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Structure and bonding in cyclic thiolate complexes of copper, silver and gold

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Abstract

The structures of $M_n(SMe)_n$ rings (M = Cu, Ag, Au; n = 2-6) and some of their PH_3 and 1,4-diaza-1,3-butadiene complexes have been calculated using DFT methods. The geometries of the calculated structures are in good agreement with representative complexes retrieved from the Cambridge Crystallographic Data Base. Though π Cu–S and M–M orbital interactions can be identified, the net bonding interaction within the ring involves σ Cu–S orbital overlap. In many cases, the observed and calculated structures bear a similarity to those of appropriate members of the C_nH_{2n} series (n = 2–8).

Keywords: Copper; Silver; Gold; Thiolate; Cyclic; DFT

1. Introduction

Copper, silver and gold form thiolate complexes which range from molecular or polymeric with an approximate 1:1 ratio of thiolate to metal, through discrete M_n metal clusters (n = 10–75) supported by thiolate ligands [1a–g] and finally to templated and supported metal nanoparticles [2a–d] and self-assembled layers on metal surfaces [3a–d] which have attracted particular attention as biosensors in the case of gold [4a–c]. Unlike copper [5a,5b], silver and gold have no known biological function. However, their strong affinity for sulfur donor ligands is known to result in bioaccumulation [6a,6b] and indeed, this property can be used to advantage in the extraction of gold from ores and mineral concentrates using microorganisms [7a–c]. In addition, the use of gold compounds in the treatment of rheumatoid arthritis is thought to depend on binding of gold at sulfur-containing amino acid residues [8a–c].

Structural characterisation of simple metal thiolates is difficult due to their insoluble, polymeric nature, though some chain structures and a range of molecular rings with from 2 up to 15 metal atoms have been characterised in the solid state, mainly using sterically demanding thiolate ligands to prevent aggregation. Even where solid state structures are available, the degree of aggregation in solution may be different; the history of the solid and solution structures of the anti-arthritic drug myocrysine (gold sodium thiomalate) provides a good example [9a,9b].

As a contribution to understanding in this area, we report here a computational study on simple ring structures of formulae $M_n(SMe)_n$ (M = Cu, Ag, Au; n = 2–6) together with substituted derivatives containing PH_3 and 1,4-diaza-1,3-butadiene (DAB); the latter ligand has been used as a computationally less demanding analogue of 1,1′-bipyridyl and 1,10-*o*-phenanthroline.

2. Computational methods

DFT calculations were performed with the GAUSSIAN-03 package [10] using a LanL2DZ basis set and the B3PW91 functional. This combination has been shown to provide satisfactory results for all three coinage metals; errors in geometry and bond dissociation energies were typically

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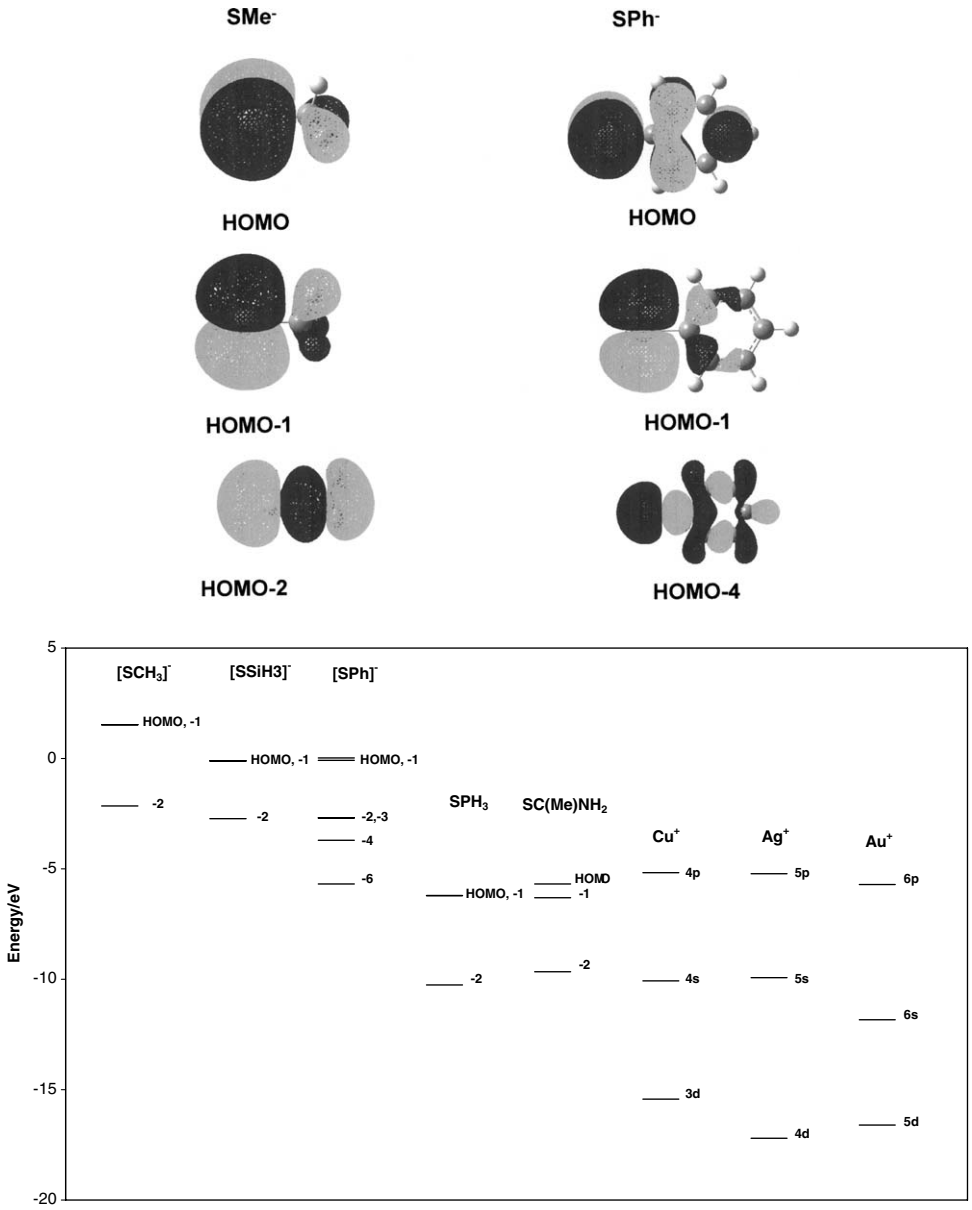

Fig. 1. Frontier molecular orbitals for 1–3 and energy level diagram for 1–5 and M^I.

3% and 10%, respectively [11]. Frequency calculations for energy minima showed no imaginary frequencies. Transition state structures exhibited one imaginary frequency. Calculated frequencies were scaled by a factor of 0.9613 [12]. Enthalpy values represent the sum of electronic and thermal enthalpies [13]. Molecular orbitals were generated using GaussView. All structures were minimised starting from a planar $M_n(SR)_n$ framework.

3. Results and discussion

3.1. $[SCH_3]^-$ as a model for $[SAr]^-$ and $[SSiR_3]^-$

For computational economy, all calculations have been performed using $[SCH_3]^-$ (**1**) as ligand. Most molecular $M_n(SR)_n$ complexes which have been structurally characterised in the solid state contain sterically demanding $[SAr]^-$ and $[SSiR_3]^-$ ligands to hinder aggregation. Using calculations on the free anions and on their CuSR complexes, an evaluation has been performed as to whether $[SCH_3]^-$ (**1**) serves as an adequate model electronically for $[SPh]^-$ (**2**) and $[SSiH_3]^-$ (**3**). All of **1**–**3** exhibit two filled orbitals perpendicular to the S–C axis and a third orbital at lower energy which is collinear with the S–C axis (Fig. 1) The HOMO/HOMO-1 pair of **2** are non-degenerate due to their differing interactions with the σ-framework of the ring. Also shown in Fig. 1 are the energies of the appropriate orbitals of SPH_3 (**4**) and thioacetamide **5**, sulfur ligands which are known to serve as neutral analogues of anionic thiolate (vide infra). The