Two enantiomers of $[Cu_3(mnt)_3]^{3-}$ as ligands to Cu(I) or Ag(I) in building $[Cu_6M_2(mnt)_6]^{4-}$ complexes (M = Cu or Ag) with the reversal of the reaction by X⁻ (X = Cl, Br)[†]

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Two enantiomers of $[Bu_4N]_3[Cu_3(mnt)_3]$ (1) formed by $Na_2(mnt)$ (mnt = maleonitriledithiolate, $[S_2C_2(CN)_2]^{2-}$) and CuCl in a 1 : 1 molar ratio react further with MCl (M = Cu or Ag) involving both the enantiomers of 1 to produce the larger complex, $[Bu_4N]_4[Cu_6M_2(mnt)_6]$ (M = Cu (2), Ag (3)) from which the capped Cu⁺ or Ag⁺ ion can readily be removed by Bu_4NX (X = Cl, Br), reverting 2 or 3 back to 1. Such reversal does not work with non-coordinating anions like BF_4^- , ClO_4^- and PF_6^- .

Introduction

The coordination chemistry of Cu¹ with 1,1- or 1,2-dithiochelating ligands is known in forming polynuclear complexes.¹⁻⁵ However, further chemistry using a polynuclear complex as ligand has not been explored. Here we report the synthesis of a new trinuclear Cu¹-maleonitriledithiolate complex structurally characterized as $[Bu_4N]_3[Cu_3(mnt)_3]$ (1). Complex 1 is used as a sulfur donor ligand to Cu¹ to synthesize $[Bu_4N]_4[Cu_8(mnt)_6]$ (2) and when Ag¹ is used the corresponding structural analogue $[Bu_4N]_4[Cu_6Ag_2(mnt)_6]$ (3) complex is formed.

Results and discussion

Synthesis

Complex 1 was isolated from the reaction of $Na_2(mnt)$ (mnt = maleonitriledithiolate, $[S_2C_2(CN)_2]^{2-}$ with CuCl in H₂O in a 1:1 molar ratio as tetrabutylammonium salt in excellent yield. Crystal structure of 1 (see X-Ray crystal structure section) showed the presence of the $[Cu_3(mnt)_3]^{3-}$ anion in two enantiomeric forms differing in their copper-sulfur binding mode (clockwise and anticlockwise fashion) in the crystal lattice. Complex 1 further reacts with CuCl to yield the known complex 2 which was synthesized by reacting Cu^I salt with mnt ligand with different stoichiometric ratio.⁵ Our approach to the creation of larger complexes using 1 as ligand was first checked with the synthesis of 2 using CuCl. This was extended to use AgCl which led to the formation of a hetero-metal complex 3 (see X-Ray crystal structure section). Interestingly, complexes 2 and 3 can be reverted back to 1 by the addition of Bu₄NBr (or Bu₄NCl), suggesting the lability of the newly formed Cu(Ag)-S bond to cleavage by a halide. The ready inter-conversion between 1 and 2 or 3 in CH₃CN is represented in Scheme 1. Addition of water to the reaction mixture (Scheme 1) led to the conversion in the forward direction but addition of diethyl ether drove the reaction backward instead.

$$2[Bu_{4}N]_{3}[Cu_{3}(mnt)_{3}] + 2MX$$
(1)
$$[Bu_{4}N]_{4}[Cu_{6}M_{2}(mnt)_{6}] + 2Bu_{4}NX$$
(2 / 3)
$$M = Ag (3), Cu (2)$$

$$X = Cl, Br$$

Scheme 1

UV-Visible spectroscopy

Such a transformation as shown in Scheme 1 can readily be followed by electronic spectroscopy and also by electrochemical study. Both 2 and 3 retained their electronic spectral features in the presence of Bu₄NBF₄ or Bu₄NClO₄, but in the presence of Bu₄NX (X = Cl or Br) the respective electronic spectra predominantly changed to 1. Similarly, the use of $M(I)ClO_4$ instead of M(I)Clled to the equilibrium reaction (Scheme 1) shifted towards the right and on addition of either water or diethyl ether led to the precipitation of only the larger complex. The addition of a coordinating anion such as Br⁻ or Cl⁻ to a solution of 2 or 3 in acetonitrile led to the enhancement of the intensity of the electronic absorption band (Fig. 1) at 377 nm, characteristic of the formation of 1 with the release of an equivalent amount of MX. The electronic spectral signature of 2 or 3 does not change on the addition of a non-coordinating or weakly coordinating anion (PF₆⁻, ClO₄⁻ or BF₄⁻).⁶ The equilibrium (Scheme 1) existed only in the presence of a coordinating ion such as a halide.

Electrochemistry

Electrochemical responses under different supporting electrolytes established the electronic spectral observation. In a typical cyclic voltammogram (CV) of **1**, an anodic peak potential (E_{Pa}) observed at +0.25 V was followed by a reversible peak ($E_{1/2}$) at +0.39 V vs. Ag/AgCl. Complex **2** displayed a reversible peak at the same potential but an anodic peak potential of the irreversible response was observed at +0.28 V vs. Ag/AgCl when a supporting electrolyte, Bu₄NClO₄ was used. On addition of Bu₄NBr to the solution of **2** (supporting electrolyte, Bu₄NClO₄), its CV changed with the shifting of the E_{Pa} from +0.28 to +0.25 V suggesting the

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Fig. 1 Change in UV-Vis absorption spectra: (a) $2(1/6 \times 10^{-4} \text{ M})$ towards 1 by addition of excess Bu₄NBr; (b) $1(1/3 \times 10^{-4} \text{ M})$ towards 2 by addition of CuBr $(1/3 \times 10^{-4} \text{ M})$; (c) $3(1/6 \times 10^{-4} \text{ M})$ towards 1 by addition of excess Bu₄NBr; and (d) $1(1/3 \times 10^{-4} \text{ M})$ towards 3 by addition of AgBr $(1/3 \times 10^{-4} \text{ M})$ in CH₃CN.

conversion of **2** to **1**. In addition, an electro-active new species with E_{Pa} at +0.69 V and E_{Pc} at +0.52 V was generated (Fig. 2). These new electro-responses were found to be due to CuBr under identical conditions (not shown).



Fig. 2 Cyclic voltammogram of $1 (1 \times 10^{-3} \text{ M})$ (red), $2 (0.5 \times 10^{-3} \text{ M})$ (black) and $[2 + Bu_4NBr (1 \times 10^{-3} \text{ M})]$ (broken line) were recorded at a scan rate of 100 mV s⁻¹ over the potential range of interest, 0 to +0.80 V in acetonitrile with 0.2 M Bu₄NClO₄ as supporting electrolyte.

NMR study

The ¹³C NMR spectrum (Fig. 3) in CD₃CN of **1** showed two resonances at 121.40 ppm for C=C carbon atoms and at 126.35 ppm for CN. The -CN and -C=C- groups present in the



Fig. 3 ¹³C NMR spectra of **1** (top) and **3** (bottom) in CD₃CN. Expanded spectra of the red-circle region for both cases are shown as insets.

coordinated mnt in **1** are under different structurally imposed environments in the solid which should have displayed four ¹³C peaks. Instead only two ¹³C peaks in CD₃CN are observed. This is due to the free rotation of two enantiomers where Cu–S arising from μ_1 -S and μ_2 -S bridgings interchange their position faster than in the NMR time scale, resulting the S atoms of mnt equivalent in solution. For the symmetrical octanuclear complex **3**, the expected two resonances appeared at 127.39 ppm for CN and at 119.44 ppm for C=C due to the coordination of dithiolene.

The strong solvent peak appeared at 118.18 ppm for -CN carbon of CD₃CN could have masked some peaks originating from compounds in that region. The ¹³C NMR spectra in d₆-DMSO solvent did not show the appearance of any other peaks in this region.⁷ The ¹³C NMR spectra of **1** and **3** (or **2**) showed only two resonances: one for C=C carbon atoms and other for CN carbon, so the solid-state structural constraint was not present in solution. When a CD₃CN solution of **1** is treated with a half equivalent of AgClO₄, its ¹³C NMR showed shifts of the 121.40 and 126.35 ppm peaks to 119.44 and 127.39 ppm respectively, demonstrating the conversion of **1** to **3** almost quantitatively.

X-Ray crystal structure†

Structural parameters of **1** and **3** were deduced from X-ray crystallography. Single crystals suitable for X-ray diffraction measurements of these complexes were obtained by slow vapor diffusion of diethyl ether into a solution of the respective complex in acetonitrile. Details of the crystallographic data and refinement parameters are provided in Table 1. The selected bond distances and angles are presented in Table 2.

The crystal structures of the cyclic trinuclear complex, $[Bu_4N]_3[Cu_3(mnt)_3]$, containing two conformers, **1a** and **1b** are shown in Fig. 4. The {Cu(mnt)} units for cyclizing in clockwise fashion (in **1a**) are enantiomers of the units for cyclizing in anticlockwise fashion (in **1b**). Each trinuclear complex in **1** is based on a cyclohexane-like six-membered {Cu₃S₃} ring in a chair conformation with alternating copper and sulfur atoms. The mnt

 Table 1
 Crystallographic data and refinements of 1 and 3

Complexes	$[Bu_4N]_3[Cu_3(mnt)_3]$	$[Bu_4N]_4[Cu_6Ag_2(mnt)_6]$ $C_{88}H_{144}Cu_6Ag_2N_{16}S_{12}$	
Formula	C ₆₀ H ₁₀₈ Cu ₃ N ₉ S ₆		
Formula weight	1338.62	2408.07	
Crystal system	Monoclinic	Monoclinic	
Space group	P21	C2/c	
Τ/Κ	100(2)	100(2)	
Ζ	6	4	
a/Å	23.8615(14)	25.554(3)	
b/Å	16.7245(10)	26.741(3)	
c/Å	29.5431(18)	16.534(3)	
a/deg	90	90	
β/deg	113.2850(10)	90.092(4)	
γ/deg	90	90	
$V/Å^3$	10829.5(11)	11298(3)	
$d_{\rm calcd}/{\rm g}~{\rm cm}^{-3}$	1.232	1.416	
μ/mm^{-1}	1.090	1.714	
θ range/deg	1.93-28.34	1.52-26.06	
R1, wR2 (all data)	0.2417, 0.2493	0.1091, 0.2227	
$\operatorname{GOF}(F^2)$	1.036	1.052	
$[I > 2\sigma(I)] R_1^a, w R_2^b$ (final)	0.0985, 0.2362	0.0699, 0.1930	
Flack parameter	0.0(3)		
$^{a}R_{1} = \sum \ F_{a}\ - \ F\ / \sum \ F_{a}\ $	$b w R_{2} = \{\sum [w(F_{2})^{2} - b w R_{2} = (F_{2})^{2} - (F_{2$	$(F^{2})^{2} [w(F_{o}^{2})^{2}]^{1/2}$	

Table 2Selected bond distances (Å) and angles (°)

Bond distances/Å		Bond angles/°		
1a				
Cu(1)-S(2)	2.218(5)	S(2)-Cu(1)-S(3)	138.16(18)	
Cu(1) - S(3)	2.234(4)	S(2)-Cu(1)-S(1)	95.60(17)	
Cu(1) - S(1)	2.278(5)	S(3)-Cu(1)-S(1)	125.01(17)	
Cu(2) - S(4)	2.207(5)	S(4)-Cu(2)-S(5)	139.35(15)	
Cu(2) - S(5)	2.213(4)	S(4)-Cu(2)-S(3)	96.10(16)	
Cu(2)-S(3)	2.264(4)	S(5)-Cu(2)-S(3)	122.73(16)	
Cu(3) - S(1)	2.205(4)	S(1)-Cu(3)-S(6)	136.33(17)	
Cu(3) - S(6)	2.214(4)	S(1)-Cu(3)-S(5)	124.95(16)	
Cu(3) - S(5)	2.260(4)	S(6)-Cu(3)-S(5)	96.73(14)	
Cu(1)– $Cu(3)$	2.781(2)			
Cu(1)-Cu(2)	2.806(2)			
Cu(2)-Cu(3)	2.759(3)			
1b				
Cu(4)–S(11)	2.228(4)	S(11)-Cu(4)-S(7)	137.08(16)	
Cu(4)-S(7)	2.244(4)	S(11)-Cu(4)-S(8)	127.19(15)	
Cu(4) - S(8)	2.281(4)	S(7)-Cu(4)-S(8)	95.47(15)	
Cu(5)–S(10)	2.205(4)	S(10)-Cu(5)-S(8)	135.03(15)	
Cu(5) - S(8)	2.213(3)	S(10)-Cu(5)-S(9)	96.70(13)	
Cu(5)–S(9)	2.279(4)	S(8) - Cu(5) - S(9)	127.93(14)	
Cu(6)–S(9)	2.206(4)	S(9)-Cu(6)-S(12)	129.19(13)	
Cu(6)–S(12)	2.225(4)	S(9)–Cu(6)–S(11)	133.12(15)	
Cu(6) - S(11)	2.259(3)	S(12)-Cu(6)-S(11)	96.92(13)	
Cu(4)– $Cu(6)$	2.783(2)			
Cu(4)– $Cu(5)$	2.827(2)			
Cu(5)–Cu(6)	2.665(2)			
3				
Cu(1) - S(2)	2.1899(19)	S(5) - Ag(1) - S(3)	115.82(6)	
Cu(1) - S(6)	2.284(2)	S(2)-Cu(1)-S(5)#1	135.69(8)	
Cu(2) - S(6)	2.208(2)	S(2)-Cu(1)-S(6)	126.44(8)	
Cu(2) - S(3)	2.2219(19)	S(5)#1-Cu(1)-S(6)	96.03(7)	
Cu(2)-S(4)	2.289(2)	S(6)-Cu(2)-S(3)	140.78(7)	
Cu(3)-S(1)	2.2418(19)	S(6)-Cu(2)-S(4)	119.40(7)	
Cu(3)-S(2)	2.267(2)	S(3)-Cu(2)-S(4)	95.97(7)	
Ag(1)-S(1)	2.4387(19)	S(4)#1-Cu(3)-S(1)	136.41(8)	
Ag(1)-S(5)	2.446(2)	S(4)#1-Cu(3)-S(2)	127.02(8)	
Ag(1)-S(3)	2.4576(18)	S(1)-Cu(3)-S(2)	95.47(7)	
Ag(1)-Cu(3)	3.1298(11)			
Ag(1)-Cu(2)	3.1800(11)			

ligand acts as a bridging bidentate ligand bound to one copper center *via* μ_1 -S and μ_2 -S to form a 5-membered chelate ring.⁸ This mnt further binds to an adjacent Cu atom to build a Cu₃S₃ sixmembered ring. The Cu– μ_1 -S distance (2.257(4) Å) associated with the five-membered chelate ring is slightly larger than the bridging Cu– μ_2 -S distance (2.213(4) Å).¹⁻⁵ Each copper atom in **1** has nearly trigonal planar geometry. The 5-membered rings are not coplanar with the Cu3-plane, with almost similar deviations of 68.7, 69.8 and 68.7°. Thus, the structures of the cyclic trimers resemble open bowl-shaped cones and exhibit approximate *C*3 symmetry.

Compound **3** crystallized in the monoclinic space group, *P*21, with one anion complex, $[Cu_6Ag_2(mnt)_6]^{4-}$ and four tetrabutyl cations. The crystal structure of **3** (**2** is similar)⁵ revealed an octanuclear complex (Fig. 5) where each metal center has a trigonal planar geometry resulting from the bonding of three μ_2 -sulfur atoms. The $(Cu \cdot \cdot Cu)_{avg}$ separation in **3** is 3.464 Å, the $(Cu-S)_{avg}$ bond distance⁵ is 2.236(9) Å and the $(Ag-S)_{avg}$ distance⁹ is 2.447(13) Å. The six Cu⁺ ions bind to the S-atoms of the mnt ligand and form a 5-membered ring that stabilizes the copper center, but the two silver centers bind through the lone pairs of the already bridging S ligands and without forming any chelate ring.⁸ This causes the lability of these two silver ions in **3** (and also equivalent copper atoms in **2**) to ready leaching out by a halide ion.



Fig. 4 The structure (ORTEP view) of anions of two conformers of **1** (1a and 1b) are shown with 30% probability thermal ellipsoids.



Fig. 5 The structure (ORTEP view) of the anion of **3** is shown with 30% probability thermal ellipsoids.

The equilibrium of 1 with 2 or 3 (Scheme 1) in solution suggests that crystallographically identified enantiomers of the anion of 1 may be available in solution, and the octanuclear core present in 2 or 3 may be built by the participation of both the enantiomers as depicted in Fig. 6. Complex 1 has two different sulfur environments, with μ_1 -S and μ_2 -S atoms.⁹ Complex 1 as ligand utilizes all its μ_1 -sulfur atoms for further coordination. The μ_1 -S atoms are positioned at a distance of 5.0 Å from each other in 1 but to utilize all these sulfurs the distance required is $\leq \sim 4.0$ Å. Therefore, it is necessary to have conformational flexibility to achieve this distance. The mnt groups in 1 have *cis*-*cis*-*cis* arrangement and an adjustment with a slightly different conformational arrangement like *cis*-*trans*-*cis* would offer further possibility of coordinating the available sulfurs. The angles and



Fig. 6 The possible interconversion between a trinuclear and an octanuclear core. From left: frame wire view (–CN parts of mnt are omitted for clarity) of enantiomer 1 with 180° rotation (shown by arrow) and on its top enantiomer 2. Middle: flipping of one of the mnt rings in each enantiomer from *cis* to *trans* position as shown in shadow. Right: (one way, above) under metallation two bi-coordinated units build planar subunits and dimerize by the formation of a cubic complex with new metal–sulfur bonds, their lability under the halide ion is shown; and (other way, below) before metallation, two units dimerize to form a $\{Cu_6(mnt)_6\}$ moiety with mnt-rings oriented alternatively in a *cis–trans–cis* way.

distances of 1 are $(Cu \cdot Cu)_{avg} = 2.76 \text{ Å and } \angle (Cu - S - Cu)_{avg} = 76^{\circ}$ while 2 (or 3) has \angle (Cu–S–Cu)_{avg} = 103.75° and (Cu···Cu)_{avg} = 3.47 Å. So, breaking of metal-sulfur bonds with the formation of newer bonds may take place in such conversion. The copper ion normally prefers a trigonal planar geometry. So the newly formed metal-ligand coordinated bonds may drag the sulfur atoms away from their earlier positions. As a result, the two enantiomers may re-organize with square bases. These further adopt an offset faceto-face arrangement to form the cubic complex 3 (and 2) as shown in Fig. 4. So in the first step, the conversion from 1 to the larger complex (2 or 3) may occur either with the intermediate formation of a hexanuclear form by the combination of two enantiomers or with the formation of a tetranuclear intermediate by the addition of a metal ion to 1 (Fig. 6). For the reverse reaction, the newly capped metal ion may be easily released from the larger complex by the interaction with a halide to form an intermediate $\{Cu_6(mnt)_6\}$ moiety which may dissociate to form 1. The $Cu \cdot \cdot Cu$ distance in 1 is in the range 2.66–2.83 Å, with \angle Cu–S–Cu angles of *ca*. 72.8–77.8°, suggesting a relatively weak Cu...Cu interaction.¹⁰ The Cu \cdot ·Cu distance of the hexanuclear core, {Cu₆(mnt)₆}, in **3** is 3.09–3.83 Å and the resultant bond angle at the bridging sulfur is 88.1–116.9°, suggesting ready dissociation of such a species to yield 1.

Conclusion

In summary, we have shown that a trinuclear complex 1 can function as a sulfur donor ligand in two enantiomeric forms to chelate a Cu^{I} or Ag^{I} ion to form an octanuclear complex 2 or 3. The introduced Cu^{I} or Ag^{I} ions in 2 or 3 can readily be removed by halide ion leaching, reverting these back to the starting trinuclear complex 1.

Experimental

General

All starting materials were purchased from commercial sources and were used without further purification. Solvents were freshly distilled over appropriate drying reagents. Na₂(mnt) was prepared as described in the literature.¹¹ All reactions were carried out under an argon atmosphere using the standard Schlenk technique unless otherwise stated. Cyclic voltammetry was performed using an Epsilon EC-20 with a scan rate of 100 mV s⁻¹. The electrolytic cell used was a conventional three-compartment cell, in which a GCE working electrode, a Pt auxiliary electrode, and a Ag/AgCl reference electrode were employed. The CV measurements were performed at room temperature using 0.2 M (ⁿBu₄N)(ClO₄) as the supporting electrolyte and CH₃CN as a solvent. The ferrocenium/ferrocene couple was used as the internal standard $(E_0 = 0.53 \text{ V})$. Electronic absorption spectra were measured with use of a USB2000 UV-Visible spectrometer. ¹³C NMR spectra were recorded on JEOL JNM-LA 400 FT-NMR machine. IR spectra were recorded by KBr pellet in the range 400-4000 cm⁻¹ on a Bruker Vertex 70, FT-IR spectrophotometer. Elemental analyses for carbon, hydrogen, nitrogen and sulfur analysis were carried out with a Perkin-Elmer 2400 microanalyser.

Synthesis

Preparation of 1. Solid CuCl (0.99 g, 10 mmol) was added to a solution of Na₂(mnt)¹¹ (1.86 g, 10 mmol) in 80 mL H₂O and the mixture was stirred for 1/2 h to dissolve the solid. Excess of Bu₄NBr was added to the solution to precipitate a yellow solid (1), which was collected by filtration, washed with H₂O, isopropanol and finally by diethyl ether. Diffraction quality crystals were obtained by vapor diffusion of diethyl ether into an acetonitrile solution of the crude product. Yield: 2.72 g (78%). Anal. calc. (found): C, 53.78 (53.73); N, 9.41 (9.38); H, 8.07 (8.08); S, 14.34 (14.37). IR (KBr, cm⁻¹): 2225 ν(C=N). UV-Vis, λ /nm (ε /M⁻¹ cm⁻¹): 377 (36600). ¹³C NMR (CD₃CN, δ , ppm); 126.35 (-CN), 121.40 (-C=C–), 59.69 (- α CH₂), 24.61 (- β CH₂), 20.51 (- γ CH₂) and 13.95 (- δ CH₃). Mp 160–162 °C.

Preparation of 2. Solid CuCl (0.099 g, 1 mmol) was added to 25 mL of acetonitrile containing 1.34 g (1 mmol) of 1 and the resultant solution was stirred for 10–15 min. The resultant solution was filtered and to this yellow solution H₂O was added dropwise to start hazy nucleation for crystallization. It was left as such at 0 °C and on standing overnight, yellow crystalline **2** was precipitated out. This was isolated by filtration, and washed with isopropanol and diethyl ether. Yield: 1.05 g (68%). IR spectral data are identical with earlier reported data.⁵ UV-Vis, λ/nm (ϵ/M^{-1} cm⁻¹): 377 (32928). Mp 195–198 °C. Crystals of **2** showed lattice parameters identical to those of the complex synthesized by another method.⁵

Preparation of 3. Solid AgCl (0.144 g, 1 mmol) was added to 25 mL of acetonitrile containing 1.34 g (1 mmol) of **1** and the resultant mixture was stirred until all solid was dissolved. The yellow solution was filtered and H₂O was added dropwise to the filtrate to make it cloudy, *i.e.* to the point of incipient crystallization, and was stored at 0 °C overnight. Orange crystals of **3** were separated out, which were isolated by filtration followed by washing with isopropanol and diethyl ether. Yield: 1.08 g (75%). Anal. calc. (found): C, 43.85 (43.88); N, 9.30 (9.28); H, 5.98 (5.95); S, 15.95 (15.97). IR (KBr, cm⁻¹): 2225 ν(C≡N). UV-Vis, λ/nm (ε/M⁻¹ cm⁻¹): 377 (32135). ¹³C NMR (CD₃CN, δ, ppm); 127.39 (-CN), 119.44 (-C=C-), 59.69 (-αCH₂), 24.55 (-βCH₂), 20.50 (-γCH₂) and 13.92 (-δCH₃). Mp 175–178 °C.

Data collection and analysis. Suitable diffraction quality crystals of 1, 2 and 3 were obtained from the crystallization procedures described in each synthesis.[†] The crystals used in the analyses were glued to a glass fiber and mounted on a Bruker SMART APEX diffractometer. The instrument was equipped with a CCD area detector and data were collected using graphite-monochromated Mo K α radiation ($\lambda = 0.71069$ Å) at low temperature (100 K). All empirical absorption corrections were applied using the SADABS program. Cell constants were obtained from the least-squares refinement of three-dimensional centroids through the use of CCD recording of narrow ω rotation frames, completing almost allreciprocal space in the stated θ range. The cell parameters of complex 2 have been found to be identical to those of the known compound reported earlier.5 All data were collected with SMART 5.628 (Bruker, 2003), and were integrated with the Bruker SAINT program. The structure was solved using SIR97 and refined using SHELXL-97.12 The respective space groups of these compounds were determined based on the lack of systematic absence and intensity statistics. The additional symmetry for all of these crystals have been checked through PLATON.¹³ Compound 1 contains nine tetrabutylammonium cations and three complex anions, $[Cu_3(mnt)_3]^{3-}$. Two of these complex anions are enantiomers (1a and 1b) to each other and the third anion is a 1a conformer. The asymmetric unit does not have any further imposed symmetry due to the slight different in core structural parameters (distance and angle) between 1a and a duplicate of this. Full-matrix leastsquares/difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters.

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