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Silver(I) complexes with quinoline based linear multidentate ligands: self-assembly of sulfur-bridged tetrametallotricyclic boxes †

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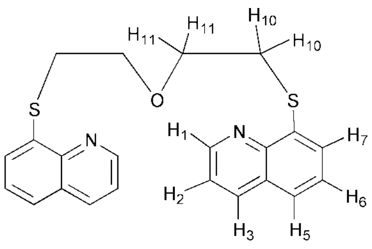
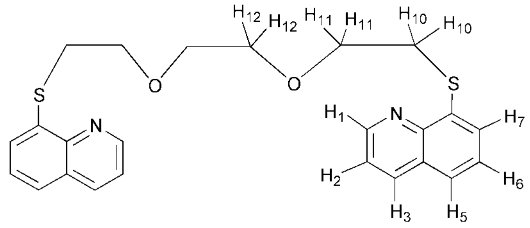
The flexible linear multidentate ligands 1,5-bis(8-quinolylsulfanyl)-3-oxapentane (OESQ) and 1,8-bis(8-quinolylsulfanyl)-3,6-dioxaoctane (ODSQ) reacted with silver(I) perchlorate affording the simple mononuclear complexes [Ag(OESQ)]ClO_4 **1** and [Ag(ODSQ)]ClO_4 **2**, respectively. However, with silver(I) nitrate, novel metallosupramolecular complexes $[Ag_4(ODSQ)_2(\eta^1\text{-}NO_3)_2(\eta^2\text{-}NO_3)_2]$ **3** and $[Ag_4(OESQ)(ODSQ)(\eta^1\text{-}NO_3)_2(\eta^2\text{-}NO_3)_2]\cdot H_2O$ **4** were obtained, in which the co-ordination motifs [Ag(OESQ)]$^+$ and [Ag(ODSQ)]$^+$ are spontaneously self-assembled by sulfur-bridged silver(I) ions into tetrametallotricyclic molecules containing the same or mixed building blocks. All four complexes have been characterized by elemental analyses, IR and ^{1}H NMR spectroscopy, and single crystal X-ray diffraction methods. The possible self-assembly process has been discussed with the aid of electrospray mass spectrometry.

Introduction

How to build metallosupramolecular species with novel molecular architectures through transition metal-directed self-assembly has received a great deal of attention in recent years,[1] and the co-ordination bond has been shown to be one of the most useful connectors in fabrication of these molecules due to the versatile geometrical modes (*e.g.* linear, trigonal, square planar, tetrahedral, octahedral) in bond formation. Often this involves the use of metal ions that have defined co-ordination numbers and stereochemical preferences, to encode the rational assembly of specific molecular architectures by recognition of the inherent properties of logically designed ligands.[1,2] However, this approach imposes natural restrictions on the architectures available, due to the limited range of angular motifs available from stereorigid metals. Thus, we pay attention to the study of the chemistry of metal ions that have less well defined co-ordination numbers and varied geometries with angular, tripodal or linear polydentate ligands.[3] This paper reports the syntheses and crystal structures of four new complexes, mononuclear [Ag(OESQ)]ClO_4 **1** and [Ag(ODSQ)]ClO_4 **2**, tetranuclear $[Ag_4(ODSQ)_2(\eta^1\text{-}NO_3)_2(\eta^2\text{-}NO_3)_2]$ **3** and $[Ag_4(OESQ)(ODSQ)(\eta^1\text{-}NO_3)_2(\eta^2\text{-}NO_3)_2]\cdot H_2O$ **4**, obtained from the reaction of silver(I) salts with linear ligands 1,5-bis(8-quinolylsulfanyl)-3-oxapentane (OESQ) and 1,8-bis(8-quinolylsulfanyl)-3,6-dioxaoctane (ODSQ).



OESQ



ODSQ

Experimental

Materials and methods

All starting materials were reagent grade obtained from commercial sources and used without further purification. The ligands OESQ and ODSQ were prepared according to previously described procedures.[4] The elemental analyses for C, H, N and S were carried out with a Varian EL elemental analyzer. The infrared spectra were recorded in the range 4000–400 cm^{-1} on a Fourier Nicolet 170 SX FT-IR spectrometer using KBr disks, ^{1}H NMR spectra on a Varian INOAN 500 instrument using $CDCl_3$ or DMSO-d_6 as solvent with TMS as internal standard at room temperature. Electrospray mass spectra (ES-MS) were recorded with a LCQ system (Finnigan MAT, USA). The samples were prepared by dissolving the silver(I) salts and the ligands in different molar ratios in 1 : 1 (v/v) methanol–acetonitrile to give *ca.* 10^{-5} M clear solutions. The spray voltage, capillary voltage and capillary temperature were set at 4.50 kV, 28.76 kV and 200 °C , respectively. The quoted *m*/*z* values represent the major peaks in the isotopic distribution.

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† Electronic supplementary information (ESI) available: electrospray mass spectra, two-dimensional layer structure of complex **4**. See http://www.rsc.org/suppdata/dt/b0/b001723j/

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Preparations

[Ag(OESQ)]ClO$_4$ 1. To a solution of OESQ (78 mg, 2 mmol) in acetonitrile (2 ml) was slowly added a solution of silver(I) perchlorate (41 mg, 2 mmol) in acetonitrile (2 ml) at room temperature. After filtration of the reaction mixture, diethyl ether was allowed to diffuse slowly into the filtrate to give colorless crystals suitable for X-ray analysis. Yield: *ca.* 60%. Found: C 43.79; H 3.17; N 4.60; S 10.56. Calc. for $C_{22}H_{20}AgClN_2O_5S_2$: C 44.15; H 3.37; N 4.68; S 10.69%. *m*/*z* (ES-MS$^+$) 501, [AgOESQ]$^+$; 455, [OESQ + 2MeOH − H]$^+$. ν_{max} (KBr) 3057, 2931, 2860, 1595, 1560, 1489, 1454, 1363, 1300, 1096s, 983, 821, 786 and 632 cm^{-1}.

[Ag(ODSQ)]ClO$_4$ 2. To a solution of ODSQ (87 mg, 2 mmol) in acetonitrile (2 ml) was slowly added a solution of silver(I) perchlorate (41 mg, 2 mmol) in acetonitrile (2 ml) at room temperature to give a clear solution. The complex was crystallized by slow diffusion of diethyl ether vapor into the reaction mixture. X-Ray quality colorless crystals formed in *ca.* 70% yield. Found: C 44.71; H 3.47; N 4.46; S 9.75. Calc. for $C_{24}H_{24}AgClN_2O_6S_2$: C 44.86; H 3.77; N 4.36; S 9.96%. *m*/*z* (ES-MS$^+$) 545, [AgODSQ]$^+$; 499, [ODSQ + 2MeOH − H]$^+$. ν_{max} (KBr) 3055, 2918, 2864, 1597, 1558, 1491, 1457, 1359, 1300, 1115s, 985, 824, 789 and 630 cm^{-1}.

[Ag$_4$(ODSQ)$_2$(η^1-NO$_3$)$_2$(η^2-NO$_3$)$_2$] 3. To 2 ml of methanol–acetonitrile (1 : 1, v/v) solution with 68 mg of silver nitrate (0.4 mmol) was added a solution of ODSQ (87 mg, 0.2 mmol) in $CHCl_3$ (2 ml) at room temperature. After filtration, slow diffusion of diethyl ether vapor into the filtrate for several days afforded colorless X-ray quality crystals in *ca.* 85% yield. Found: C 36.94; H 3.49; N 7.26; S 8.24. Calc. for $C_{12}H_{12}AgN_2SO_4$: C 37.21; H 3.12; N 7.24; S 8.26%. *m*/*z* (ES-MS$^+$) 545, [AgODSQ]$^+$; 499, [ODSQ + 2MeOH − H]$^+$. ν_{max} (KBr) 3050, 2917, 2860, 1595, 1560, 1496, 1433s, 1384s, 1293s, 1110, 983, 821, 786 and 660 cm^{-1}.

[Ag$_4$(OESQ)(ODSQ)(η^1-NO$_3$)$_2$(η^2-NO$_3$)$_2$]·H$_2$O 4. To 2 ml of a mixture of OESQ (39 mg, 0.1 mmol) and ODQS (44 mg, 0.1 mmol) in $CHCl_3$ was slowly added 2 ml of 1 : 1 methanol–acetonitrile (v/v) solution containing 68 mg silver nitrate (0.4 mmol). The resulting solution was filtered. After slow diffusion of diethyl ether vapor for several days, colorless X-ray quality crystals were obtained in *ca.* 80%. Found: C 35.86; H 3.41; N 7.03; S 7.65. Calc. for $C_{23}H_{23}Ag_2N_4O_8S_2$: C 36.27; H 3.05; N 7.36; S 8.04%. *m*/*z* (ES-MS$^+$) 545, [AgODSQ]$^+$; 455, [OESQ + 2MeOH − H]$^+$; 499, [ODSQ + 2MeOH − H]$^+$. ν_{max} (KBr) 3064, 2931, 2860, 1588, 1560, 1489, 1454s, 1384s, 1307s, 983, 828, 786 and 625 cm^{-1}.

X-Ray crystallographic studies

The diffraction intensities of complexes **1**, **2** and **4** were collected (hemisphere technique) on a Bruker SMART 1K diffractometer with a CCD area detector. Absorption corrections were performed using the SADABS program.[5a] Data collection for **3** was performed on a Siemens R3m four-circle diffractometer. An empirical absorption correction based on psi scans of several reflections was applied. All the structures were solved by direct methods and refined by full-matrix least squares against F^2 of all data using SHELXTL software.[5b] Anisotropic thermal factors were assigned to most of the non-hydrogen atoms with the exceptions of the perchlorate anion in **1** and the water molecule in **4**. The hydrogen atoms were included in the calculations isotropically but not refined. Both the perchlorate anions in **1** and **2** are axially disordered about one Cl–O bond. The site occupancy factors (s.o.f.s) of the disordered oxygen atoms in **1** were refined by setting the free variable as 0.6 for O(11), O(12) and O(13), and 0.4 for O(11)′, O(12)′ and O(13)′. The disordered oxygen atoms in **2** were anisotropically refined with half occupancy. The water molecule in **4** was disordered over two 2-fold symmetry-related positions and refined isotropically with the fractional site occupancy factor of 0.5. The final Fourier difference map revealed that a couple of peaks had height of 1.42 e Å^{-3} lying close to the silver(I) ions. A summary of parameters for the data collections and refinements is given in Table 2.

CCDC reference number 186/1970.

See http://www.rsc.org/suppdata/dt/b0/b001723j/ for crystallographic files in .cif format.

Results and discussion

Syntheses and spectroscopy

The compounds OESQ and ODSQ are flexible linear ligands containing soft backbones $CH_2(CH_2OCH_2)_nCH_2$ ($n = 1$, OESQ; $n = 2$, ODSQ) and rigid 8-sulfanylquinoline as terminal chelating groups. The mixed donor set OSN enables the compounds to behave as multidentate ligands which show versatile co-ordination modes towards transition metal ions. Mononuclear complexes will be formed when the ligands wrap around one metal ion,[4c] while dinuclear or polynuclear complexes will be afforded if they bridge two metal ions with each sulfanylquinoline group chelating with an individual metal ion.[4b,6] In addition, the thioether sulfur atom is a potential bridging donor[3c] which makes it possible to aggregate simple complexes into large molecules by careful selection of metal ions and counter anions.[7] These considerations prompted us to investigate the co-ordination behaviour of the ligands OESQ and ODSQ with silver(I) ions.

Silver(I) perchlorate was first selected with the purpose to construct polymeric structures.[6] However, simple mononuclear complexes [Ag(OESQ)]ClO$_4$ **1** and [Ag(ODSQ)]ClO$_4$ **2** were isolated whether the ligands react with silver(I) perchlorate in 1 : 1 or 1 : 2 molar ratio. The compositions of **1** and **2** were deduced from elemental analyses and their molecular structures confirmed by X-ray crystallography. This finding suggests that the ligands incline to chelate one metal ion without additional auxiliary forces. Accordingly, silver(I) nitrate was used considering the stronger co-ordination ability of the nitrate anion. It is interesting that the reaction of ODSQ with silver(I) nitrate in 1 : 2 molar ratio afforded a unprecedented tetranuclear complex [Ag$_2$(ODSQ)(NO$_3$)$_2$]$_2$ **3**. The molecule can be seen as two [Ag(ODSQ)]$^+$ co-ordination motifs similar to that in **2** assembled by two Ag(NO$_3$)$_2^-$ through sulfur atom bridging, suggesting that large metallosupramolecular complexes could be aggregated by utilization of these electron rich bridging sulfur atoms. Interestingly, a mixture of silver(I) nitrate with equimolar OESQ–ODSQ in 2 : 1 molar ratio also afforded a closely similar tetranuclear complex [Ag$_4$(OESQ)(ODSQ)(NO$_3$)$_4$]·H$_2$O **4**. The elemental analysis is in good agreement with the structure, and the X-ray analysis unambiguously certifies the result, confirming the assumption that both building blocks [Ag(OESQ)]$^+$ and [Ag(ODSQ)]$^+$ are present in solution. The attempt to assemble tetranuclear complexes with OESQ alone was not successful due to the greater constraint of a shorter $CH_2CH_2OCH_2CH_2$ backbone as will be discussed below. The ligand ODSQ reacted with silver(I) nitrate in 1 : 1 molar ratio giving only a crystalline precipitate which was not suitable for X-ray single crystal analysis to clarify its structure, although the ES-MS spectrum indicated the formation of a mononuclear [Ag(ODSQ)]$^+$ cation (*m*/*z* 543) in mixed methanol–acetonitrile solution.

^{1}H NMR spectra of the ligands OESQ, ODSQ and the complexes **1**–**4** were recorded at room temperature. The co-ordination of OESQ and ODSQ to silver(I) ion results in a set of well resolved proton signals relative to those of the "free" ligands as exemplified by ODSQ and its complexes **2** and **3** shown in Fig. 1. The chemical shifts and coupling constants are

Table 1 ^{1}H NMR spectroscopic data[a] for OESQ, ODSQ and complexes **1**–**4**

Compounds	H^1	H^2	H^3	H^5	H^6	H^7	H^{10}	H^{11}	H^{12}	$^2J(H^1H^2)$	$^3J(H^1H^3)$	$^2J(H^2H^3)$	$^2J(H^5H^6)$	$^3J(H^5H^7)$	$^2J(H^6H^7)$	$^2J(H^{10}H^{11})$
OESQ	8.96	7.45	8.15	7.60	7.48	7.56	3.31	3.85	—	4.0	1.5	8.0	8.0	1.0	7.5	7.0
ODSQ	8.96	7.44	8.14	7.59	7.47	7.57	3.32	3.83	3.67	4.0	1.5	8.0	8.0	1.0	7.5	7.0
1	9.05	7.76	8.65	8.13	7.77	8.26	3.41	3.55	—	4.5	1.5	8.0	8.0	1.0	7.5	5.0
2	8.90	7.73	8.63	8.19	7.78	8.36	3.36	3.48	3.43	4.3	1.5	8.3	8.0	1.0	7.5	5.0
3	9.00	7.85	8.71	8.33	7.89	8.53	3.36	3.58	3.46	4.3	1.5	8.3	8.0	[b]	7.5	5.0
4(OESQ)	9.11	7.77[c]	8.71	8.21	7.82[c]	8.37	3.29[c]	3.51[c]	—	4.5	1.3	8.0	8.1	[b]	7.4	5.0
4(ODSQ)	8.92	7.77[c]	8.68	8.25	7.82[c]	8.44	3.29[c]	3.51[c]	3.40	4.3	1.2	8.0	8.1	[b]	7.3	5.0

[a] Spectra were measured in $CDCl_3$ for OESQ and ODSQ, in DMSO-d_6 for **1**–**4**, with the chemical shifts in ppm and coupling constants *J* in Hz, ^2J for 1,2-positioned protons and ^3J for 1,3. [b] Not observed. [c] Overlapped.

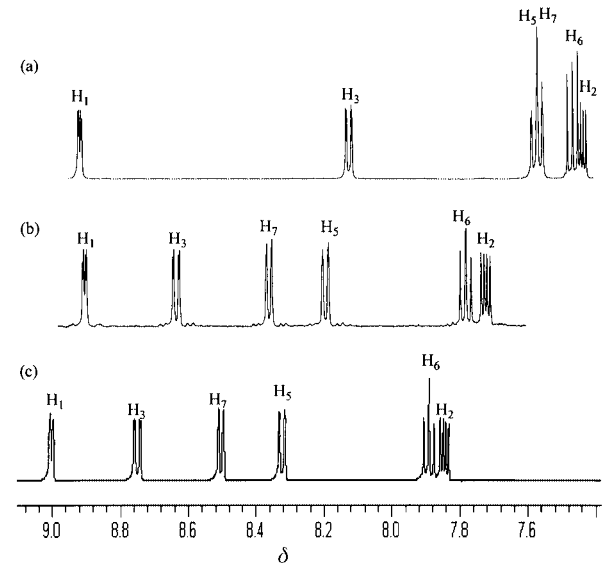


Fig. 1 Partial ^{1}H NMR spectra of the ligand ODSQ in $CDCl_3$ (*a*), complex **2** in DMSO-d_6 (*b*) and complex **3** in DMSO-d_6 (*c*).

given in Table 1. Coupling constants ^2J and ^3J in the ranges 4–8 and 1–1.5 Hz conform to the normal values for *ortho* and *meta* protons,[8] respectively. In general, the protons of the quinoline rings show a significant downfield shift for the complexes as compared with those of the "free" ligands with the exception of H^1. The largest change is found for H^7 ($\Delta\delta = 7$–10 ppm) as a consequence of adjacency to the sulfur atom bonded to the silver(I) ion. The *para* protons H^3 and H^5 also shifted downfield by 5–7 ppm, while the *meta* protons H^2 and H^6 shifted downfield by 3–4 ppm. So the signal of H^7 appears in a lower field region than H^5 in all complexes, contrary to that of the "free" ligand. Protons H^5 and H^7 are well resolved for the complexes, while for the "free" ligand they are partially merged. What is unusual is the *ortho* proton H^1 to the quinoline nitrogen atom; it shows slight change after co-ordination of the nitrogen atom to the silver(I) ion. For complex **4** two sets of aromatic protons can be distinguished corresponding to the two ligands OESQ and ODSQ although some of the peaks are overlapped. The protons in the $CH_2(CH_2OCH_2)_nCH_2$ backbone show various changes of less than 3.5 ppm.

Electrospray mass spectrometry (ES-MS) was employed to investigate the solution speciation of the reaction of the ligands with either silver(I) perchlorate or nitrate in various molar ratios. Samples were prepared in dry 1 : 1 MeOH–MeCN (v/v) by mixing measured amounts of the ligand and the silver(I) salt, and selected spectra are available as Electronic Supplementary Information. With silver(I) perchlorate and ODSQ a base peak at *m*/*z* 545.2 corresponding to $[Ag(ODSQ)]^+$ was observed, together with a peak at *m*/*z* 499.1 attributed to $[ODSQ + 2MeOH - H]^+$.[9] This spectral pattern remains unchanged for metal to ligand ratios up to 3 : 1. The spectrum with OESQ resembles that with ODSQ, suggesting the formation of mononuclear complexes in both cases even in the presence of an excess of silver(I) perchlorate. With silver(I) nitrate these two peaks are still dominant in the reaction mixture of ODSQ but with the relative abundance reversed. Since **3** is electrically neutral, the expected ionization pathways would reasonably be expected to be the loss of nitrate anions. However, no remarkable polynuclear species was observed, suggesting that the tetranuclear molecule is not present at low concentration ($\approx 10^{-5}$ M), or could not be detected under the present experimental conditions. Anyway, the existence of the $[Ag(ODSQ)]^+$ co-ordination motif, however small the peak is in the ES-MS spectra, indicates that it can serve as a building block to construct tetranuclear structures. This is evidenced by ES-MS investigation of the reaction of silver(I) nitrate with OESQ. The reaction mixture at 1 : 1 metal to ligand ratio showed a base peak at *m*/*z* 455.3 corresponding to $[OESQ + 2MeOH - H]^+$, and a somewhat small peak at *m*/*z* 501 due to $[Ag(OESQ)]^+$ cation, indicating the formation of $[Ag(OESQ)]^+$ building blocks. However, the 2 : 1 mixture afforded the remarkable solvated species but no other significant peaks. This observation indicates that the reaction of silver(I) nitrate with OESQ in no less than 2 : 1 ratio may result in a complex with entirely different structure whose preliminary X-ray analysis revealed a trinuclear framework deviating from the topology discussed in this paper.[10] It is unexpected to find no peak of $[Ag(OESQ)]^+$ in this 2 : 1 mixture though the peaks of mononuclear species are always small and those of polynuclear species never appear as discussed above in either 1 : 1 $AgNO_3$–OESQ or 1 : 1 and 2 : 1 $AgNO_3$–ODSQ reaction mixtures. Anyway, since the peak of $[Ag(OESQ)]^+$ is evidently present in the arbitrary ratio (1 : 1 up to 3 : 1) $AgClO_4$–OESQ and in 1 : 1 $AgNO_3$–OESQ reaction mixtures it is rational to assume that the $[Ag(OESQ)]^+$ cation should be initially produced even in a 2 : 1 $AgNO_3$–OESQ mixture to act as building block to form the final thermodynamically stable polynuclear complexes whose ES-MS spectrum may not reveal significant mono- and poly-nuclear species as discussed above. The spectrum of the reaction mixture of 2 : 1 : 1 $AgNO_3$–OESQ–ODSQ displays three peaks, a base peak at *m*/*z* 499.3 corresponding to the major species $[ODSQ + 2MeOH - H]^+$, a relatively smaller peak at *m*/*z* 455.3 for $[OESQ + 2MeOH - H]^+$, and another peak at *m*/*z* 545.1 resulting from the cation $[Ag(ODSQ)]^+$ in agreement with the previous assignments. Unfortunately the strong parent peak of $[ODSQ + 2MeOH - H]^+$ with 1 dalton separated isotopic distribution patterns makes it impossible to distinguish the possible low abundance peak of $[Ag(OESQ)]^+$ cation from the spectrum. Nonetheless, although no polynuclear species was observed as in 2 : 1 $AgNO_3$–OESQ and $AgNO_3$–ODSQ reaction mixtures discussed above, the construction of a tetranuclear molecule utilizing the present building blocks is possible, and is confirmed by the structural analyses discussed below.

Structural results

The X-ray structural analyses revealed that complexes **1** and **2** are mononuclear with discrete cations $[Ag(OESQ)]^+$ for **1**,

Table 2 Crystallographic data for complexes **1**–**4**

	1	**2**	**3**	**4**
Formula	$C_{22}H_{20}AgClN_2O_5S_2$	$C_{24}H_{24}AgClN_2O_6S_2$	$C_{48}H_{48}Ag_4N_8O_{16}S_4$	$C_{46}H_{46}Ag_4N_8O_{16}S_4$
Formula weight	599.84	643.89	1552.66	1526.63
Crystal system	Triclinic	Triclinic	Orthorhombic	Orthorhombic
Space group	$P\bar{1}$	$P\bar{1}$	*Pcab*	*Pbcn*
a/Å	10.618(2)	9.088(1)	14.981(4)	17.211(3)
b/Å	11.047(2)	11.064(1)	16.923(4)	14.572(3)
c/Å	11.621(2)	14.898(2)	21.999(7)	21.810(4)
α/°	69.48(3)	92.90(1)		
β/°	68.38(3)	105.69(2)		
γ/°	72.25(3)	113.98(2)		
V/Å^3	1162.4(4)	1295.6(3)	5577(3)	5469.9(18)
Z	2	2	4	4
μ/mm^{-1}	1.199	1.085	1.608	1.638
T/K	293(2)	293(2)	293(2)	293(2)
No. unique reflections	3323	5511	5458	6266
No. observed reflections [$I > 2\sigma(I)$]	2716	4848	3331	2426
R	0.0439	0.0310	0.0506	0.0620
wR	0.1231	0.0831	0.1033	0.1868

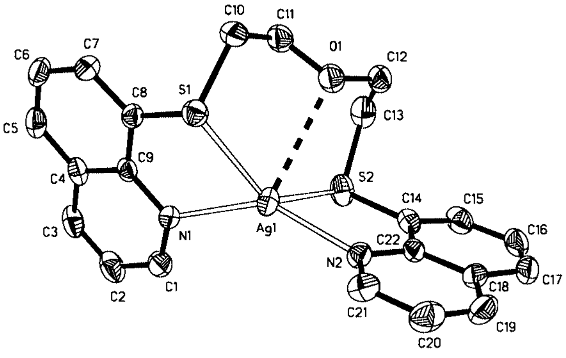


Fig. 2 Cationic structure of complex **1** with thermal ellipsoids drawn at 30% probability level. Hydrogen atoms are omitted for clarity.

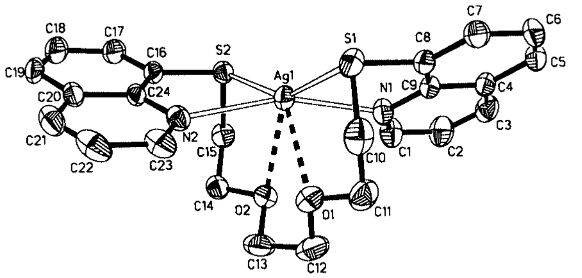


Fig. 3 Cationic structure of complex **2**. Details as in Fig. 2.

$[Ag(ODSQ)]^+$ for **2**, and counter anion ClO_4^-. Figs. 2 and 3 show the cations, with the atomic numbering schemes. The silver(I) ion in both complexes is four-co-ordinated by the two quinoline nitrogen atoms and the two thioether sulfur atoms from the ligands. The co-ordination geometry of Ag^I in **1** may be described as a strongly distorted tetrahedron and that in **2** a tetrahedrally distorted square plane. The difference comes from the N–Ag–N and S–Ag–S angles. In **1** they are 143.25(15) and 131.49(16)°, in **2** 161.95(9) and 149.23°, respectively (Table 3). The distortion caused by restriction of the bidentate chelation in the bite angle N–Ag–S is nearly the same (average 76.39° for **1** and 75.22° for **2**). The Ag–N bond distances of **1** (2.263(4) and 2.312(4) Å) are shorter than those of **2** (2.444(2) and 2.512(2) Å). On the contrary, the Ag–S bond distances of **1** (2.6163(17) and 2.6747(18) Å) are longer than those of **2** (2.5412(8) and 2.5595(8) Å). This change is easily understood taking into account the different lengths of the polyethylene glycol fragments in OESQ and ODSQ. In both complexes the flexible $SCH_2CH_2OCH_2CH_2S$ and $SCH_2(CH_2OCH_2)_2CH_2S$ chains wrap around the central ions. The triethylene glycol fragment in **2** is long enough to co-ordinate the silver(I) ion without much strain, resulting in a larger S–Ag–S angle with the Ag directed inward, while the shorter diethylene glycol fragment in **1** only spans above the ion with a restricted small S–Ag–S angle. This difference also results in different dihedral angles (**1** 77.4 and **2** 54.2°) between the two coplanar quinoline rings, which would be critical for the assembly of tetranuclear complexes discussed below. The distances between the ether oxygen atom and the silver(I) ion are 2.881(4) Å for **1** and 2.646(2) and 2.752(2) Å for **2**, indicating the existence of ether oxygen–silver interactions.[11]

Table 3 Selected bond distances (Å) and angles (°) for complexes **1** and **2**

	2	**1**
Ag(1)–N(1)	2.444(2)	2.312(4)
Ag(1)–N(2)	2.512(2)	2.263(4)
Ag(1)–S(2)	2.5412(8)	2.6747(18)
Ag(1)–S(1)	2.5595(8)	2.6163(17)
Ag(1)–O(1)	2.646(2)	2.881(4)
Ag(1)–O(2)	2.752(2)	
N(1)–Ag(1)–N(2)	161.95(9)	143.25(15)
N(1)–Ag(1)–S(2)	110.10(6)	107.85(11)
N(2)–Ag(1)–S(2)	74.67(6)	76.86(11)
N(1)–Ag(1)–S(1)	75.77(6)	75.91(11)
N(2)–Ag(1)–S(1)	109.44(6)	129.08(11)
S(2)–Ag(1)–S(1)	149.23(3)	131.49(6)
N(1)–Ag(1)–O(1)	81.00(8)	124.11(13)
N(2)–Ag(1)–O(1)	83.85(8)	92.16(13)
S(2)–Ag(1)–O(1)	135.83(6)	70.01(9)
S(1)–Ag(1)–O(1)	74.32(6)	69.03(9)
N(1)–Ag(1)–O(2)	83.54(7)	
N(2)–Ag(1)–O(2)	81.02(7)	
S(2)–Ag(1)–O(2)	74.68(5)	
S(1)–Ag(1)–O(2)	135.78(5)	
O(1)–Ag(1)–O(2)	64.01(7)	

Complex **3** can be considered as a dimer of $[Ag_2(ODSQ)(\eta^1\text{-}NO_3)(\eta^2\text{-}NO_3)]$ (Fig. 4(*a*)) related by a crystallographically imposed inversion lying in the center of the tetranuclear molecule. In each dinuclear moiety there are two co-ordination geometries for the silver atoms: a square planar Ag(1) co-ordinated to the two quinoline nitrogen atoms and the two thioether sulfur atoms of the same ODSQ ligand and a square pyramidal Ag(2) co-ordinated to two thioether sulfur atoms of two different ODSQ and three oxygen atoms of two nitrate groups one of η^1 and the other of η^2 co-ordination. Thus, each sulfur atom acts as a bridge to assemble the dinuclear monomer into a tetranuclear dimer as shown in Fig. 4(*b*). The crystal

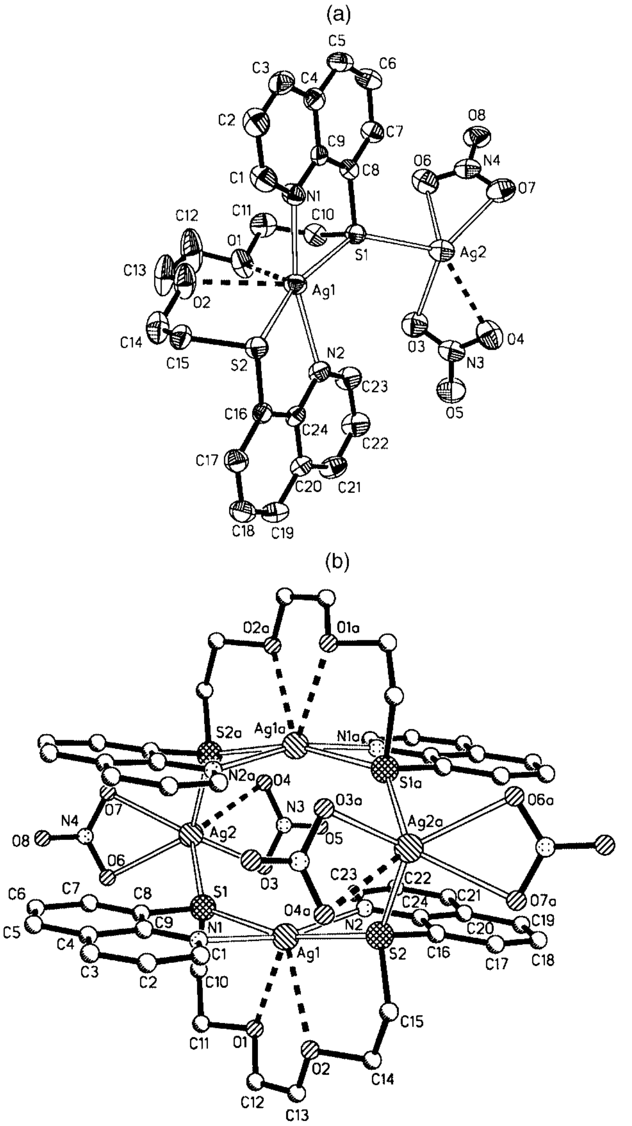


Fig. 4 Molecular geometry of complex **3** with the atomic numbering scheme. (*a*) Asymmetric monomer of $[Ag_2(ODSQ)(NO_3)_2]$. (*b*) Inversion related tetranuclear molecule emphasizing the co-ordination environments of the silver(I) ions. Hydrogen atoms are omitted for clarity.

structure of **4** consists of a lattice water molecule and a discrete neutral tetranuclear $[Ag_4(OESQ)(ODSQ)(\eta^1\text{-}NO_3)_2(\eta^2\text{-}NO_3)_2]$ molecule which is composed of ten components: two flexible linear ligands OESQ, ODSQ, four silver(I) ions and four NO_3^- anions with a similar topology to that of **3**. There is a crystallographically imposed twofold symmetry axis passing through O(2), the center of bond C(12)–C(12a), Ag(1) and Ag(2), so that the asymmetric unit contains only half of a tetranuclear molecule. From Fig. 5(*b*) it may be seen that ligands OESQ and ODSQ exhibit similar co-ordination modes with the quinoline nitrogen atoms and the thioether sulfur atoms of each chelating one silver(I) ion, giving two cymbal-like $[Ag(OESQ)]^+$ and $[Ag(ODSQ)]^+$ motifs closely resembling the cations in **1** and **2**, respectively. The sulfur atoms further co-ordinate to another silver(I) atom whose co-ordination sphere is filled as that in complex **3**. Thus, two $[Ag(NO_3)_2]^-$ co-ordination motifs bridge $[Ag(OESQ)]^+$ and $[Ag(ODSQ)]^+$ to result in a neutral hybrid tetranuclear molecule. The four silver(I) ions also show two kinds of co-ordination: a tetrahedrally distorted square planar one co-ordinated by a N_2S_2 donor set from OESQ (or ODSQ) and a square pyramidal one similar to that in **3**. It is obvious that the two bridging silver(I) ions in **3** and **4** have the same co-ordination geometry while the two chelated ions show slight differences which can be seen from the S–Ag–S and N–Ag–N angles: 164.39(6) and 165.00(19)° in **3** and 158.48(7) and 172.08(17)° in **4**, respectively (Tables 4 and 5). The Ag–N bond distances (2.308(5), 2.336(5) Å in **3** and 2.297(3) and 2.351(3) Å in **4**) are slightly longer than those in the pyridyl complexes (2.135–2.218 Å).[3b,c,11] The Ag–S bond distances range from 2.5739(17) to 2.7354(17) Å showing significant diversification due to the bridging co-ordination in **3** and **4**. Compared with the non-bridging in **1** and **2** this bridging results in a slight elongation of the Ag–S bonds which also are longer than those in silver(I) complexes of chelating

Table 4 Selected bond distances (Å) and angles (°) for complex **3**

Ag(1)–N(1)	2.308(5)	Ag(1)–O(1)	2.678(6)
Ag(1)–N(2)	2.336(5)	Ag(1)–O(2)	2.764(6)
Ag(1)–S(2)	2.6757(17)	Ag(2)–O(3)	2.396(6)
Ag(1)–S(1)	2.7071(17)	Ag(2)–O(4)	2.678(6)
Ag(2)–S(2a)	2.5739(17)	Ag(2)–O(6)	2.473(6)
Ag(2)–S(1)	2.7354(17)	Ag(2)–O(7)	2.558(6)
N(1)–Ag(1)–N(2)	165.00(19)	O(3)–Ag(2)–O(7)	125.82(18)
N(1)–Ag(1)–S(2)	107.38(12)	O(6)–Ag(2)–O(7)	50.7(2)
N(2)–Ag(1)–S(2)	73.76(12)	O(3)–Ag(2)–S(2a)	116.88(15)
N(1)–Ag(1)–S(1)	75.21(12)	O(6)–Ag(2)–S(2a)	131.28(14)
N(2)–Ag(1)–S(1)	99.72(12)	O(7)–Ag(2)–S(2a)	94.40(14)
S(2)–Ag(1)–S(1)	164.39(6)	O(3)–Ag(2)–S(1)	96.13(15)
O(3)–Ag(2)–O(6)	111.55(19)		

Symmetry transformation used to generate equivalent atoms: a $-x + 2, -y, -z$.

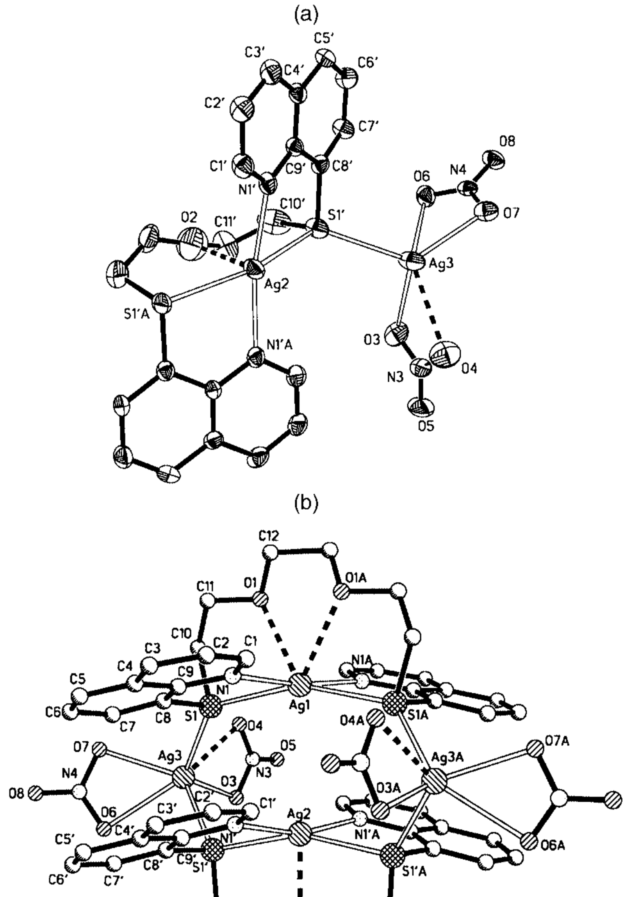


Fig. 5 Molecular geometry of complex **4** with the atomic numbering scheme. (*a*) Monomer containing OESQ ligand $[Ag_2(OESQ)(NO_3)_2]$. (*b*) Twofold axis related tetranuclear molecule emphasizing the co-ordination environments of the silver(I) ions. Hydrogen atoms are omitted for clarity.

Table 5 Selected bond distances (Å) and angles (°) for complex **4**

Ag(1)–N(1)	2.351(3)	Ag(1)–O(1)	2.685(3)
Ag(2)–N(1′)	2.297(3)	Ag(2)–O(2)	2.685(5)
Ag(1)–S(1)	2.6807(12)	Ag(3)–O(3)	2.392(4)
Ag(2)–S(1′)	2.6157(13)	Ag(3)–O(4)	2.648(5)
Ag(3)–S(1)	2.6574(14)	Ag(3)–O(6)	2.595(4)
Ag(3)–S(1′)	2.6856(16)	Ag(3)–O(7)	2.457(4)
N(1)–Ag(1)–N(1a)	172.08(17)	S(1′)–Ag(2)–S(1′a)	159.32(8)
N(1)–Ag(1)–S(1)	75.11(8)	O(3)–Ag(3)–O(7)	120.04(13)
N(1a)–Ag(1)–S(1)	106.43(8)	O(3)–Ag(3)–O(6)	105.24(12)
N(1)–Ag(1)–S(1a)	106.43(8)	O(7)–Ag(3)–O(6)	50.06(12)
N(1a)–Ag(1)–S(1a)	75.11(8)	O(3)–Ag(3)–S(1)	120.37(10)
S(1)–Ag(1)–S(1a)	158.48(7)	O(7)–Ag(3)–S(1)	99.82(9)
N(1′)–Ag(2)–N(1′a)	164.35(18)	O(6)–Ag(3)–S(1)	134.29(8)
N(1′)–Ag(2)–S(1′)	76.15(9)	O(3)–Ag(3)–S(1′)	98.65(10)
N(1′a)–Ag(2)–S(1′)	106.76(9)	O(7)–Ag(3)–S(1′)	127.54(9)
N(1′)–Ag(2)–S(1′a)	106.76(9)	O(6)–Ag(3)–S(1′)	88.49(8)
N(1′a)–Ag(2)–S(1′a)	76.15(9)		

Symmetry transformation used to generate equivalent atoms: a $-x$, y, $-z + \frac{1}{2}$.

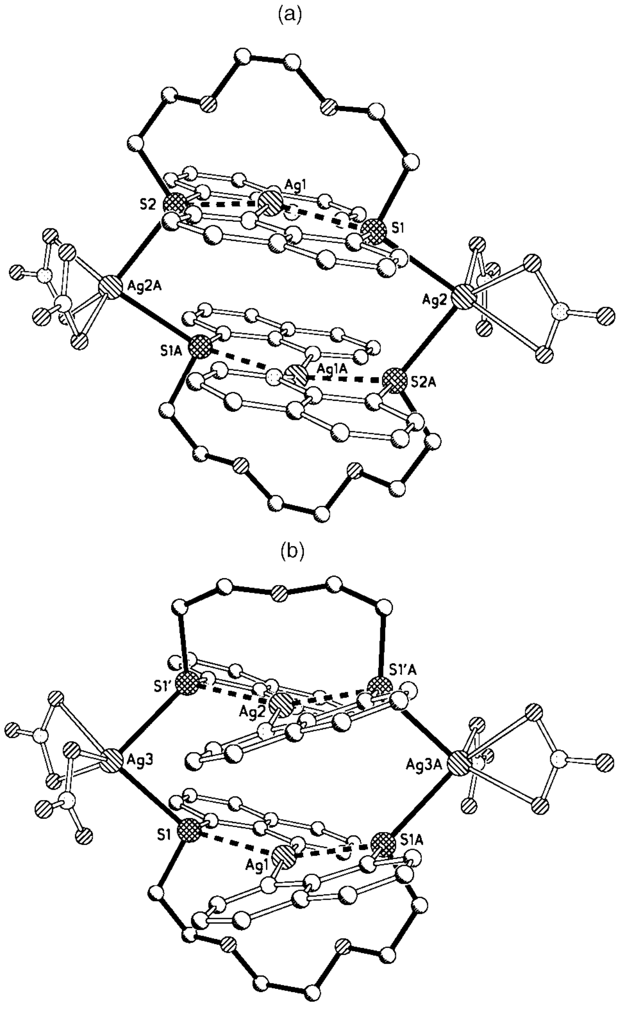


Fig. 6 Top view of the box-like [Ag$_4$(ODSQ)$_2$(NO$_3$)$_4$] **3** (*a*) and [Ag$_4$(OESQ)(ODSQ)(NO$_3$)$_4$] **4** (*b*) showing metallotricyclic rings and distortion of the box in **4**.

MPTQ (8-((2-pyridylmethyl)sulfanyl)quinoline) ligand (2.5481–2.5496 Å),[3c] but fall well within the Ag–S bond distance range found in other sulfur donor silver(I) complexes.[12] The Ag–O bond distances in **3** and **4** are essentially the same showing unremarkable features and resemble those in other anion co-ordinated complexes.[3b,c,11] There are a number of Ag···O interactions: Ag(1)···O(1) 2.678(6), Ag(1)···O(2) 2.764(6) and Ag(2)···O(4) 2.687(7) Å in **3** and Ag(1)···O(1) 2.685(3), Ag(2)···O(4) 2.685(5) and Ag(3)···O(4) 2.648(5) Å in **4**, exhibiting flexibility of the silver(I) co-ordination environments.

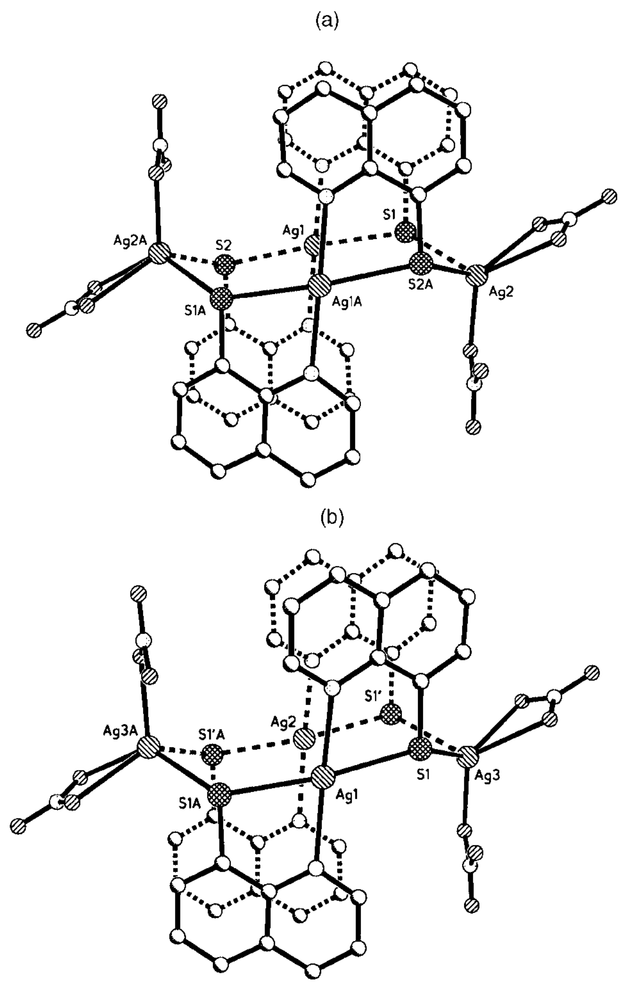
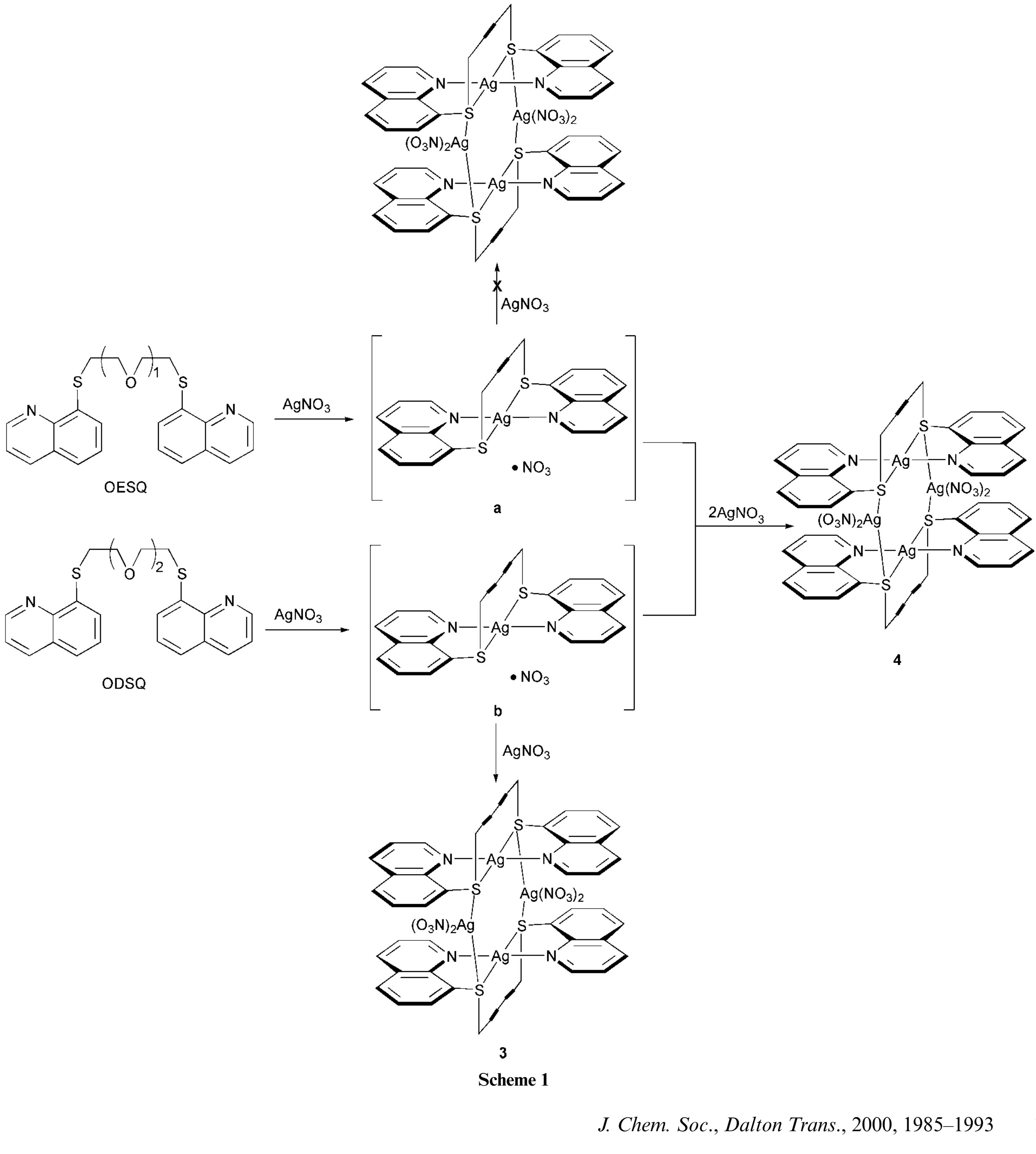


Fig. 7 Side view of the box-like [Ag$_4$(ODSQ)$_2$(NO$_3$)$_4$] **3** (*a*) and [Ag$_4$(OESQ)(ODSQ)(NO$_3$)$_4$] **4** (*b*) showing the chair-like central ring Ag$_4$S$_4$. The polyethylene glycol backbones are omitted for clarity.

Noteworthily, the molecules in complexes **3** and **4** can be considered as tetrametallotricyclic boxes consisting of two cymbal-like Ag(ODSQ) (or Ag(OESQ)) moieties with the fragments CH$_2$(CH$_2$OCH$_2$)$_n$CH$_2$ as the handles and the two cymbals (quinoline rings) as two opposite faces, which are bridged by the two five-co-ordinated Ag(NO$_3$)$_2^-$ species as the other two faces of the box. Thus a large metallomacrocycle is formed in which the four quinoline rings stand face-to-face in pairs to form the box with approximate dimensions 3.6 × 8.6 × 10.5 Å closed by four nitrate anions flanking the sides. As shown in Fig. 6, the 22-membered metallomacrocycle of approximate dimensions 8.7 × 11.2 Å in **3** is made up of three smaller rings with the eight-membered fragments CH$_2$(CH$_2$OCH$_2$)$_2$CH$_2$ as the two end-rings (handles of the cymbals) and the eight-membered Ag$_4$S$_4$ skeleton as the central ring. A similar 19-membered metallotricycle is formed in **4** but comprises two different fragments: five-membered CH$_2$CH$_2$-OCH$_2$CH$_2$ and eight-membered CH$_2$(CH$_2$OCH$_2$)$_2$CH$_2$ with approximate dimensions 8.6 × 10.0 Å. The relatively small end-ring from OESQ lifts up the two sulfur atoms in **4** causing one of the silver(I) ions to orient outwards towards the other, while both silver(I) ions wrapped by ODSQ are oriented inward. The Ag···Ag distance for **3** is 4.41 and for **4** is 3.73 Å. However the eight-membered central ring consisting of alternately arranged silver(I) and S atoms shows a similar chair-like conformation in both **3** and **4** as shown in Fig. 7.

Despite the similar structural topology shared by complexes **3** and **4**, distinct differences can be found between them. Two pairs of face-to-face quinoline rings are essentially parallel in both **3** and **4** with dihedral angles of only 1.6 and 2.2°, respectively, yet the two quinoline rings belonging to the same ligand are different. In **3** the two rings of each ODSQ are nearly coplanar (dihedral angle 1.6°) giving a normal box, while in **4** the smaller end-ring from OESQ causes the two rings to be inclined to one another at an angle of 32°. Correspondingly, the larger end-ring from ODSQ allows counter-turn rotation of its two quinoline rings at an angle of 30°, so that the four aromatic rings are still parallel in pairs giving a distorted box.

A comparison of the common features of complexes **3** and **4** together with the simple co-ordination motifs in **1** and **2** may provide insight into the self-assembly process of the tetranuclear complexes as demonstrated in Scheme 1. That is, if the mononuclear $[Ag(OESQ)]^+$ and $[Ag(ODSQ)]^+$ motifs are considered as building blocks, reaction of OESQ or ODSQ with silver(I) nitrate in equimolar ratio affords first the mononuclear intermediate **a** or **b** with a similar co-ordination motif to that in **1** or **2** as manifested by ES-MS spectra. On reaction with a second molecule of $AgNO_3$, two **b** will assemble into tetranuclear **3**, or one **a** and one **b** cross-assemble into **4**. The main driving force of the self-assembly is definitely the co-ordination of the sulfur-bridging silver(I) ions whose vacant co-ordination sites are occupied by the oxygen atoms of auxiliary NO_3^- anions. The separation of 3.61 and 3.54 Å between the two parallel aromatic pairs in **3** and **4**, respectively, suggests that the $\pi\cdots\pi$ interactions also make some contribution to the assembly which is critical particularly in the case of OESQ. As discussed above, the orientations of the two quinoline rings of OESQ are restricted by the short diethylene glycol backbone while the longer triethylene glycol only loosely wraps around the silver(I) ion to make the two quinoline rings adjustable to adapt to the requirement for self-assembly. Thus no matter whether the building block $[Ag(ODSQ)]^+$ is assembled with itself or with $[Ag(OESQ)]^+$, face-to-face $\pi\cdots\pi$ interactions are present. However, once two $[Ag(OESQ)]^+$ are assembled, the close edge-to-edge repulsion will prevent formation of a stable tetranuclear complex. The anions play an important role in the assembly. The weaker co-ordinating ClO_4^- anion does not enable the two sulfur atoms to bridge another silver(I) ion with the remaining co-ordination positions free, while the stronger co-ordinating NO_3^- anions satisfactorily meet the requirements by acting as auxiliary ligands.



Scheme 1

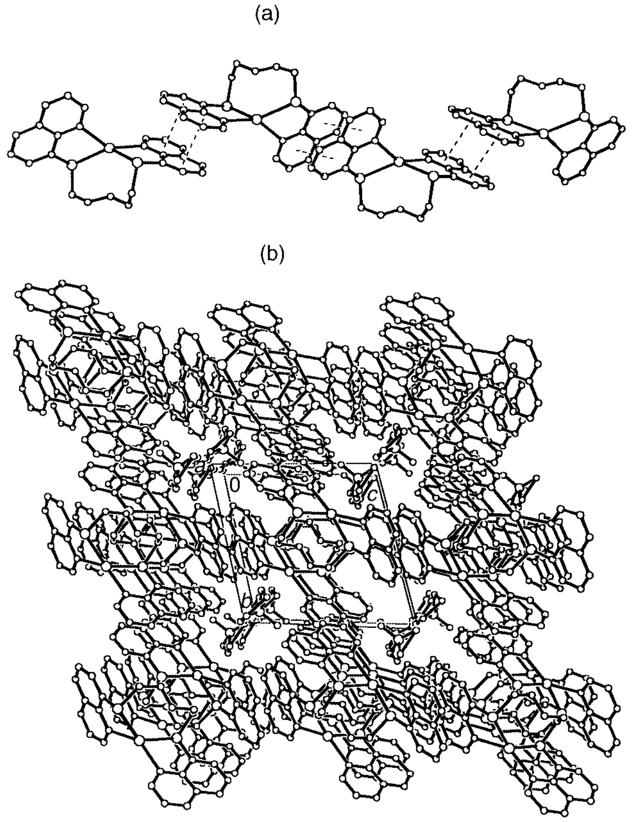


Fig. 8 (*a*) View of the weak face-to-face π···π interactions formed between the [Ag(OESQ)]$^+$ cations in complex **1**, resulting in a zigzagged chain extended along the *bc* direction. (*b*) Crystal packing of **1** viewed down the *a* axis, showing square channels that accommodate the guest ClO_4^- anions.

Crystal packing

In the mononuclear complex **1** each quinoline ring forms weak face-to-face π···π interactions[13] with two adjacent [Ag(OESQ)]$^+$ cations with the centroid-to-centroid distances of 3.73 and 4.02 Å as shown in Fig. 8(*a*). These π···π interactions assemble the [Ag(OESQ)]$^+$ cations into one dimensional zigzagged chains extending along the *bc* directions. The inversion symmetry-related array of such chains results in square channels in the *a* direction in which disordered ClO_4^- guest anions are accommodated (Fig. 8(*b*)). The [Ag(ODSQ)]$^+$ cations in **2** are discrete with the closest silver(I) ions 8.02 Å away. In **4** every [Ag_4(OESQ)(ODSQ)$(NO_3)_4$] molecule is connected to four neighbouring molecules by O···O hydrogen bonding with water molecules. A two-dimensional network is thus generated. The crystal structure is stacked by overlapped arrangement of these layers. Such a crystal packing may be more influenced by the molecular shape of the tetranuclear complex than by hydrogen bonding because a similar crystal packing is also formed in **3** without any water molecules. The presence of two relative larger triethylene glycol chains $CH_2(CH_2OCH_2)_2CH_2$ in **3** compared with one smaller diethylene glycol $CH_2CH_2OCH_2CH_2$ in **4** may account for exclusion of water molecules in the crystal of **3**, and the ability of solvated water molecules to enter the crystal lattice may also depend on the crystallization conditions.

Conclusion

Two novel tetrametallotricyclic complexes which have similar box-like topology but different building blocks have been constructed by spontaneous self-assembly of ten components. The self-assembly process has been clarified with the help of two mononuclear complexes and ES-MS investigation of the solution speciation in the reaction mixtures. The soft polyethylene glycol backbones and rigid 8-sulfanylquinoline terminal groups facilitate the self-assembly of flexible linear ligands with silver(I) nitrate, as the former has been known to easily wrap around a metal ion[14] while the latter can chelate the metal ion with the exodentate sulfur atoms ready for further bridging. This unique conformation obviously takes advantage of the mixed OSN donor set as the C–O bond prefers *anti* placement while the C–S bond prefers *gauche*.[3c,4d,15] The different lengths of the polyethylene glycol backbones in OESQ and ODSQ have significant influence on the co-ordination geometry of the silver(I) ion, which consequently decides the assembly outcome and dictates the resulting molecular shape. The anions play an important role in the assembly depending upon their co-ordination ability. Acting as an auxiliary ligand, nitrate controls the formation of tetranuclear molecules while perchlorate gives only mononuclear complexes. Construction of metallo-supramolecular species with novel molecular architectures, such as squares, boxes, cages, helicates, catenates, pseudorotaxanes and polyrotaxanes, in which some are of nanoscale, from the reaction of silver(I) salts with various heterocyclic ligands has been vigorously reported in recent years.[16] However, the present complexes have features of molecular stoichiometry, dimensions and topology which are different from those of any previous structures.

Acknowledgements

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