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Isolation of the Single Cubane-like Re–S–Cu–Cl Cluster $[ReS_4(CuCl)_3Cl]^{2-}$

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The tetrathiometallate anions of Mo(VI) and W(VI) have been used widely in transition metal coordination chemistry, often as bidentate ligands to a later transition metal [1]. Other syntheses employing these $[MS_4]^{2-}$ ions have led to the formation of cubane-like clusters including M'_3MS_4 (M' = Fe) [2], M'_3MS_3Cl, and $M'_4M_2S_6$ (M' = Cu or Ag) frameworks [1, 3, 4]. Recently, the first example of a Re–S–Cu–Cl cluster, $[ReS_4Cu_5Cl_7]^{3-}$, was reported and shown to possess a novel double cubane-like structure [5]. Herein we report the synthesis, structural, spectroscopic and electrochemical characterization of $[ReS_4(CuCl)_3Cl]^{2-}$, the first example of a single cubane-like Re–S–Cu–Cl cluster.

$[NPr^n_4][ReS_4]$ [6] was allowed to react with CuCl (1:3) in degassed MeCN overnight at room temperature; emerald green crystals of $[NPr^n_4]_2[ReS_4(CuCl)_3Cl]$ were obtained by slow addition of diethyl ether and cooling to 0 °C. *Anal.* Calc. for $C_{24}H_{56}N_2Cl_4Cu_3ReS_4$: C, 28.3; H, 5.5; N, 2.7; Cl, 13.9; Cu, 18.7; Re, 18.3; S, 12.6. Found: C, 29.2; H, 5.8; N, 3.2; Cl, 14.0; Cu, 18.7; Re, 16.9; S, 12.2%. These crystals proved suitable for X-ray crystallographic investigation. $[NPr^n_4]_2[ReS_4(CuCl)_3Cl]$ crystallizes in the orthorhombic space group *Pccn* with $a = 28.147(8)$, $b = 17.943(4)$ and $c = 16.316(4)$ Å, $U = 8240$ Å^3, $Z = 8$, $D_c = 1.644$ g cm^{-3}, $F(000) = 4064$, $\mu = 4.98$ mm^{-1} for Mo Kα radiation ($\lambda = 0.71073$ Å). Data were collected to $2\theta_{max} = 45°$ on a Siemens AED2 diffractometer at room temperature and corrected semiempirically for absorption. The structure was solved by heavy atom methods and refined by least-squares on F with $w^{-1} = \sigma^2(F)$, anisotropic thermal parameters for atoms of the anion, and geometrical restraints for the cations (C–C = 1.5 Å, C–C–C = 109.5°). For 3016 reflections with $F > 4\sigma(F)$, $R = 0.156$ and $R_w = 0.102$.

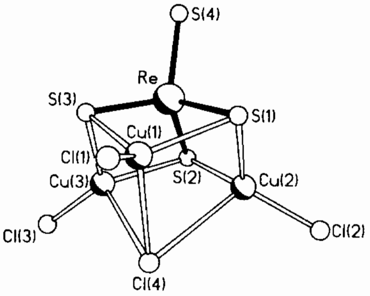

Fig. 1. Structure of $[ReS_4(CuCl)_3Cl]^{2-}$.

TABLE I. Dimensions of $[ReS_4(CuCl)_3Cl]^{2-}$ [a]

Bond	Length (Å)	Atoms	Angle (°)
Re–S(1)	2.20	S(1)–Re–S(4)	108.6
Re–S(2)	2.24	S(2)–Re–S(4)	109.5
Re–S(3)	1.93	S(3)–Re–S(4)	109.8
Re–S(4)	2.10	S(1)–Re–S(2)	108.3
		S(1)–Re–S(3)	114.2
		S(2)–Re–S(3)	106.5
Cu(1)–Cl(1)	2.19		
Cu(2)–Cl(2)	2.11	Cl(1)–Cu(1)–Cl(4)	115.5
Cu(3)–Cl(3)	2.11	Cl(2)–Cu(2)–Cl(4)	116.6
		Cl(3)–Cu(3)–Cl(4)	111.9
Cu(1)–Cl(4)	2.58		
Cu(2)–Cl(4)	2.87	Cl(1)–Cu(1)–S(1)	118.5
Cu(3)–Cl(4)	2.74	Cl(1)–Cu(1)–S(3)	127.7
		Cl(2)–Cu(2)–S(1)	124.9
Cu(1)–S(1)	2.32	Cl(2)–Cu(2)–S(2)	116.8
Cu(1)–S(3)	2.31	Cl(3)–Cu(3)–S(2)	118.7
Cu(2)–S(1)	2.28	Cl(3)–Cu(3)–S(3)	127.7
Cu(2)–S(2)	2.19		
Cu(3)–S(2)	2.27	Cl(4)–Cu(1)–S(1)	97.8
Cu(3)–S(3)	2.08	Cl(4)–Cu(1)–S(3)	94.2
		Cl(4)–Cu(2)–S(1)	91.2
Re---Cu(1)	2.63	Cl(4)–Cu(2)–S(2)	93.1
Re---Cu(2)	2.61	Cl(4)–Cu(3)–S(2)	94.7
Re---Cu(3)	2.60	Cl(4)–Cu(3)–S(3)	95.0
		S(1)–Cu(1)–S(3)	97.0
		S(2)–Cu(2)–S(1)	107.2
		S(2)–Cu(3)–S(3)	100.1

[a] e.s.d.s are 0.01 Å and 0.5°.

Unfortunately, the C_3H_7 chains of the cations are significantly disordered and/or subject to very high thermal motion, which reduced the overall precision of the refinement; however, the positions of all of the atoms of the anion are well defined. The structure of the anion is shown in Fig. 1 and comprises a cubane-like $Re(\mu_3\text{-}S)_3Cu_3(\mu_3\text{-}Cl)$ framework, with the coordination about each metal being completed by bonding to an atom external to the cluster, in an arrangement analogous to that of $[MoS_4(CuPPh_3)_3Cl]$ [4]. The dimensions of the cluster are summarized in Table I, and it is observed that the major irregularity in the cubane frame is the relatively long distance from each copper to the μ_3-Cl atom (Cl(4)).

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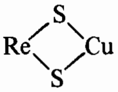
This leads to a significantly distorted tetrahedral coordination geometry at each copper, whereas the ReS_4 moiety closely approximates to a tetrahedron. The average length of the Re–S bonds for $[ReS_4(CuCl)_3Cl]^{2-}$ (2.12 Å) is slightly shorter than that (2.29 Å) for the double cubane, $[ReS_4Cu_5Cl_7]^{3-}$ [5], presumably as a consequence of the former involving one terminal and three μ_3-S atoms whereas the latter involves four μ_4-S atoms. The Re---Cu separations over the



rhombs is similar in each of these Re–S–Cu–Cl structures (2.61 and 2.65 Å, respectively). Also, each cluster involves Cu–Cl(terminal) bonds of length *ca.* 2.15 Å and Cu–S(bridging) bonds of length *ca.* 2.25 Å and the average Cu–Cl(bridging) distance is similar (*ca.* 2.8 Å) even though the range of these last distances is much narrower for $[ReS_4(CuCl)_3Cl]^{2-}$ (2.58–2.87 Å) than for $[ReS_4Cu_5Cl_7]^{3-}$ (2.50–3.32 Å).

$[NPr^n_4]_2[ReS_4(CuCl)_3Cl]$ dissolves in MeCN to give a purple coloured solution [λ_{max} (nm) (ϵ (dm^3 mol^{-1} cm^{-1})) 538(3375) 319(11600) 258(12340)] the lowest energy band experiencing a red shift from that (508 nm) of $[NPr^n_4][ReS_4]$. The IR spectrum of a nujol mull of $[NPr^n_4]_2[ReS_4(CuCl)_3Cl]$ contains bands at 525, 470, and 439 cm^{-1} and the powdered solid shows clear Raman effects at *ca.* 520 and 440 cm^{-1}. We assign these vibrational modes, approximating the symmetry of the anion to C_{3v}, to the Re–S stretching modes as: A_1 (Re–S(terminal)) 525 cm^{-1}; E (Re–S(assym. bridging)) 470 cm^{-1}; A_1 (Re–S(symm. bridging)) 439 cm^{-1}.

Cyclic voltammetric studies of [NPrn4]2[ReS4-
bridging)) 470 cm^{-1}; A_1 (Re–S(symm. bridging)) 439 cm^{-1}.

Cyclic voltammetric studies of $[NPr^n_4]_2[ReS_4(CuCl)_3Cl]$ in MeCN solution, containing $[NBu^n_4][BF_4]$ as the carrier electrolyte, identified a reduction process at $E_{1/2} = -0.45$ V (*versus* S.C.E.) and $\Delta E_p = 160$ mV which compares with the reduction of $[ReS_4]^-$ at $E_{1/2} = -1.21$ V and $\Delta E_p = 90$ mV under the same conditions.

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