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Molecular orbital studies of luminescent silver(I) chalcogenido clusters $[Ag_4(\mu\text{-dppm})_4(\mu_4\text{-E})]^{2+}$ (dppm = $Ph_2PCH_2PPh_2$)†

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The electronic structures of the μ_4-chalcogenido silver(I) complexes $[Ag_4(\mu\text{-dppm})_4(\mu_4\text{-E})][O_3SCF_3]_2$ (E = S **1**, Se **2** or Te **3**; dppm = $Ph_2PCH_2PPh_2$) have been calculated by use of the Fenske–Hall molecular orbital method. The results indicate that complexes **1**–**3** show similar electronic structures, with the highest occupied molecular orbital being mainly of Ag–E character while the lowest unoccupied molecular orbital is of metal–metal interaction character. A correlation between the results of these calculations with the spectroscopic properties of this class of complexes is described.

There has been a growing interest in the photophysical properties of polynuclear d^{10} metal complexes.[1–8] The electronic structures of related systems have also been the focus of considerable attention.[2c,9] Recently, we reported the syntheses and structural characterization of a novel class of luminescent tetranuclear d^{10} chalcogenido clusters of copper(I)[8j,k] and silver(I),[8l] $[M_4(\mu\text{-dppm})_4(\mu_4\text{-E})]^{2+}$ (M = Ag, E = S **1**, Se **2** or Te **3**; M = Cu, E = S **4** or Se **5**; dppm = $Ph_2PCH_2PPh_2$). The clusters have been found to possess rich photophysical and photochemical properties. Excitation of the complexes in the solid state and in fluid solutions with $\lambda > 350$ nm results in intense and long-lived green to orange luminescence. The solid-state emission energies follow the orders: **1** > **2** > **3**; **4** > **5**; **1** > **4** and **2** > **5**. In view of the σ-donating ability of chalcogenides and the observed trends in emission energies (see above), the excited states of these clusters are expected to possess a high parentage of ligand-to-metal charge-transfer l.m.c.t. ($E^{2-}\rightarrow M_4$) character. In order to gain more insight into the electronic structures and the nature of the excited states of these luminescent complexes, a Fenske–Hall molecular-orbital calculation on the series $[Ag_4(\mu\text{-dppm})_4(\mu_4\text{-E})][O_3SCF_3]_2$ has been performed.

Computational Details

Non-parametrized Fenske–Hall MO calculations[10] were carried out on the model complexes $[Ag_4(\mu\text{-}H_2PCH_2PH_2)_4(\mu_4\text{-E})]^{2+}$ in terms of the orbital interactions between the fragments $Ag_4(\mu\text{-}H_2PCH_2PH_2)_4^{2+}$ and E. This model is based on a self-consistent-field method, which is an approximation of the Hartree–Fock–Roothaan procedure. The molecular geometry and the atomic basis sets used completely determine the resulting eigenvalues and eigenvectors. The geometry of each complex was taken directly from that crystallographically determined for complexes **1**–**3** with hydrogen atoms replacing the phenyl groups on the dppm ligand (P–H taken to be 1.41 Å and C–H 0.95 Å) and idealized to C_{2v} point group. The relative positions of the four silver atoms were adjusted to form a rectangle. A perspective drawing of the idealized complex $[Ag_4(\mu\text{-}H_2PCH_2PH_2)_4(\mu_4\text{-E})]^{2+}$ (E = S **1a**, Se **2a** or Te **3a**) is shown in Fig. 1. Bond angles and distances, based on those of structures **1**–**3**, are summarized in Table 1. The basis sets used were those provided with the Fenske–Hall program package (version 5.1). All calculations were carried out on a VAX 780 computer at The University of Hong Kong.

Table 1 Selected bond distances (Å) and angles (°) for the idealized cationic complexes $[Ag_4(\mu\text{-}H_2PCH_2PH_2)_4(\mu_4\text{-E})]^{2+}$ (E = S **1a**, Se **2a** or Te **3a**)

Complex	E–Ag	Ag–Ag	Ag–P	P–C
1a	2.514	3.160, 3.038	2.504	1.872
2a	2.620	3.222, 3.055	2.514	1.846
3a	2.757	3.257, 3.071	2.513	1.827

	Ag(1)–E–Ag(2′)	E–Ag(1)–P(2)	Ag(1)–P(2)–C(1)	P(2)–C(1)–P(1)	Ag(1′)–Ag(1)–P(3)
1a	121.35	102.85	112.30	111.04	123.50
2a	115.87	101.28	110.49	112.86	123.30
3a	111.22	101.21	109.83	114.90	123.12

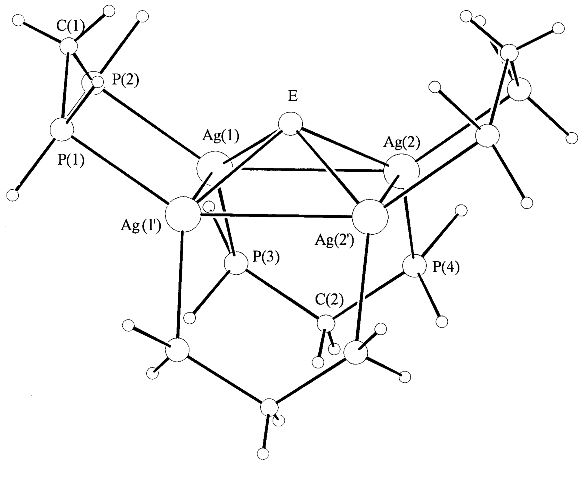

Fig. 1 Perspective drawing of the idealized model complexes **1a**–**3a** for Fenske–Hall MO calculations; C_{2v} point-group symmetry is assumed and all phenyl groups in the dppm ligands are replaced by hydrogen atoms

Results and Discussion

Fig. 2 shows the molecular orbital diagrams for complexes **1a**–**3a**. The electronic structures for all three complexes are similar. Since the bonding interactions between the chalcogen atom and four silver atoms are the main contributors to the highest occupied molecular orbital (HOMO) (MO64), they undoubtedly play an important role in the determination of the molecular properties. This interaction can be further investigated in terms of the interactions between the two fragments $Ag_4(\mu\text{-}H_2PCH_2\text{-}$

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† *Non-SI unit employed:* eV ≈ 1.60×10^{-19} J.

Table 2 Mulliken overlap populations for orbital interactions between the fragment $Ag_4(\mu\text{-}H_2PCH_2PH_2)_4^{2+}$ and S in the model compound $[Ag_4(\mu\text{-}H_2PCH_2PH_2)_4(\mu_4\text{-}S)]^{2+}$

FMO of $[Ag_4(\mu\text{-}H_2PCH_2PH_2)_4]^{2+}$	Atomic orbitals of S			
	3s	$3p_x$	$3p_y$	$3p_z$
$59(b_1)$		−0.026		
$61(b_1)$ HOMO		0.539		
$62(b_2)$ LUMO			0.538	
$63(a_1)$	0.050			0.286

Table 3 Energies and percentage compositions for the frontier orbitals of complexes **1a**–**3a**

Complex	Molecular orbital	Energy/eV	% Composition E	4 Ag	$4\ H_2PCH_2PH_2$
1a	LUMO $65(a_2)$	−4.14	0.00	96.54	3.46
	HOMO $64(b_1)$	−11.08	46.12	42.00	11.88
2a	LUMO $65(a_2)$	−4.52	0.00	96.52	3.48
	HOMO $64(b_1)$	−10.75	50.16	39.26	10.58
3a	LUMO $65(a_2)$	−5.16	0.00	96.30	3.70
	HOMO $64(b_1)$	−10.55	51.64	38.40	9.96

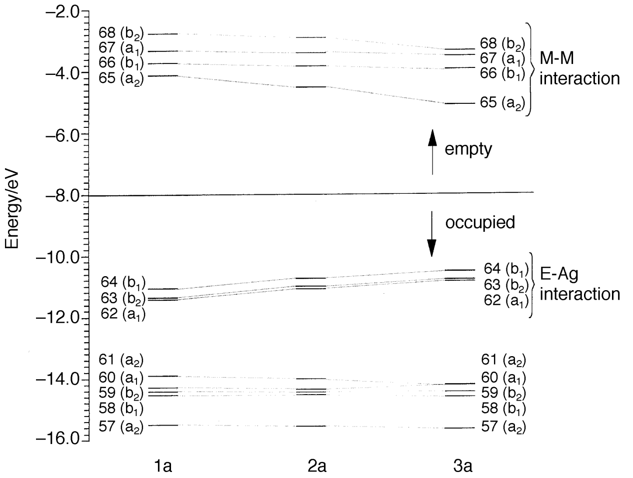

Fig. 2 Molecular orbital diagrams of complexes **1a**–**3a**

$PH_2)_4^{2+}$ and E (S, Se or Te). Similar results have been found for complexes **1a**–**3a**. However, for the purpose of discussion, only **1a** will be described in detail.

Fig. 3 shows the MO correlation diagram for complex **1a**. The lowest unoccupied molecular orbital (LUMO) [fragment molecular orbital FMO62(b_2)] of the metal core fragment possesses major contributions from the Ag atoms with little contribution from the $H_2PCH_2PH_2$ units. The metal–metal interactions involve mainly those of the 5s and 5p orbitals with little contributions from the 4d orbitals. It can also be seen that only the 3p orbitals on the S atom could have appropriate symmetry and energies to interact with the frontier orbitals of the metal-core fragment. Our calculations indicate that the three high-lying occupied orbitals MO64(b_1), MO63(b_2) and MO62(a_1) of complex **1a** (Fig. 4) are mainly comprised of the bonding interaction of the low-lying metal core FMO61(b_1), FMO62(b_2) and FMO63(a_1) of the Ag_4 fragment with the $3p_x$, $3p_y$ and $3p_z$ orbitals of S, respectively. In fact, the interfragment orbitals [FMO61(b_1)–p_x], [FMO62(b_2)–p_y] and [FMO63(a_1)–p_z] together contribute 99% of the total interfragment interactions. The interfragment Mulliken overlap populations for the interactions of $3p_x$, $3p_y$ and $3p_z$ of S and the frontier MOs of the $Ag_4(\mu\text{-}H_2PCH_2PH_2)_4^{2+}$ unit are listed in Table 2. The substantial lowering of the energy levels for the FMOs 61(b_1), 62(b_2) and 63(a_1) of the metal-core fragment as a result of Ag–E bonding interactions is also displayed in Fig. 3.

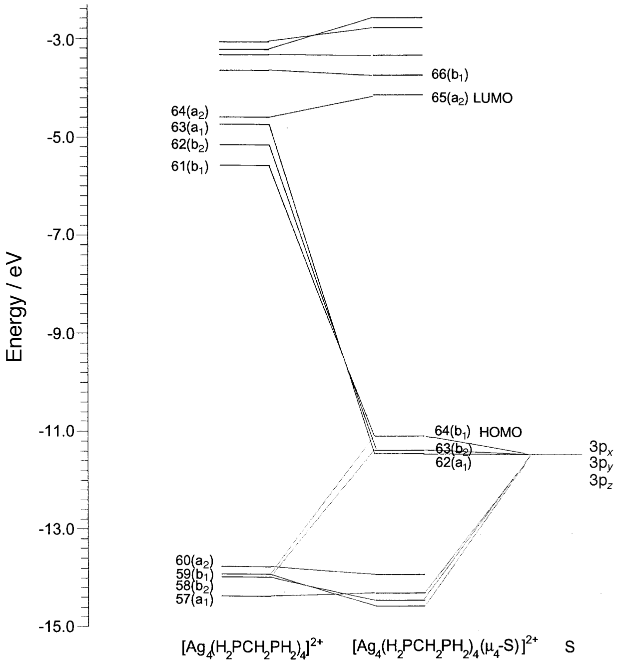

Fig. 3 The MO correlation diagram for the idealized complex $[Ag_4(\mu\text{-}H_2PCH_2PH_2)_4(\mu_4\text{-}S)]^{2+}$

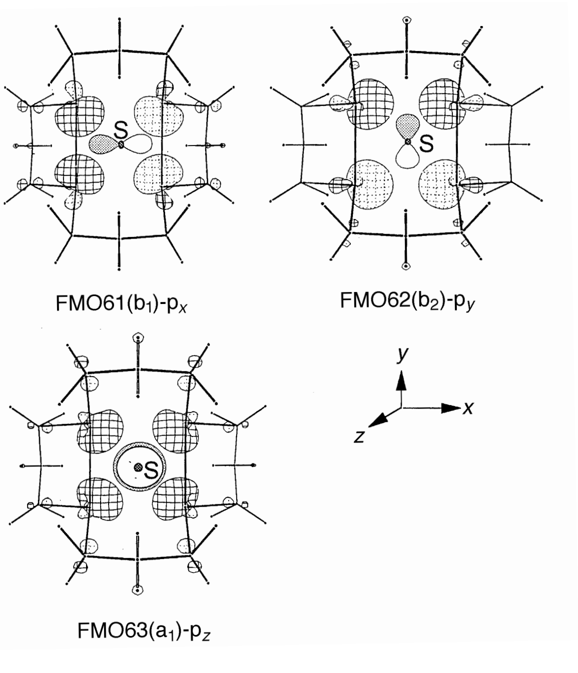

Fig. 4 Three high-lying occupied orbitals MO64(b_1), MO63(b_2) and MO62(a_1) of complex **1a** resulting from major overlaps between $Ag_4(\mu\text{-}H_2PCH_2PH_2)_4^{2+}$ and S

The compositions of the frontier molecular orbitals for complexes **1a**–**3a** are summarized in Table 3. The calculation results reveal that the composition of the HOMO is approximately 50% chalcogen, with most of the remainder metal-based. However, the LUMO is almost metal-localized. Correlation of the compositions of the frontier orbitals with the emission energies of clusters **1**–**3** have been pursued. The emission energies of the solid-state luminescence at 298 K, follow the order **1** (516 nm) > **2** (527 nm) > **3** (574 nm),[8l] in line with the changes in the ionization potentials of the chalcogens,[11] and the calculated decreasing HOMO − LUMO energy gaps from **1a** to **3a** (6.94 > 6.23 > 5.39 eV).

In view of fact that the HOMOs of the complexes are mainly of Ag–E bonding character and the LUMOs are essentially metal-based, the transitions associated with the emissions of the silver(I) clusters **1**–**3** originate essentially from a ligand-to-metal charge-transfer l.m.c.t. ($E^2 \rightarrow Ag_4$) excited state, with mixing of a metal-centred (d–s/d–p) silver(I) state. Similar assignments have also been suggested for other luminescent polynuclear d^{10} thiolato,[2b,d,4a,d,5b,6] halogeno[2a,c,d] and alkynyl[8c,e–g,i] systems.

The present work describes the electronic structures of the novel luminescent silver(I) chalcogenido clusters, and the nature of the excited state of such complexes. Related work on other polynuclear d^{10} luminescent systems is in progress.

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