA)_{12}Cl]\cdot nH_2O$, 71733-80-7; $[Co(NH_3)_6]_5[Cu^{II}_6Cu^{I}_8(MIBA)_{12}Cl]_3$, 71786-24-8.

Supplementary Material Available: A table of observed and calculated structure factor amplitudes (24 pages). Ordering information is given on any current masthead page.

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(8) Abbreviations used in this article: H_2Pen = penicillamine, $HSC(CH_3)_2CH(COO^-)NH_3^+$; H_2MIBA = α-mercaptoisobutyric acid, $HSC(CH_3)_2COOH$; HDMC = β,β-dimethylcysteamine, $HSC(CH_3)_2CH_2NH_2$. Deprotonated ligands are abbreviated as Pen, MIBA, and DMC, respectively. *i*-MNT = 1,1-dicyanoethylene-2,2-dithiolate, $(CN)_2C{=}C(S^-)_2$; DED = dicarbethoxy-2,2-ethylenedithiolate, $(EtOOC)_2C{=}C(S^-)_2$; DTS = dithiosquarate, $(S^-)C{=}C(S^-)COCO$.
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