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Synthesis, molecular and electronic structure of an incomplete cuboidal Re_3S_4 cluster with an unusual quadruplet ground state†

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A Re(IV) cluster complex $[Re_3(\mu_3\text{-}S)(\mu\text{-}S)_3(dppe)_3Br_3]^+$ with nine cluster skeletal electrons (CSE) and a quadruplet ground state has been prepared by treatment of $[Re_3S_7Br_6]Br$ with 1,2-bis(diphenylphosphino)ethane (dppe) in MeCN.

Triangular clusters with incomplete cuboidal $M_3(\mu_3\text{-}Q)(\mu\text{-}Q)_3$ cores (Q = S, Se) are basic units in the chemistry of the heaviest group six transition metal cluster chalcogenides.[1] With a single reported exception,[2] M_3Q_4 (M = Mo, W) clusters are electron precise with six CSE for the formation of three metal–metal bonds that results in stable diamagnetic complexes.[3] These M_3Q_4 compounds are building blocks for the formation of heterobimetallic M_3Q_4M' species with variable CSE populations ranging from 13 to 17 electrons. The catalytic potential of these cubane-type clusters has been recently reviewed.[4]

Unlike numerous examples of molybdenum and tungsten M_3Q_4 clusters, their Re analogues remain much less investigated.[5] In 1990 the first synthesis of a family of Re(V) trinuclear cluster chalcogenides of formula $[Re_3Q_7X_6]X$ (Q = S, Se; X = Cl, Br) was reported.[6] In these systems with six CSE and three metal–metal bonds, the rhenium atoms define an equilateral triangle with a capping chalcogen and three bridging dichalcogenides. The cluster core in $[Re_3Q_7X_6]X$ shares structural and electronic features with the $M_3(\mu_3\text{-}Q)(\mu\text{-}Q_2)_3$ unit found in the polymeric $\{M_3Q_7X_{4/2}X_2\}_\infty$ (M = Mo, W) phases, widely used as starting materials for the preparation of molybdenum and tungsten M_3Q_4 cuboidal complexes upon treatment with phosphanes. The extension of this synthetic strategy to rhenium using $[Re_3S_7X_6]X$ and monophosphanes as precursors was widely explored by Saito *et al.* in the nineties.[7] Re(V) in the starting material is partially or totally reduced to Re(IV) to yield monocapped (with one μ_3-S ligand) $[Re_3S_4Cl_6(PEt_3)_3]^-$ with 8 CSE or bicapped (with two μ_3-S) $[Re_3S_4Cl_5(PEt_3)_3]$ and $[Re_3S_4Br_4(PEt_3)_4]$ with 9 and 10 CSE, respectively. Subtle changes in reaction conditions produce cluster species with different molecular and electronic structures. The use of PPh_3 instead of PEt_3 produces a mixture of co-crystallized bicapped clusters with 9 and 10 CSE.[8] Heterometallic Re_3Q_4M' cubanes (M′ = Co, Ni and Cu) with terminal phosphanes are also known.[9]

Motivated by the chemistry developed on molybdenum and tungsten $[M_3Q_4(diphosphane)_3X_3]^+$ cuboidal complexes,[1c,10–12] we decided to investigate the reactivity of $[Re_3S_7Br_6]Br$ towards diphosphanes. Refluxing of a mixture of $[Re_3S_7Br_6]Br$ and dppe in acetonitrile leads to $[Re_3S_4(dppe)_3Br_3]Br$ ([**1**]Br) with 9 CSE.‡ During the reaction Re(V) is reduced to Re(IV) by means of dppe. Diphosphane also serves as a sulfur acceptor, converting μ-S_2 ligands into μ-S. The structure of [**1**]Br·3MeCN (Fig. 1) was established by single crystal X-ray diffraction experiments§ and it shares structural features with its molybdenum and tungsten analogues. The metal atoms in Re_3S_4 define an almost equilateral triangle (average Re–Re distance 2.780[9] Å) with one capping μ_3-S atom and three bridging μ-S. The Re_3S_4 unit can also be regarded as an incomplete cube in which the metal and sulfur atoms occupy adjacent vertex with a missing rhenium atom. The Re–(μ-S) distances that are roughly *trans* to a Re–P bond are noticeably (by 0.05 Å) longer than those *trans* to the Re–Br bond. The two types of Re–P distances also differ, the one *trans* to μ_3-S ligand being *ca.* 0.03 Å shorter (see Table 1). The specific coordination of the diphosphane ligands results in cubane-type sulfido clusters with backbone chirality.

The mixed-halide $[Re_3S_4(dppe)_3Br_{1.6}Cl_{1.4}]Br\cdot4.5CH_2Cl_2$ ([**2**]Br·4.5CH_2Cl_2) cluster is isolated when dichloromethane is used as a reaction solvent, even at room temperature, or upon crystallization of [**1**]Br from the dichloromethane/ether mixture. Halogen composition of $\mathbf{2}^+$ was determined by X-ray diffraction and confirmed by ES mass spectrometry. A similar situation has

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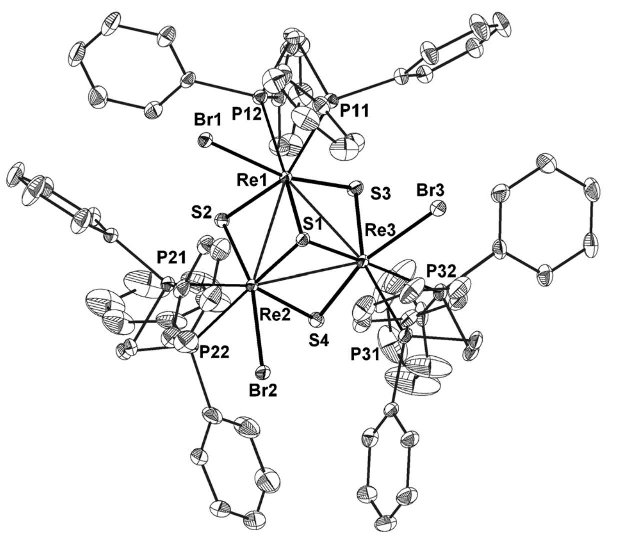

Fig. 1 Molecular structure of 1^+ cluster cation depicting thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity.

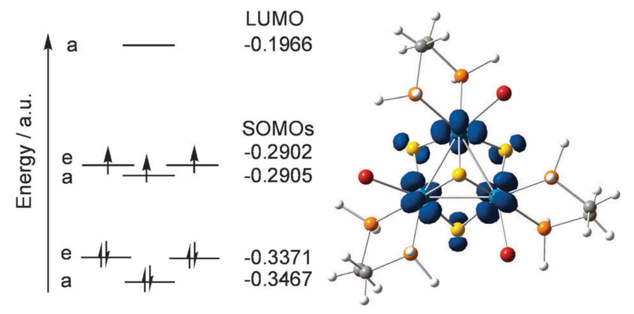

Fig. 2 Schematic MO diagram and isocontour plot of unpaired electron spin density for 1^+ calculated at the DFT level (cut-off value 0.02).

also been observed in their homologous molybdenum and tungsten cluster complexes but only at high temperatures.[11] This observation suggests that 1^+ can activate C–Cl bonds at room temperature. Halogen substitution doesn't have a significant effect on the cluster unit geometry (see Table 1).

In spite of the structural similarities existing between the Re_3S_4 cluster unit and the molybdenum and tungsten M_3Q_4 cores, their electronic count differs by three CSE. According to the Cotton–Haas scheme, six CSE enter the low energy $1a_1$ and 1e metal cluster orbitals which in the case of Mo and W clusters results in electron precise species with three M–M bonds.[13] For rhenium, the three extra electrons would occupy $2a_1$ and 2e orbitals which are predicted to be approximately M–M non-bonding. This non-bonding character is in agreement with the fact that Re–Re distances in 1^+ and 2^+ differ only slightly from Mo–Mo bond lengths in Mo_3S_4 clusters with 6 CSE (Table 1). However, discrepancies exist regarding the energy ordering and character of these last orbitals which are certainly influenced by the nature of the ligands.[3,14] To get a deeper insight into the electronic structure of the Re_3S_4 core we decided to investigate the magnetic properties of 1^+ in combination with DFT calculations.

Magnetic susceptibility measurements of [**1**]Br·3MeCN show an almost constant μ_{eff} value (Fig. S1, ESI†) in the 30–300 K temperature range, as expected for a nearly perfect paramagnetic system. Unexpectedly, at 300 K μ_{eff} equals 3.87 BM in agreement with the presence of three unpaired electrons per formula unit. This fact makes clusters with Re_3S_4 cores attractive building blocks for the construction of high-spin arrays. Due to its paramagnetic nature [**1**]Br does not show any signals in the $^{31}P\{^1H\}$ NMR-spectrum.

A DFT study at the B3LYP level has been carried out using $[Re_3S_4(H_2PCH_2CH_2PH_2)_3Br_3]^+$ as a molecular model of 1^+. The experimental geometry is well reproduced by gas-phase geometry optimizations (Table S4, ESI†). The cluster cation presents a quadruplet ground state lying 4.61 kcal mol^{-1} below the doublet state. Fig. 2 shows the orbital energy ordering in the SOMO–LUMO region together with an isocontour plot of the unpaired electron spin density for 1^+. Within the C_3 symmetry of the cluster, the three extra CSE occupy almost degenerate metal–metal non-bonding orbitals of symmetry a and e to afford an unusual high spin configuration for the incomplete cuboidal Re_3S_4 cluster complex. The molecular orbital overlap population between rhenium atoms for the three SOMO has been calculated (Table S5, ESI†), yielding values of 0.006, −0.024 and −0.011. These values are close to zero proving the non-bonding M–M character of these orbitals. Unpaired electrons are basically located on the metal atoms (65%) and to a lower extent on the bridging sulfides (35%).

The calculated electronic structure for 1^+ was confirmed by variable temperature EPR studies. A single line with parallel and perpendicular components at *ca.* 5200 and 12 900 G (corresponding to g = 4.70 and 1.90, respectively) emerges below 100 K (Fig. 3), suggesting that the three unpaired electrons are delocalized over the three Re centres at high temperatures but they progressively become localized as the temperature decreases below 100 K.

Table 1 Selected bond lengths in [**1**]Br, [**2**]Br and their Mo analogues

Average distance[a]/Å	[**1**]Br·3MeCN	[**2**]Br·4.5CH$_2$Cl$_2$	$[Mo_3S_4(dmpe)_3Cl_3]PF_6$	$[Mo_3S_4(dppe)_3Br_{0.75}Cl_{2.25}](BF_4)_{0.5}Cl_{0.5}$
M–M	2.780[9]	2.775[4]	2.766(4)	2.777[6]
M–(μ$_3$-S)	2.344[4]	2.340[5]	2.360(9)	2.359[5]
M–(μ-S)[b]	2.327[5]	2.336[10]	2.336(7)	2.320[4]
M–(μ-S)[c]	2.283[9]	2.296[13]	2.290(7)	2.280[5]
M–Hal	2.586[12]	2.549[11]	2.473(7)	2.51[4]
M–P[d]	2.536[15]	2.522[7]	2.605(8)	2.658[12]
M–P[e]	2.511[8]	2.504[7]	2.536(8)	2.576[6]
Reference	This work	This work	**10**	**11**

[a] Standard deviations for averaged values are given in square brackets. [b] Distance *trans* to the M–P bond. [c] Distance *trans* to the M–Hal bond. [d] Distance *trans* to the M–(μ-S) bond. [e] Distance *trans* to the M–(μ$_3$-S) bond.

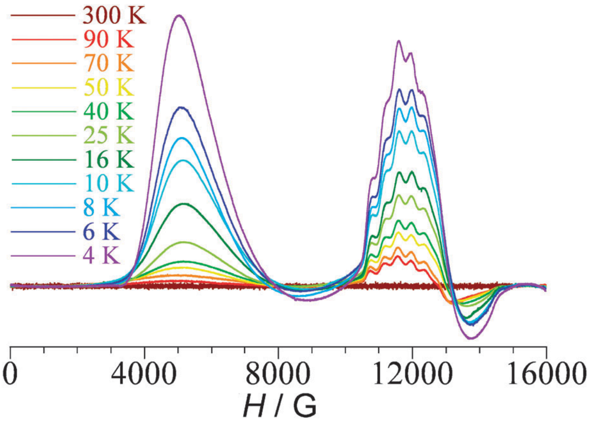

Fig. 3 Thermal variation of the EPR spectrum of [**1**]Br·3MeCN in the 4–300 K range.

Electron density localization below 100 K is confirmed by the presence of hyperfine coupling of *ca.* 375 G clearly observed in the perpendicular component as a group of six lines. This coupling arises from the coupling of the electron spin with the nuclear spin $I = 5/2$ of the ^{185}Re and ^{187}Re isotopes (with natural abundances of 37.4 and 62.6%, respectively). This result agrees with the MO calculations that locate most of the spin density on the Re $d_{x^2-y^2}$ orbital. The thermal dependence of the EPR signal shows an almost paramagnetic behaviour from *ca.* 100 to 30 K and a decrease of μ_{eff} below *ca.* 30 K in agreement with the behaviour observed in the SQUID magnetic measurements.

Thus it has been shown that the $[Re_3(\mu_3\text{-}S)(\mu\text{-}S)_3(dppe)_3X_3]^+$ clusters can be prepared by the reaction of $[Re_3S_7Br_6]Br$ with dppe. The quadruplet ground state of these compounds makes them promising building blocks for heterospin magnetic arrays.

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Notes and references

‡ All manipulations were performed under a purified argon atmosphere using the standard Schlenk technique. The solvents were degassed and dried and distilled prior to use. Magnetic measurements were performed using a Quantum Design MPMS SQUID magnetometer. Preparation of $[Re_3(\mu_3\text{-}S)(\mu\text{-}S)_3(dppe)_3Br_3]Br\cdot 3MeCN$ ([**1**]Br·3MeCN): a mixture of $Re_3S_7Br_7$ (236 mg, 0.176 mmol) and dppe (373 mg, 0.936 mmol) was refluxed in MeCN (20 mL) for 12 h. Dark brown solution was filtered through celite to remove the black residue, evaporated to half of volume *in vacuo* and left at +5 °C. Black crystals were collected in several days. Yield 60 mg (15%). Found: C, 42.8; H, 3.3%. Calc. for $C_{78}H_{72}Br_4P_6Re_3S_4$: C, 42.55; H, 3.30%. UV-VIS, λ_{max}(MeCN)/nm 560sh (log ε/dm^3 mol^{-1} cm^{-1} 3.32), 630sh (3.13), 830 (2.70). ES-MS (MeCN), *m*/*z*: 2121.9 ($[Re_3S_4(dppe)_3Br_3]^+$, 6%).

$[Re_3(\mu_3\text{-}S)(\mu\text{-}S)_3(dppe)_3Br_{1.6}Cl_{1.4}]Br\cdot 4.5CH_2Cl_2$ ([**2**]Br·4.5CH$_2$Cl$_2$): a mixture of $Re_3S_7Br_7$ (356 mg, 0.265 mmol) and dppe (530 mg, 1.330 mmol) was stirred in CH_2Cl_2 (20 mL) for 24 h. Dark brown solution was filtered through celite to remove the black residue and evaporated *in vacuo*. The dark residue was washed with Et_2O (3 × 10 mL), re-dissolved in 10 mL CH_2Cl_2 and filtered. Et_2O (15 mL) was layered over this solution to form black crystals. Yield 130 mg (20%). Found: C, 39.3; H, 3.2%. Calc. for $C_{82.5}H_{81}Br_{2.6}Cl_{10.4}P_6Re_3S_4$: C, 39.29; H, 3.24%. UV-VIS, λ_{max}(MeCN)/nm 400sh (log ε/dm^3 mol^{-1} cm^{-1} 3.67), 445sh (3.47), 545sh (3.30), 820 (2.28). ES-MS (MeCN), *m*/*z*: 2122.1 ($[Re_3S_4(dppe)_3Br_3]^+$, 4%), 2078.1 ($[Re_3S_4(dppe)_3Br_2Cl]^+$, 9%), 2032.1 ($[Re_3S_4(dppe)_3BrCl_2]^+$, 6%), 1988.2 ($[Re_3S_4(dppe)_3Cl_3]^+$, 2%).

§ Crystal data were collected using a Bruker X8APEX CCD diffractometer with MoKα radiation (λ = 0.71073 Å) and a graphite monochromator. A semiempirical absorption correction was applied based on equivalent reflections. [**1**]Br·3MeCN: $C_{84}H_{81}Br_4N_3P_6Re_3S_4$, M = 2324.82 g mol^{-1}, monoclinic, $C2/c$, a = 44.6606(12) Å, b = 13.7072(4) Å, c = 29.2555(8) Å, β = 98.4630(10)°, V = 17714.4(9) Å^3, Z = 8, ρ_{calcd} = 1.743 g cm^{-3}, μ = 6.140 mm^{-1}, T = 100.0 K. 54 964 reflections (26 356 unique) in the θ range 1.68–31.62°, R_{int} = 0.0234, R_1 [21 811 $I > 2\sigma(I)$] = 0.0339, wR_2 (all data) = 0.0976 for 975 parameters. GOF = 1.049. CCDC 855429. [**2**]Br·4.5CH$_2$Cl$_2$: $C_{82.5}H_{81}Br_{2.6}Cl_{10.4}P_6Re_3S_4$, M = 2521.58 g mol^{-1}, triclinic, $P\bar{1}$, a = 13.6395(3) Å, b = 15.3991(3) Å, c = 22.8431(5) Å, α = 80.5320(10)°, β = 72.6390(10)°, γ = 83.4320(10)°, V = 4506.04(17) Å^3, Z = 2, ρ_{calcd} = 1.857 g cm^{-3}, μ = 5.723 mm^{-1}, T = 100.0 K. 47 320 reflections (23 261 unique) in the θ range 1.89–31.57°, R_{int} = 0.0273, R_1 [17 767 $I > 2\sigma(I)$] = 0.0497, wR_2 (all data) = 0.1290 for 1032 parameters and 11 restraints. GOF = 1.059. CCDC 855430.†

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