Electronic structure of the mononuclear Ag(II) complex $[Ag([18]aneS_4O_2)]^{2+}$ ([18]aneS$_4$O$_2$ = 1,10-dioxa-4,7,13,16-tetrathiacyclooctadecane)†

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The structure of $[Ag([18]aneS_4O_2)](PF_6)_2{\cdot}CH_2Cl_2$ shows a highly unusual and unexpected boat conformation for the macrocycle with square-planar S_4-coordination at the formal Ag(II) centre and the two ether O-centres lying on the same side of the S_4 plane; the SOMO in $[Ag([18]aneS_4O_2)]^{2+}$ possesses 22.7% Ag 4d$_{xy}$ character, as determined by multi-frequency EPR spectroscopy and supported by DFT calculations.

Complexes incorporating formal Ag(II) centres have been used as oxidants in organic synthesis[1] and have been identified in radioactive waste processing.[2] The reported structures of mononuclear Ag(II) complexes are dominated by N-donor ligands of porphyrins,[3] macrocycles,[4] bipyridines[5] and pyridine-2-carboxylate derivatives[6] in which the metal centre is bound in a square-planar geometry with weak axial interaction(s) to counter-anions or co-ligands. Sulfur-based ligands[7] and thioether macrocycles[8,9] have also been used to complex redox-active Ag centres. However, crystal structures of mononuclear Ag(II) complexes with S-donor ligands remain very rare, the only reported example is the homoleptic thioether macrocyclic complex $[Ag([18]aneS_6)](ClO_4)_2$ ([18]aneS$_6$ = 1,4,7,10,13,16-hexathiacyclooctadecane).[10] As part of our on-going studies of complexes containing unusual metal oxidation states,[11] we were interested in defining the extent to which homoleptic thioether coordination stabilises a formal Ag(II) centre. Thus, we modified the ligand donor set from S_6- to S_4O_2-coordination *via* incorporation of two ether O-donors, and report herein the results of structural and electronic investigations of $[Ag([18]aneS_4O_2)](PF_6)_2$ ([18]aneS$_4$O$_2$ = 1,10-dioxa-4,7,13,16-tetrathiacyclooctadecane) for direct comparison with its $[Ag([18]aneS_6)](ClO_4)_2$ counterpart.[10]

$[Ag([18]aneS_4O_2)]PF_6$ was prepared by reaction of [18]aneS$_4$O$_2$ with $AgPF_6$ in CH_2Cl_2–MeOH, and a single crystal of $[Ag([18]aneS_4O_2)]PF_6{\cdot}MeCN$ suitable for X-ray crystallography‡ was obtained by diffusion of Et_2O into a solution of the complex in MeCN at −20 °C. There is minor disorder in the macrocyclic ring of one of the two independent cations in each asymmetric unit. The structure of the $[Ag([18]aneS_4O_2)]^+$ cation shows *meso* coordination of the macrocycle with four S-donors bound to Ag^{I} in a distorted tetrahedral coordination geometry with a dihedral angle of 70.0(2)° between the planes defined by S(4)Ag(1)S(7) and S(13)Ag(1)S(16) consistent with a formal Ag(I) oxidation state in this complex [Fig. 1(a)]. The O-donors remain unbound to the Ag^{I} centre [Ag(1)···O(1) 3.092(3) and Ag(1)···O10 3.022(3) Å]. The Ag–S bond lengths [Ag(1)–S(4) 2.5746(11), Ag(1)–S(7) 2.6094(13), Ag(1)–S(13) 2.5745(11) and Ag(1)–S(16) 2.5724(11) Å] in $[Ag([18]aneS_4O_2)]^+$ are shorter than the Ag–S bond lengths [2.6665(12) and 2.7813(10) Å] in $[Ag([18]aneS_6)]^+$ consistent[9] with the lower coordination number of $[Ag([18]aneS_4O_2)]^+$.

The cyclic voltammogram of $[Ag([18]aneS_4O_2)]PF_6$ in CH_2Cl_2 containing 0.4 M NBu_4PF_6 at a scan rate of 100 mV s^{-1} shows an oxidative process at E_p^a = +1.09 V *vs.* Fc^+/Fc at 253 K with a return wave observed at E_p^c = +0.95 V (ΔE = 140 mV) (see ESI†). This contrasts with the fully irreversible process with no return wave observed at E_p^a = +0.93 V for $[Ag([18]aneS_6)]PF_6$ under the same experimental conditions. This suggests a degree of increased kinetic inertness for Ag(II) with the [18]aneS$_4$O$_2$ macrocycle. In addition, the general broadening of the cyclic voltammetric response for $[Ag([18]aneS_4O_2)]PF_6$ is consistent with changes in coordination at the metal centre upon oxidation. Coulometric measurements at

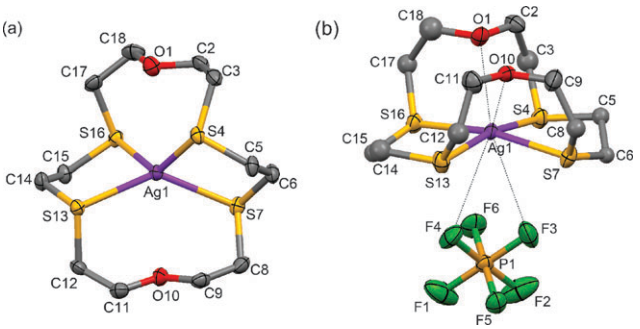

Fig. 1 (a) View of one of the two crystallographically independent $[Ag([18]aneS_4O_2)]^+$ cations in the asymmetric unit. (b) View of $[Ag([18]aneS_4O_2)]^{2+}$ showing interactions with O-donor atoms and with PF_6^- anion in the solid state. One of the two equally-occupied disorder components of the atoms C3, C5, C6, C8, C12, C14, C15, C17 and C18 in the macrocylic ring is omitted for clarity.

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† Electronic supplementary information (ESI) available: Synthesis and structural data of Ag(I) and Ag(II), cyclic voltammograms of $[Ag([18]aneS_4O_2)]PF_6$ and $[Ag([18]aneS_6)]PF_6$, EPR physical measurements and EPR theoretical calculation, experimental details of DFT calculations. See DOI: 10.1039/b717647c

+1.12 V *vs.* Fc^+/Fc confirm that the oxidation of [Ag([18]aneS$_4$O$_2$)]PF_6 is a one-electron process, but this quantitative oxidation is accompanied by precipitation of the product during the course of the bulk experiment. Controlled potential electrolysis in a thin quartz cell ($40 \times 10 \times 0.5$ mm^3) at +1.12 V *vs.* Fc^+/Fc in CH_2Cl_2 containing 0.4 M NBu_4PF_6 under Ar at 253 K provided a route for the electrocrystallisation of [Ag([18]aneS$_4$O$_2$)]$(PF_6)_2 \cdot CH_2Cl_2$ as blue needle crystals. These crystals, suitable for X-ray crystallography,‡ were deposited on the surface of the Pt/Rh gauze working electrode after *ca.* 1 h of electrolysis.

The single-crystal X-ray structure of [Ag([18]aneS$_4$O$_2$)]$(PF_6)_2 \cdot CH_2Cl_2$ [Fig. 1(b)] shows a highly unusual and unexpected boat conformation for the [18]aneS$_4$O$_2$ macrocycle that is significantly different from the structure of the parent [Ag([18]aneS$_4$O$_2$)]$PF_6 \cdot$MeCN complex. The majority of the macrocyclic carbon atoms are each disordered over two alternative sites, a common feature in cyclic thioether complexes. The Ag centre in [Ag([18]aneS$_4$O$_2$)]$(PF_6)_2 \cdot CH_2Cl_2$ possesses a primary square-planar S$_4$-coordination sphere with the Ag–S distances [Ag(1)–S(4) 2.487(4), Ag(1)–S(7) 2.537(4), Ag(1)–S(13) 2.501(4), Ag(1)–S(16) 2.518(4) Å] significantly shorter than those in six-coordinated [Ag([18]aneS$_6$)]$(ClO_4)_2$ [Ag(1)–S(1) 2.569(7), Ag(1)–S(2) 2.720(6) Å],[10] consistent with the lower coordination number in the former complex. Interestingly and unusually, the two macrocyclic O-donors in [Ag([18]aneS$_4$O$_2$)]$(PF_6)_2$ are located in *cis*-positions relative to the S$_4$-plane [Ag(1)···O(1) 2.814(9), Ag(1)···O(10) 2.797(10) Å] rather than in the expected *trans*-positions as observed in [Ag([18]aneS$_4$O$_2$)]PF_6 (see above).[10] In [Ag([18]aneS$_4$O$_2$)]$(PF_6)_2$, the Ag(II) ion lies 0.26 Å out of the least-squares S$_4$ plane of the macrocycle and towards the O-centres with one of the PF_6^- counter-anions occupying a site below the cation [Ag–F 3.295(13) and 3.240(12) Å] on the opposite side of the S$_4$ plane to the macrocyclic ether centres. Thus, although the primary coordination at Ag(II) is square-planar *via* binding four thioether S-donors of the macrocycle, there is some evidence, at least in the solid state, of potential long-range interactions with ether O-donors and two F centres in the PF_6^- anion to give a twist square-prismatic stereochemistry [Fig. 1(b)].

We have shown previously that high-valent transition metal complexes of thioether crowns are stabilised in acidic solutions.[12] Therefore, this approach was used to stabilise $[Ag([18]aneS_4O_2)]^{2+}$ in solution to facilitate spectroscopic studies. Electrochemically prepared microcrystals of [Ag([18]aneS$_4$O$_2$)]$(PF_6)_2 \cdot CH_2Cl_2$ were dissolved in 70% $HClO_4$ and the resultant sample was studied by multi-frequency EPR spectroscopy in fluid (293 K, X-band) and frozen solutions (125 K, S-, X- and Q-band, Fig. 2). The fluid-solution X-band spectrum of $[Ag([18]aneS_4O_2)]^{2+}$ shows a doublet that results from hyperfine coupling to ^{107,109}Ag nuclei (^{107,109}Ag $I = 1/2$, 100% combined natural abundance) and simulation gave $g_{iso} = 2.0273$ and $|A_{iso}| = 34 \times 10^{-4}$ cm^{-1} [Fig. 2(a)]. The frozen-solution Q-band spectrum is axial with ^{107,109}Ag hyperfine that is clearly resolved in the $g_\parallel$ and $g_\perp$ regions [Fig. 2(d)]. Simulation of this spectrum gave $g_\perp = 2.0163$, $g_\parallel = 2.0415$; $|A_\perp| = 31 \times 10^{-4}$ cm^{-1} and $|A_\parallel| = 43 \times 10^{-4}$ cm^{-1}. These spin Hamiltonian parameters were verified

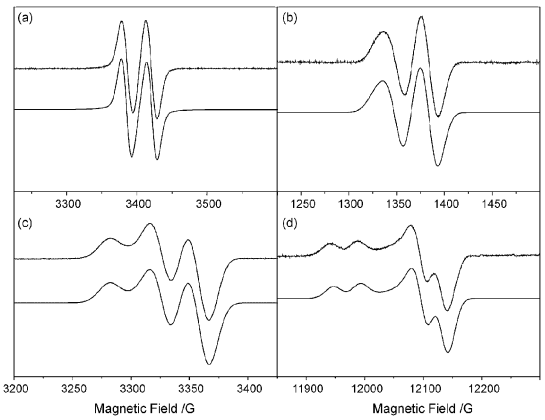

Fig. 2 Multi-frequency EPR spectra of $[Ag([18]aneS_4O_2)]^{2+}$ in 70% $HClO_4$ solution. (a) X-Band fluid spectrum at 293 K (top) and simulation (bottom) with $g_{iso} = 2.0273$, $|A_{iso}| = 34 \times 10^{-4}$ cm^{-1}; (b) S-band frozen spectrum; (c) X-band frozen spectrum; (d) Q-band frozen spectrum at *ca.* 125 K (top) and simulations (bottom) with $g_{11} = g_{22} = 2.0163$, $g_{33} = 2.0415$; $|A_{11}| = |A_{22}| = 31 \times 10^{-4}$ cm^{-1}, $|A_{33}| = 43 \times 10^{-4}$ cm^{-1}. Gaussian linewidths of $W_{iso} = 14 \times 10^{-4}$ cm^{-1} for X-band fluid spectrum; $W_{11} = W_{22} = W_{33} = 25 \times 10^{-4}$ cm^{-1} for Q-band frozen spectrum; $W_{11} = W_{22} = W_{33} = 17 \times 10^{-4}$ cm^{-1} for X- and S-band frozen spectra.

by the simultaneous simulation of the frozen-solution S- and X-band spectra [Fig. 2(b) and (c)]. The simulated hyperfine coupling constants require the sign of the A values to be either all positive or negative such that $A_{iso} = (A_\parallel + 2A_\perp)/3$.

The axial EPR spectra of $[Ag([18]aneS_4O_2)]^{2+}$ are consistent with the approximate square-planar molecular structure determined by X-ray crystallography. Thus, the z-axis was defined as being perpendicular to the S$_4$ plane with $g_\parallel$ and $A_\parallel$ lying along this axis, with the x-axis defined as pointing along the bisector of the S(4)–Ag(1)–S(16) angle. Thus, crystal-field theory predicts a 4d$_{xy}$-based SOMO in $[Ag([18]aneS_4O_2)]^{2+}$ consistent with the observed $g_\parallel > g_\perp > g_e$ pattern in the EPR spectra of the complex. Analysis of the simulated g and A-values from the multi-frequency EPR spectra gave $\alpha^2 = 22.7\%$ with $A_{zz} \equiv A_\parallel$ and $g_{zz} = g_\parallel$ (see ESI†). Negative A-values gave invalid negative values for α^2. Thus, the contribution of 4d$_{xy}$ metal orbital to the SOMO is 22.7% as determined by multi-frequency EPR spectroscopy.

The experimentally determined composition of the SOMO was compared with that determined by unrestricted relativistic DFT calculations (see ESI†). These calculations were carried out using the Amsterdam Density Functional (ADF) suite version 2005.01.[13,14] An unconstrained model, based on the crystallographic structure of $[Ag([18]aneS_4O_2)]^{2+}$, converged to a similar geometry but with Ag–S bond lengths that are on average 0.07 Å longer than those in the experimental structure. In contrast the Ag···O distances for the calculated geometry are 0.12 Å shorter than in the experimental structure, which may point towards a weak interaction involving the O-donors in this complex that may be associated with the displacement of the Ag ion out of the S$_4$ plane (see above). It is likely that the principal differences between the calculated and experimental geometries result from the omission of a weakly bound PF_6^- counter-anion in the model employed for the calculations.

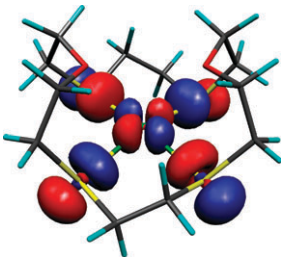

Fig. 3 Isosurface plot of the α-spin SOMO of $[Ag([18]aneS_4O_2)]^{2+}$ derived from a BP-TZP relativistic DFT calculation.

The calculated composition of the SOMO is 18.4% Ag $4d_{xy}$ and 68.4% S 3p (Fig. 3). The calculated Ag $4d_{xy}$ contribution is 4.3% less than that derived from the EPR spectroscopic studies; a similar difference was also observed for $[Ag([18]aneS_6)]^{2+}$,[10] for which the calculated SOMO possesses 22% Ag $4d_{xy}$ character and EPR spectroscopic studies reveal a SOMO composition of 26% Ag $4d_{xy}$. Our spectroscopic and theoretical studies point to a slightly (4%) lower metal composition of the SOMO in $[Ag([18]aneS_4O_2)]^{2+}$ than $[Ag([18]aneS_6)]^{2+}$, and that the equatorial S-donors are capable of buffering these differences in the Ag contributions to the SOMO. It is interesting to note that the average in-plane Ag–S distance for $[Ag([18]aneS_4O_2)]^{2+}$ is 5% shorter than for $[Ag([18]aneS_6)]^{2+}$ suggesting greater Ag–S orbital overlap, and potentially greater covalency.

In summary, we have prepared $[Ag([18]aneS_4O_2)](PF_6)_2$ and shown that the macrocycle binds to the Ag(II) centre in a unique conformation. EPR spectroscopic and theoretical calculations on this complex show that $[Ag([18]aneS_6)]^{2+}$ and $[Ag([18]aneS_4O_2)]^{2+}$ possess similar Ag $4d_{xy}$ ground-states with significant spin density on the equatorial thioether S-donors. These results imply an overriding importance for equatorial thioether coordination in the stabilization of Ag(II) by crown thioether macrocycles. This notwithstanding, long-range interactions at and around axial sites with O-centres and PF_6^- anion may stabilize the formal Ag(II) centre in $[Ag([18]aneS_4O_2)]^{2+}$ in the solid state, although no Ag···F coupling was observed in solution by EPR spectroscopy.

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Notes and references

‡ *Crystal data*: $C_{14}H_{27}NO_2S_4PF_6Ag$, M = 622.45, orthorhombic, space group $Pna2_1$, a = 21.0076(4), b = 17.5973(6), c = 12.5610(7) Å, V = 4643.5(3) Å^3, T = 150(2) K, Z = 8, D_c = 1.781 g cm^{-3}, 11085 unique reflections (R_{int} = 0.0282), final $R_1[F > 2\sigma(F)]$ = 0.030, wR_2 (all data) = 0.0705.
$C_{13}H_{26}O_2S_4Cl_2P_2F_{12}Ag$, M = 811.29, monoclinic, space group $P2_1/n$ (alt. $P2_1/c$, no. 14), a = 11.190(2), b = 10.510(2), c = 22.990(5) Å, β = 91.00(3)°, V = 2703.4(9) Å^3, T = 150(2) K, Z = 4, D_c = 1.993 g cm^{-3}, 4733 unique reflections (R_{int} = 0.177). Application of disorder modelling and distance restraints to the macrocyclic C and solvent Cl atoms led to stable refinement and final $R_1[F > 2\sigma(F)]$ = 0.0944, wR_2 (all data) = 0.251.
CCDC 667819 and 667820. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b717647c

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