$(NBu^n{}_4{}^+)_3[Re_6S_8Cl_6]^{3-\cdot}$: synthesis and luminescence of the paramagnetic, open shell member of a hexanuclear chalcohalide cluster redox system

Christophe Guilbaud,[a] André Deluzet,[a] Benoît Domercq,[a] Philippe Molinié,[a] Claude Coulon,[b] Kamal Boubekeur[a] and Patrick Batail*[a]

[a] *Institut des Matériaux Jean Rouxel, UMR 6502 CNRS-Université de Nantes, 2, rue de la Houssinière, 44322 Nantes, France. E-mail: patrick.batail@cnrs-imn.fr*
[b] *Centre de Recherche Paul Pascal, CNRS, Avenue Dr. Schweitzer, 33600 Pessac, France*

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The chemical and electrochemical synthesis, X-ray crystal structure, magnetic characterization, absorption and luminescence spectra of $(NBu^n{}_4)_3[Re_6S_8Cl_6]$, the 23-electron cluster core member of the reversible redox couple $[Re_6S_8Cl_6]^{4-}$–$[Re_6S_8Cl_6]^{3-\cdot}$ is reported.

Amongst the series of molecular, hexanuclear sulfidohalide and sulfido cluster anions, $(NBu^n{}_4{}^+)_n[Re_6S_{4+n}Cl_{4-n}Cl_6]^{n-}$ (n = 1–4),[1,2] the latter tetra-anion stands out because of its unusual redox behaviour, characterised by a reversible one-electron oxidation process at the remarkably low potential of $E_{1/2} = 0.27$ V *vs.* SCE in acetonitrile.[2] This is a salient feature since, within this set of isostructural and isoelectronic cluster anions, either no oxidation ($n = 1$) or reversible oxidation processes (n = 2,3) are observed albeit at the higher potential values of 0.99 ($n = 2$) and 1.04 ($n = 3$) V *vs.* SCE.[1] Both the low potential value, which qualifies $[Re_6S_8Cl_6]^{4-}$ as an electron donor comparable to tetrathiafulvalene (0.33 V *vs.* SCE in acetonitrile), and the reversible character of the redox process suggest that the paramagnetic 23-electron Re_6 cluster core anion might be isolated, an unprecedented opportunity in this chemistry of molecular forms of mineral clusters prepared by high temperature solid state synthesis.

Reactions of acetonitrile solutions of $(NBu^n{}_4)_4[Re_6S_8Cl_6]$[2] with $SOCl_2$, ferrocenium or $TCNQF_4$ afford crystalline precipitates the X-ray powder pattern of which differs from that of the starting material, and appears very similar to those of $(NBu^n{}_4)_3[Re_6S_7Cl_7]$[3,4] and $(NBu^n{}_4)_3[Re_6S_7(SH)Cl_6]$[2] simulated from the single crystal X-ray structure data. Thus, an excess of $SOCl_2$ (0.8 mL) was added under stirring at room temperature to a yellow solution of $(NBu^n{}_4)_4[Re_6S_8Cl_6]$ (263 mg, 0.1 mmol) in acetonitrile (30 mL), upon which the solution rapidly turned red. After 30 min, the solution was evaporated to dryness and the residual solid washed with water, ethanol and toluene, then dried under vacuum. Crystallisation in acetonitrile–ethanol (2 : 1) afforded red orange plate-like crystals (yield 221 mg, 93%).

Red single crystals were grown by anodic, constant low direct current oxidation (1.6 μA cm^{-2}) at a platinum wire electrode of a solution of 60 mg of $(NBu^n{}_4)_4[Re_6S_8Cl_6]$ dissolved in 12 mL THF–DMF (3 : 1). The solution slowly turned from yellow to pink red in the anodic compartment of the two-compartment electrocrystallization cell within a few days. The crystals harvested after 10 days lose THF molecules and recrystallisation of the latter in acetonitrile yielded high quality red orange stable single crystals which are identical to those obtained by the chemical route described above (Anal. for $C_{48}H_{108}Cl_6N_3Re_6S_8$. Calc.: C, 24.91; H, 4.75; N, 1.82; S, 11.08; Cl, 9.19. Found: C, 24.87; H, 4.61; N, 1.78; S, 11.13; Cl, 9.25%). In order to ensure that both the chemical and electrochemical syntheses were conducted on pristine $(NBu^n{}_4)_4[Re_6S_8Cl_6]$, with no $(NBu^n{}_4)_3[Re_6S_7Cl_7]$, the purity of the starting material has been qualified by X-ray powder pattern and elemental analysis.

The X-ray structure determination reveals that a single phase, formulated as $(NBu^n{}_4)_3[Re_6S_8Cl_6]$, is obtained by the two routes and is isostructural to triclinic $(NBu^n{}_4)_3[Re_6S_7Cl_7]$,[4] containing the closed shell, 24-electron cluster core trianion prepared by metathesis of solutions of $Cs_3[Re_6S_7Cl_7]$.[3] The asymmetric unit consists of two half-clusters located on inversion centres and three tetrabutylammonium cations in general positions. The analysis of the structure determined at room temperature indicates that the Re–Re bond lengths within the cluster core (Fig. 1) [$<d_{Re–Re}> = 2.600(1)$ Å] and the Re–(inner)μ$_3$-S bond lengths [$<d_{Re–S}> = 2.408(3)$ Å] are similar to those observed in the structure of $(NBu^n{}_4{}^+)_4[Re_6S_8Cl_6]^{4-}$, $<d_{Re–Re}> = 2.601(4)$ Å and $<d_{Re–S}> = 2.403(9)$ Å, respectively.[2] Of particular interest is the present opportunity to extend the structural correlation between the lengthening of the rhenium–μ-chloride distances with the increase of the net cluster anion charge revealed previously within the series of cluster anion forms with the same counter cation, $(NBu^n{}_4{}^+)_n$-$[Re_6S_{4+n}Cl_{4-n}Cl_6]^{n-}$ [from 2.344(4), to 2.362(2), to 2.415(3) Å for n = 1, 2, 3, respectively).[1,4] Thus, $<d_{Re–Cl}> = 2.418(3)$ Å for $[Re_6S_8Cl_6]^{3-\cdot}$ is shorter than $<d_{Re–Cl}> = 2.451(4)$ Å determined for $(NBu^n{}_4{}^+)_4[Re_6S_8Cl_6]^{4-}$,[2] as expected.[1] This is also consistent with theoretical calculations for $[Re_6S_8X_6]^{4-}$ (X = Cl, Br, I) made available recently by Arratia-Perez *et al.*[5] which demonstrate that the pronounced halogen-based cluster HOMO has a large Re–(apical)halide antibonding character. In addition, $<d_{Re–Cl}> = 2.418(3)$ Å for $(NBu^n{}_4{}^+)_3[Re_6S_8Cl_6]^{3-\cdot}$ is identical to that obseved for the triclinic structure of $(NBu^n{}_4{}^+)_3[Re_6S_7Cl_7]^{3-}$ [$<d_{Re–Cl}> = 2.415(3)$ Å][4] and to that determined for $(NBu^n{}_4{}^+)_3[Re_6S_6(SH)Cl_7]^{3-}$ [$<d_{Re–Cl}> = 2.419(6)$ Å].[2]

The paramagnetic character of $(NBu^n{}_4{}^+)_3[Re_6S_8Cl_6]^{3-\cdot}$ is demonstrated both by (i) static magnetic susceptibility data, properly fitted to a Curie law down to low temperatures (C = 0.523 cm^3 mol^{-1}) with a calculated effective magnetic moment ($\mu_{eff} = 2.045\ \mu_B$) larger than the spin ½-only value (μ_{SO} = 1.73

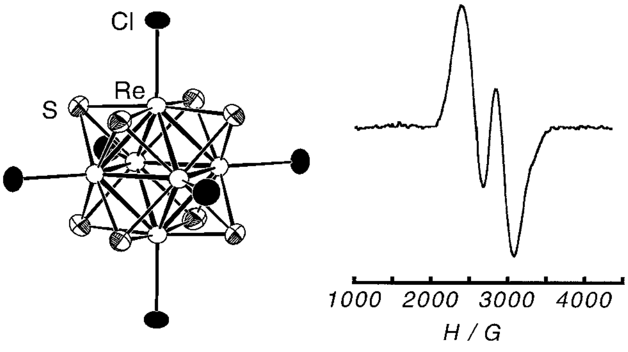

Fig. 1 Structure with thermal ellipsoids at the 50% probability level, labelling scheme and EPR spectrum of a single crystal of $(NBu^n{}_4)_3$-$[Re_6S_8Cl_6]$ at 3.8 K. The two broad resonance lines with $g = 2.44$ and ΔH = 260 G are associated with two different orientations of the cluster in the triclinic unit cell.

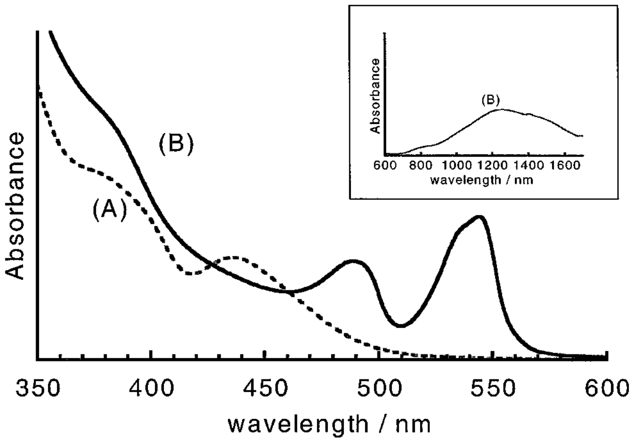

Fig. 2 Electronic absorption spectra for acetonitrile solutions (c = 2.8 × 10^{-4} M) of $(\mathrm{NBu^n_4})_4[\mathrm{Re_6S_8Cl_6}]$ [(A) two poorly resolved shoulders at 335 and 380 nm and a peak of larger intensity at 436 nm (ε_M = 8.6 × 10^2 dm^3 mol^{-1} cm^{-1})] and $(\mathrm{NBu^n_4})_3[\mathrm{Re_6S_8Cl_6}]$ [(B), one poorly resolved shoulder (381 nm), two large peaks (489 nm, ε_M = 8.5 × 10^2 dm^3 mol^{-1} cm^{-1}; 544 nm, ε_M = 1.23 × 10^3 dm^3 mol^{-1} cm^{-1}) and a very wide band centred around 1250 nm (700–1750 nm, ε_M = 4 × 10^2 dm^3 mol^{-1} cm^{-1})].

μ_B), a manifestation of spin–orbit coupling; and (ii) by single crystal EPR experiments (g = 2.44, Fig. 1). The g values for the paramagnetic hexanuclear molybdenum cluster anions $[\mathrm{Mo_6(X_7Q)X_6}]^{2-\cdot}$ (X = Cl, Br, Q = S, Se) and $[\mathrm{Mo_6(Cl_6Se_2)Cl_6}]^{3-\cdot}$ obtained in frozen solution at 77 K are in the range 2.05–2.23.[6,7] The higher g value observed for the present rhenium cluster is consistent with a higher spin–orbit coupling.

The UV–VIS spectrum for $(\mathrm{NBu^n_4}^+)_4[\mathrm{Re_6S_8Cl_6}]^{4-}$ in acetonitrile (Fig. 2) is essentially identical to that reported earlier by Holm and coworkers except for the absence in Fig. 2 of a weak peak at 537 nm.[2] Within the series $[\mathrm{Re_6S_{4+\mathit{n}}Cl_{4-\mathit{n}}Cl_6}]^{n-}$, the intense absorption at 436 nm for the tetra-anion (n = 4) is remarkable since it is not observed for n = 1, 2, 3[8] and has been shown[2] to be very sensitive to the nature of the apical halide, a likely indication of ligand-to-metal charge transfer. The spectrum for acetonitrile solutions of $(\mathrm{NBu^n_4}^+)_3[\mathrm{Re_6S_8Cl_6}]^{3-\cdot}$ (Fig. 2) is strikingly different from the former. These salient differences between the spectra in Fig. 2 demonstrate that a significant change of the electronic structure of the cluster anion occurs upon the one-electron oxidation. The wide near-IR absorption band may be attributed to electronic transitions from a fully to a partially occupied metal orbital. A similar absorption band has been observed for the paramagnetic hexanuclear molybdenum clusters anions $[\mathrm{Mo_6(X_7Q)X_6}]^{2-\cdot}$ (X = Cl, Br, Q = S, Se) and $[\mathrm{Mo_6(Cl_6Se_2)Cl_6}]^{3-\cdot}$.[6,7]

Emission spectra for acetonitrile solutions of $[\mathrm{Re_6S_8Cl_6}]^{4-}$ and $[\mathrm{Re_6S_8Cl_6}]^{3-\cdot}$ are shown in Fig. 3(a) and (b), respectively, for excitations at 250 and 393 nm. As anticipated by Arratia-Pérez *et al.*,[5] the tetra-anion $[\mathrm{Re_6S_8Cl_6}]^{4-}$ is luminescent. Altogether, the luminescence for the tetra-anion is very similar to that for the hexanuclear molybdenum(II) cluster $[\mathrm{Mo_6Cl_{14}}]^{2-}$.[9,10] Note that the mono-, di-, and tri-anion within the chalcohalide series $[\mathrm{Re_6S_{4+\mathit{n}}Cl_{4-\mathit{n}}Cl_6}]^{n-}$ (n = 1, 2, 3) do not present any such luminescence.

Strikingly, the luminescence spectra for acetonitrile solutions of $(\mathrm{NBu^n_4}^+)_3[\mathrm{Re_6S_8Cl_6}]^{3-\cdot}$ [Fig. 3(b)] exhibit emission bands which are typically more intense than those for solutions of $(\mathrm{NBu^n_4}^+)_4[\mathrm{Re_6S_8Cl_6}]^{4-}$. Time-resolved photoluminescent experiments in solution as well in the solid state are in progress in order to elucidate the nature of the excited state of the paramagnetic radical cluster anion in $(\mathrm{NBu^n_4}^+)_3[\mathrm{Re_6S_8Cl_6}]^{3-\cdot}$.

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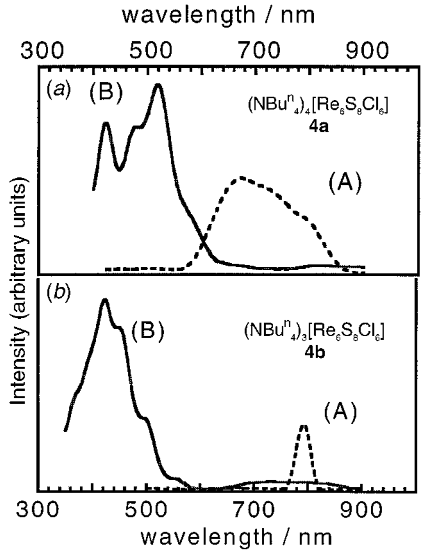

Fig. 3 (a) Luminescence spectra for an acetonitrile solution of $(\mathrm{NBu^n_4})_4[\mathrm{Re_6S_8Cl_6}]$ (5 × 10^{-4} M) for excitations at 393 nm [(A), maximum at 660 nm] and 250 nm [(B), maxima at 418, 460 and 497 nm]. (b) Luminescence spectra for an acetonitrile solution of $(\mathrm{NBu^n_4})_3[\mathrm{Re_6S_8Cl_6}]$ (1.4 × 10^{-4} M) for excitations at 393 nm [(A), maximum at 796 nm] and 250 nm [(B), maxima at 420, 455 and 500 nm].

Notes and references

† *Crystal structure analysis* for $(\mathrm{NBu^n_4})_3[\mathrm{Re_6S_8Cl_6}]$: $\mathrm{C_{48}H_{108}Cl_6N_3Re_6S_8}$, triclinic, space group $P\bar{1}$, a = 12.378(1), b = 17.229(1), c = 18.205(2) Å, α = 96.39(1), β = 106.33(1), γ = 103.57(1)°, V = 3555.6(12) Å^3, D_c = 2.161 g cm^{-3}, Z = 2. Red–orange plate-like crystal (0.56 × 0.23 × 0.02 mm). Data were collected at 293 K on a Stoe IPDS single ϕ axis diffractometer with a 2D area detector based on imaging plate technology with Mo-Kα radiation (λ = 0.71073 Å) (250 frames recorded using the rotation method ($0 \leqslant \phi \leqslant 250°$) with $\Delta\phi$ = 1° increments, an exposure time of 5 min and a crystal-to-plate distance of 60 mm).[11] A total of 35884 reflections were collected up to θ = 25.8° of which 13220 are independent among 9098 observed $[F_o^2 > 2\sigma(F_o^2)]$. The structure solution (SHELXS-86)[12] and refinements on F_o^2 (SHELXL-97)[13] gave R(obs.) = 0.0329 [R(all) = 0.0546)] and R_w(obs.) = 0.0674 [R_w(all) = 0.0712] for 669 parameters and two restraints; min. and max. residual electron densities were 1.78 and 1.76 e Å^{-3}.

CCDC 182/1360. See http://www.rsc.org/suppdata/cc/1999/1867/ for crystallographic files in .cif format.

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