Two different types of folding of isomeric macrocycles induced by metal ion co-ordination

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The crystal structure of the dicopper(I) complex of a novel 30-membered macrocyclic Schiff-base type ligand with two dithiadiimine co-ordination sites, linked by two *meta*-substituted benzene rings, has revealed an achiral folding of the macrocycle ('squeezed ring'), with two tetrahedral co-ordination sites and π-stacked benzene rings. The dicopper(I) compound of the isomeric 32-membered macrocycle with π-stacked *para*-substituted benzene rings has a chiral double helical ('twisted ring') conformation. The co-ordination geometries of the two copper(I) chromophores of both structures are very similar, and this emerges also from the solid-state UV/VIS spectra [metal-to-ligand charge-transfer transitions at 375 and 355 nm for the dicopper(I) species with the 30- and 32-membered macrocycle, respectively]. Proton NMR experiments and UV/VIS spectroscopy indicate that the folded structures are preserved in solution and that the metal-free compounds both have an open cyclic structure.

The folding of large macrocyclic rings is an important feature in the biological, applied and fundamental chemistry of macrocyclic ligands. There are a number of naturally occurring cyclic peptides in bacteria, fungi, plants and marine organisms (*e.g.* Ascidiacyclamide, Patellamide D and Cyclosporin A), and their unique properties may in part be related to their folding, in both metal-free and co-ordinated states.[1] Also, transition-metal compounds of macrocyclic ligand systems have often been used to model the active sites of metalloproteins, and an understanding of the topological properties of these species is an important feature.[2] In this and other areas, the preorganization of the metal-free compounds (metal-ion selectivity) and of the complexes (substrate binding) are of particular interest.

Metal ion-induced helicity has attracted much attention in recent years,[3] and polypyridine-based ligands have been of major importance in this area.[4] Recently, a series of large macrocyclic Schiff-base type compounds with $(N_2S_2)_2$ donor sets was discovered, which, upon co-ordination to two copper(I) ions, lead to chiral 'figure-of-eight loop' double helical compounds (Scheme 1, 'twisted' conformation).[5] The simplicity of this new structural motif is both aesthetically satisfying and, due to the versatility of the synthetic procedure, useful in the study of factors contributing to a particular type of chiral self-organization. The syntheses are based on a well documented [2 + 2] condensation reaction.[6] The imine and thioether donors both favour soft metal ions and thus stabilize the +I oxidation state of copper, which prefers tetrahedral co-ordination geometry. All the structurally characterized dicopper(I) compounds of this type of macrocyclic ligand exhibit similar structural features, *i.e.* (distorted) tetrahedral co-ordination geometries of the two copper(I) sites and π-stacked benzene spacer groups.[5,7] Nuclear magnetic resonance experiments indicate that the metal-free compounds have an open 'cyclic' structure, and that the chiral double helical geometry of the dicopper(I) compounds pertains in solution, when a non-co-ordinating solvent is used.[5,7,8]

There are two possible effects contributing to the metal ion-induced double helical folding of the ligands, *i.e.* the preference of copper(I) for tetrahedral co-ordination geometry in combination with ligand-centred steric contributions, and π stacking of the benzene rings. Stabilization by π stacking is a minor[9] but not necessarily insignificant contribution. This also follows from the fact that the metal-free compounds exhibit 'cyclic' structures and no π stacking (see Scheme 1; proof for the 'cyclic' structure for the metal-free compounds emerges from the ^{1}H NMR spectra, see below). There exist various strategies to study the two possible contributing factors for the helical structures separately. The two approaches that have been used so far are (*i*) to preorganize the ligand by linking the co-ordinating loops to a paracyclophane group,[8] and therefore to exclude the structural influence of π stacking, and (*ii*) to modify structurally the benzene spacer groups in order to discourage the metal ion-induced folding to a 'twisted' conformation. The latter approach is described here. We report the synthesis of a unique pair of isomeric compounds with all-ethylene-bridged donor sets and *para*- or *meta*-substituted benzene spacer groups, leading to 32- and 30-membered macrocycles, respectively, and the synthesis, structural, spectroscopic and electrochemical characterization of the corresponding dicopper(I) compounds with strikingly different structural properties (see Scheme 1).

Results and Discussion

Syntheses and structural analyses

The addition of stoichiometric amounts of tere- or isophthalaldehyde to solutions (MeCN or toluene, respectively) of 1,8-diamino-3,6-dithiaoctane yields the isomeric compounds L^1 and L^2, respectively, as white solids in good yields (48–71%; Scheme 1). Addition of $[Cu(MeCN)_4]ClO_4$ to solutions of L^1 or L^2 in MeCN–CH_2Cl_2 (1:1) produces an orange or yellow solution, respectively, of the dicopper(I) complexes **1** and **2**, from which air-stable orange (yellow) crystals, suitable for X-ray diffraction, were isolated, after slow evaporation of the solvents at ambient temperature.

The crystal structure analyses of complexes **1** and **2** reveal that the two isomers belong to two different structural types, *i.e.* the modification of the benzene spacer groups leads to a new structural motif (the molecular cations are plotted in Fig. 1, which also defines the nomenclature used in Table 1 where selected bond distances and valence angles are listed). While the dinuclear compound **1** occurs in the chiral 'twisted figure-of-

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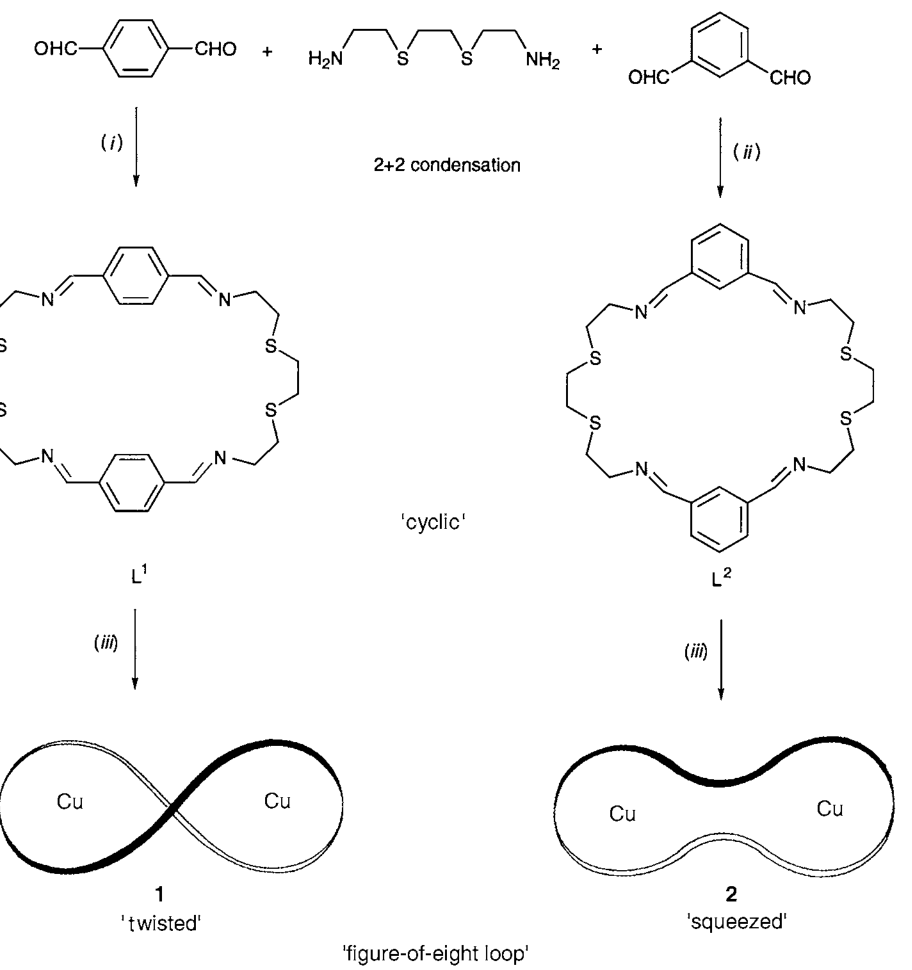


Scheme 1 (*i*) MeCN; (*ii*) toluene; (*iii*) Cu$^+$

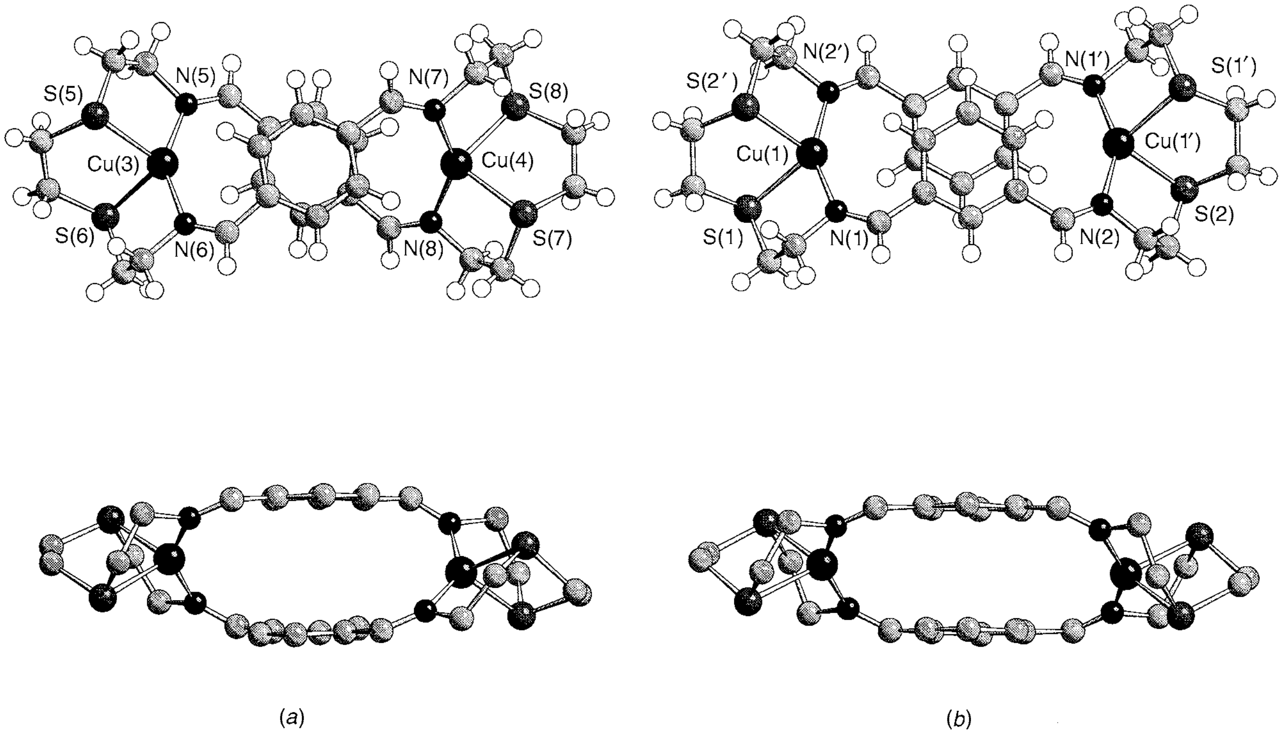
Table 1 Average bond lengths (Å) and angles (°) for the 'twisted' complex **1** and the 'squeezed' dicopper(I) complex **2**

	1	**2**
Cu–S	2.380	2.429
Cu–N	2.013	1.994
Cu···Cu	7.825	8.145
$C^{benz}\cdots C^{benz}$	3.432	3.394
benzene···benzene	3.588	3.259
S–Cu–S	91.0	88.24
S–Cu–N	115.1	113.25
S–Cu–N^{bite}	90.8	89.65
N–Cu–N	144.1	148.5

eight loop' form, also found for all other dicopper(I) compounds with the same type of ligand,[5,7] **2** exhibits a new type of folding with an achiral 'squeezed figure-of-eight loop' conformation. Similar types of folding have been observed with 2:2 metallamacrocycles involving linear bis(bidentate) ligands with aromatic spacer groups.[11,12] The common features of structures **1** and **2** are: (*i*) similar, distorted tetrahedral co-ordination geometries of the copper(I) centres, and (*ii*) a parallel arrangement of the two benzene rings (see Fig. 1 and Table 1 which summarizes the salient structural features). The difference in the folding of the two macrocycles leads to a slightly lager Cu···Cu distance for **2** (8.15 *vs.* 7.83 Å). The distance between the two parallel benzene ring planes is smaller for the 'squeezed' conformation of **2** than for the 'twisted' ring of **1** [3.26 *vs.* 3.59 Å; the inter-ring distance for all the structurally characterized 'twisted' dicopper(I) complexes is rather constant,[5,7] and the shortest C···C distances between carbon atoms of the two parallel rings are also slightly different [3.43 *vs.* 3.39 Å; there is a second set of C···C distances in **2** (3.43 Å) with slightly longer distances]. The small difference in C···C distances is the result of the two different modes of stacking of the parallel benzene rings: in **1** there is a torsion of 16° around the perpendicular vector connecting the two benzene rings, and in **2** there is a horizonal translation of 1.06 Å. The amount of stabilization by π stacking is probably similar in the two types of folded structures (*ca.* 2–3 kJ mol^{-1}).[9] In both structures this stabilization is largely compensated by a considerable strain induced to the C^{imine}–C^{benzene} torsional angle (*ca.* 32° in the four imines each in both structures), leading to a torsional strain of *ca.* 1–2 kJ mol^{-1} per torsion.[6e]

^{1}H NMR spectroscopy

The ^{1}H NMR coupling patterns of the geminal protons have been used to analyse the solution structures of helical compounds.[5,13] The signals of the methylene groups of the 1,2-dithiaethane fragments are well separated, and singlets at δ 2.74 and 2.77 are observed for the metal-free compounds L^1 and L^2, respectively, typical of non-stereogenic sites, and thus indicating an open 'cyclic' structure of the ligands. In the ^{1}H NMR spectra in nitromethane of the corresponding dicopper(I) complexes **1** and **2** (see Table 2) these methylene groups exhibit an AX spin pattern with a geminal coupling of 10.2 and 10.0 Hz, and a chemical shift difference $\Delta\delta$ of 257.3 and 253.1 Hz, respectively, typical of diastereotopic protons (considering the well defined methylene protons between the two sulfur donors), and indicating that the complexes with the 'twisted' and 'squeezed' figure-of-eight loop geometries are kinetically inert on the NMR timescale. This indicates that metal-ion co-ordination is an important driving force for the ligand folding.



(*a*) (*b*)

Fig. 1 Crystal structure of (*a*) $[Cu_2L^1][ClO_4]_2\cdot 0.5MeCN\cdot 0.5H_2O$ **1** [two independent molecular cations with very similar structures in the unit cell, Cu(1), Cu(2) and Cu(3), Cu(4); the second is plotted] and (*b*) $[Cu_2L^2][ClO_4]_2\cdot MeCN$ **2** (SCHAKAL plot[10])

Table 2 Proton NMR data for the chelate ethylene bridges in the 'twisted' complex **1** and the 'squeezed' complex **2**

	1	**2**
δ	3.65 (d, 4 H)	3.61 (d, 4 H)
$^2J_{AX}$/Hz	10.1	10.0
δ	2.80 (d, 4 H)	2.77 (d, 4 H)
$^2J_{AX}$/Hz	10.2	10.0
$\Delta\nu$/Hz	257.3	253.1

UV/VIS spectroscopy and electrochemistry

The UV/VIS spectra of complexes **1** and **2** and similar double helical dicopper(I) compounds[7] are dominated by a transition around 350–380 nm with a moderately high intensity ($\varepsilon \approx 4000$ dm^3 mol^{-1} cm^{-1}), tentatively assigned to a metal-to-ligand charge-transfer (m.l.c.t.) transition, and signals between 200 and 300 nm with higher intensities ($\varepsilon \approx 50\,000$ dm^3 mol^{-1} cm^{-1}), tentatively assigned to intraligand transitions (the metal-free compounds have similar transitions in the UV region). The most significant differences between the solution spectra (MeCN) of **1** [λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 376 (4070), 271 (43 301) and 203 (58 713)] and **2** [345 (4183), 295 (sh) and 230 (62 440)] occur, as expected (different substitution patterns of the benzene spacer group), in the area of the intraligand transitions. Owing to the electronically similar donor set and the roughly identical co-ordination geometries of **1** and **2** (see Table 1), there is a significant but small shift of the charge-transfer transition (lower energy for the 'squeezed' ring compound **2**; 345 *vs.* 376 nm). The fact that the position of these m.l.c.t. transitions of **1** and **2** does not change much upon dissolution of the compounds (solid-state spectra λ_{max}/nm: **1**, 375; **2**, 355) supports the interpretation obtained from NMR spectroscopy (see above) that the folded structures are preserved in solution.

The electrochemical behaviour of complexes **1** and **2** is comparable to that of other double helical compounds with $(N_2S_2)_2$ donor sets.[5,7,8] The cyclic voltammogram of the helicate **1** shows a reversible oxidation wave due to copper(II), centred at +1.067 V *vs.* normal hydrogen electrode (NHE) ($\Delta E_p = 58$ mV; scan rate range 10–100 mV s^{-1}). Oxidation of the 'squeezed ring' dicopper(I) compound **2** is irreversible (quasi-reversible after addition of the ferrocene standard), with the oxidation wave centred around +1.18 V *vs.* NHE. The voltammograms indicate that, in both compounds, the two copper(I) centres each at a distance of *ca.* 8 Å behave independently, and this was expected from earlier studies.[5,6e,7,8] The soft donor sets and the tetrahedral co-ordination geometry stabilize the reduced form of the dinuclear complexes.

Experimental

General

1,8-Diamino-3,6-dithiaoctane was prepared as described.[14] The iso- and tere-phthalaldehyde are commercially available. The NMR spectra (CD_3NO_2) were obtained with a Bruker AS 200 instrument at 300 and 75.5 or 50.32 MHz for ^{1}H and ^{13}C, respectively, infrared spectra (KBr pellets) with a Perkin-Elmer 16PC FT-IR instrument and UV/VIS spectra with a Cary 1E (solutions) or 2300 (powders) instrument. Electrochemical measurements of 0.01 mmol dm^{-3} solutions of the complexes in $MeNO_2$, containing 0.1 mol dm^{-3} tetrabutylammonium perchlorate as electrolyte and ferrocene as internal standard (+0.44 V *vs.* NHE), were made with a BAS 100B system with a glassy carbon working electrode, a platinum auxiliary electrode and a Ag–$AgNO_3$ reference electrode. Mass spectra (3-nitrobenzyl alcohol matrix) were recorded with a Finnigan 8400 spectrometer. Elemental analyses were obtained from the microanalytical laboratory of the chemical institutes of the University of Heidelberg.

Syntheses

For the syntheses of the macrocycles L^1 and L^2 terephthalaldehyde (4.0 g, 30 mmol; dissolved in 500 cm^3 MeCN) or isophthalaldehyde (6.71 g, 50 mmol, dissolved in 250 cm^3 toluene) was added slowly (24 h) to a stirred solution of 1,8-diamino-3,6-dithiaoctane (5.4 g, 30 mmol, dissolved in 800 cm^3 MeCN; or 9.0 g, 50 mmol dissolved in 250 cm^3 toluene, respectively). The isolated white solids were recrystallized twice from $MeCN–CH_2Cl_2$ (1 : 1).

Compound L^1: yield 6.0 g (10.8 mmol, 71%) (Found: C, 57.95; H, 6.3; N, 9.85; S, 22.2. Calc. for $C_{28}H_{36}N_4S_4$: C, 58.5; H, 6.65; N, 9.75; S, 22.3). Positive-ion FAB mass spectrum: *m*/*z* 557 (M^+, 10%). NMR ($CDCl_3$): ^{1}H (300.1 MHz), δ 8.18 (s, 4 H, NCH), 7.74 (s, 8 H, aryl CH), 3.77 (t, 8 H, $^3J_{HH} = 6.6$, NCH_2), 2.83 (t, 8 H, $^3J_{HH} = 6.5$ Hz, NCH_2CH_2) and 2.74 (s, 8 H, SCH_2); ^{13}C (75.5 MHz), δ 33.1 (SCH_2), 33.3 (CH_2CH_2N), 62.7 (NCH_2), 128.5 (*o*-C of aryl), 138,0 (aryl *C*CHN) and 161.4 (NCH). IR (KBr): 1636s, [ν(C=N)].

Compound L^2: yield 6.7 g (12.05 mmol, 48%) (Found: C, 60.5; H, 6.35; N, 9.6; S, 23.55. Calc. for $C_{28}H_{36}N_4S_4$: C, 60.4; H, 6.5; N, 10.05; S, 23.05%). Positive-ion FAB mass spectrum: *m*/*z* 557 (M^+, 18%). NMR ($CDCl_3$): ^{1}H (300.1 MHz), δ 8.29 (s, 4 H, NCH), 8.02 [s, 2 H, aryl C(2)H], 7.77 [d, 4 H, $^3J_{HH} = 8.8$ aryl, C(4)H, C(6)H], 7.40 [t, 2 H, $^3J_{HH} = 7.6$, aryl C(5)H], 3.77 (t, 8 H, $^3J_{HH} = 6.2$ NCH_2), 2.83 (t, 8 H, $^3J_{HH} = 6.7$ Hz, NCH_2CH_2) and 2.77 (s, 8 H, SCH_2); ^{13}C (75.5 MHz) δ 32.60 (SCH_2), 32.97 (NCH_2CH_2), 61.59 (NCH_2), 128.7 [aryl C(5)], 128.97 [aryl C(4)], 130.15 [aryl C(2)], 136.42 [aryl C(1)] and 161.56 (NCH). IR (KBr): 1638s cm^{-1} [ν(C=N)].

Dry and degassed solvents were used for the syntheses of complexes **1** and **2** in an argon atmosphere. An excess of freshly prepared $[Cu(MeCN)_4]ClO_4$ in MeCN was added slowly to a stirred solution of L^1 or L^2 (200 mg, 0.36 mmol) in MeCN–CH_2Cl_2 (1 : 1. 200 cm^3). The yellow-orange (yellow) solution was filtered after 1 h and reduced to 50 cm^3 by evaporation of the solvent under reduced pressure to afford yellow-orange (yellow) crystalline solids. Recrystallization of the products from MeCN afforded suitable crystals for structure determinations.

Complex **1**: yield 190 mg (0.1 mmol, 60%) (Found: C, 38.15; H, 4.2; N, 6.55; S, 13.9. Calc. for $C_{28}H_{36}Cl_2Cu_2N_4O_8S_4\cdot0.5CH_3CN\cdot0.5H_2O$: C, 38.55; H, 3.85; N, 6.9; S, 14.05%). Positive-ion FAB mass spectrum: *m*/*z* 782 ($Cu_2LClO_4^+$, 100%). ^{1}H NMR (300.1 MHz, CD_3NO_2): δ 8.75 (s, 4 H, NCH), 7.63 (s, 8 H, aryl CH), 4.12 (td, 4 H, $^2J_{AX} = 14.0$, $^3J_{HH} = 4.0$, NCH_2), 4.05–3.97 (m, 4 H, NCH_2CH_2), 3.30 (td, 4 H, $^2J_{AX} = 14.2$, $^3J_{HH} = 3.4$, NCH_2, $\Delta\nu = 212.8$), 3.65 (d, 4 H, $^2J_{AX} = 10.1$, SCH_2) and 2.80 (d, 4 H, $^2J_{AX} = 10.2$ Hz, SCH_2, $\Delta\nu = 257.3$ Hz). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 33.2 (SCH_2), 34.4 (CH_2CH_2N), 59.2 (NCH_2), 129.1 (*o*-C of aryl), 138.4 (aryl *C*CHN) and 166.3 (NCH). IR (KBr): 1622s, [ν(C=N)] and 1088s (br) cm^{-1} [ν(Cl–O)].

Complex **2**: yield 126 mg (0.142 85 mmol, 40%) (Found: C, 37.8; H, 4.15; N, 6.25; S, 14.25. Calc. for $C_{28}H_{36}Cl_2Cu_2N_4O_8S_4$: C, 38.1; H, 4.1; N, 6.35; S, 14.55%). Positive-on FAB mass spectrum: *m*/*z* 783 ($Cu_2LClO_4^+$, 39), 683 (Cu_2L^+, 14) and 619 (CuL^+, 41%). NMR (CD_3NO_2): ^{1}H (300.1 MHz), δ 2.77 (d, 4 H, $^2J_{AX} = 10.0$, SCH_2), 3.01–3.27 (m, NCH_2, NCH_2CH_2), 3.61 (d, 4 H, $^2J_{AX} = 10.0$, SCH_2, $\Delta\nu = 253.1$ Hz), 3.93–4.11 (m, NCH_2, NCH_2CH_2), 7.01 [d, 4 H, $^3J_{HH} = 7.62$, aryl C(4)H + C(6)H], 7.21 [t, 2 H, $^3J_{HH} = 7.7$ Hz, aryl C(5)H], 8.08 [s, 2 H, aryl C(2)H] and 8.68 (s, 4 H, NCH); ^{13}C (50.3 MHz), δ 31.61 (SCH_2), 33.04 (CH_2CH_2N), 57.57 (NCH_2), 125.81 [aryl C(5)], 127.74 [aryl C(4)], 128.56 [aryl C(2)], 134.02 [aryl C(1)] and 164.09 (NCH). IR (KBr): 1090 (br) [ν(Cl–O)] and 1622s cm^{-1} [ν(C–N)].

Crystallography

Complex 1. *Crystal data.* $C_{29}H_{48.5}Cl_2Cu_2N_{4.5}O_{8.5}S_4$, $M = 912.23$, yellow-orange prismatic crystals, crystal dimensions 0.40 × 0.25 × 0.20 mm, monoclinic, space group $P2_1/c$, $a = 12.974(3)$, $b = 36.045(7)$, $c = 17.033(4)$ Å, $\beta = 106.99(2)°$, $U = 7604(2)$ Å^3, $Z = 8$, $D_c = 1.591$ g cm^{-3}, $F(000) = 3744$, $\mu = 51.36$ cm^{-1}, minimum, maximum relative transmission 0.655, 0.997, $N = 11\,622$, $N_{unique} = 10\,298$, $N_o = 4046$, ρ_{max} 1.10, ρ_{min} −0.51 e Å^{-3}.

Lattice parameters were measured at 21 °C on a Rigaku AFC7R four-circle diffractometer employing graphite-monochromated Cu-Kα radiation ($\lambda = 1.5418$ Å); ω–2θ scan ($1 < \theta < 60°$). Data reduction and application of Lorentz-polarization, absorption (empirical ψ scan) and decomposition corrections were carried out using the TEXSAN system;[14] the structure was solved by direct methods using SHELXS 86.[15] Hydrogen atoms were included at calculated sites with fixed isotropic thermal parameters. Full-matrix least-squares methods were used to refine 900 variables using 4046 reflections with $I > 2.5\sigma(I)$ and converged at $R = 0.084$ and $R' = 0.088$ $\{w^{-1} = \sigma^2(F), R' = [\Sigma w(|F_o|-|F_c|)^2/\Sigma wF_o^2]^{\frac{1}{2}}\}$. The *R* value is higher than desirable and the data to parameter ratio lower but, given the large size of the asymmetric unit (>1800) and the highly mobile perchlorate anions, they are the best that could be obtained.

Complex 2. *Crystal data.* $C_{28}H_{36}Cl_2Cu_2N_4O_8S_4$, $M = 923.75$, yellow plates (crystal dimensions 0.22 × 0.10 × 0.08 mm), triclinic, space group $P\bar{1}$, $a = 10.728(2)$, $b = 11.145(1)$, $c = 9.600(1)$ Å, $\alpha = 96.448(8)$, $\beta = 103.624(10)$, $\gamma = 63.907(8)°$, $U = 1010.8(2)$ Å^3, $Z = 1$, $D_c = 1.517$ g cm^{-3}, $F(000) = 474$, $\mu = 48.30$ cm^{-1}, minimum, maximum relative transmission 0.745–1.00, $N = 3175$, $N_{unique} = 2992$, $N_o = 2035$, ρ_{max} 0.44, ρ_{min} −0.32 e Å^{-3}.

Lattice parameters at 21 °C were determined by least-squares fits to setting parameters of 25 independent reflections, measured and refined on an AFC-7 four-circle diffractometer employing graphite-monochromated Cu-Kα radiation ($\lambda = 1.5418$ Å); ω–2θ scan ($1 < \theta < 60°$). Data reduction and correction, structure solution and treatment of H atoms were as above. Full-matrix least-squares methods were used to refine 260 variables using 2035 reflections with $I > 2.5\sigma(I)$ and converged at $R = 0.044$ and $R' = 0.047$ $\{w^{-1} = \sigma^2(F), R' = [\Sigma w(|F_o|-|F_c|)^2/\Sigma wF_o^2]^{\frac{1}{2}}\}$.

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997. Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/462.

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