

## EPR and Theoretical Studies on the Electronic Structures of Thioether Macrocyclic Complexes of Gold(II) and Silver(II)

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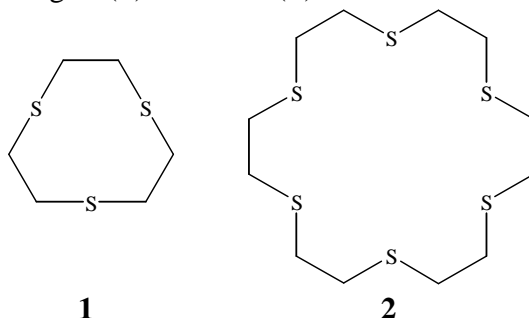
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In recent years several complexes of gold and silver in their unusual oxidation state of II have been isolated and studied.<sup>1</sup> However, to date, full elucidation of their electronic structures has not been undertaken. The aims of this work are to fully characterise and investigate the electronic structures of two such complexes.

Thioether macrocycles are capable of modifying their coordination to accommodate a range of transition-metal stereochemistries and, as such, are suited to facilitate the study of the redox chemistry of transition-metal complexes.<sup>2</sup> The thioether macrocycles 1,4,7-trithiacyclononane ([9]aneS<sub>3</sub>) (**1**) and 1,4,7,10,13,16-hexathiacyclooctadecane ([18]aneS<sub>6</sub>) (**2**) are known to stabilise gold(II) and silver(II).<sup>1</sup>



The complexes [Au([9]aneS<sub>3</sub>)<sub>2</sub>][BF<sub>4</sub>]<sub>2</sub> and [Ag([18]aneS<sub>6</sub>)](ClO<sub>4</sub>)<sub>2</sub> were synthesised and studied. The unique crystal structure of [Ag([18]aneS<sub>6</sub>)](ClO<sub>4</sub>)<sub>2</sub> has been solved at 150 K and 30 K. This is the first crystal structure of a Ag(II) complex with a sulfur donor ligand. At 150 K the individual Ag(II)-S bond lengths are not resolved and average to 2.642(3) Å and at 30 K two crystallographically independent Ag(II)-S distances which are equivalent within errors are observed; this leads to two groups of three Ag(II)-S distances which are essentially the same at 2.619(5) and 2.613(5) Å.

Multi-frequency EPR studies have been carried out in order to probe the electronic structure of the complex. Calculations based on the spin-Hamiltonian parameters from simulations of the EPR data are compared to a model of the SOMO generated by DFT calculations.

<sup>1</sup> A.J. Blake, J.A. Greig, A.J. Holder, T.I. Hyde, A. Taylor, M. Schröder, *Angew. Chem., Int. Ed. Eng.*, 1990, **29**, 197-198, R. Kirmse, M. Kampf, R.-M. Olk, M. Hildebrand and H. Krautscheid, *Z. Anorg. Allg. Chem.*, 2004, **630**, 1433-1436 and A.J. Blake, R.O. Gould, A.J. Holder, T.I. Hyde and M. Schröder, *Polyhedron*, 1989, **8**, 513-518

<sup>2</sup> M. Schröder, *Pure Appl. Chem.*, 1988, **60**, 517 and references therein