Synthesis, Crystal Structures, and Bonding of the Molybdenum Cubane Compounds $[Mo(\mu\text{-}C_5H_4Pr^i)(\mu^3\text{-}S)]_4{}^{n+}$, where $n = 0, 1,$ and 2

Judith A. Bandy,[b] **Cathryn E. Davies,**[a] **Jennifer C. Green,**[a] **Malcolm L. H. Green,**[a] **Keith Prout,**[b] **and Damian P. S. Rodgers**[a]

[a] *Inorganic Chemistry Department, South Parks Road, Oxford OX1 3QR, U.K.*
[b] *Chemical Crystallography Laboratory, 9 Parks Road, Oxford OX1 3PD, U.K.*

The compounds $[Mo(\eta\text{-}C_5H_4Pr^i)(\mu^3\text{-}S)]_4{}^{n+}$, where $n = 0, 1,$ or 2 have been prepared and *X*-ray crystal structure determinations show them to have a cubane structure: the compounds are related by reversible one electron oxidation–reduction reactions and the photoelectron spectrum for the neutral compound, $n = 0$, provides a description of the bonding in the cubane system.

Transition metal–sulphur cubane systems are of current interest since they occur in biological materials such as ferredoxins[1] and, possibly, in nitrogen fixing enzymes.[2]

During a study of organo-molybdenum–sulphur chemistry we found that treatment of the dimer $[Mo(\eta\text{-}C_5H_4Pr^i)(\mu\text{-}Cl)_2]_2$ (**1**) with lithium hydrosulphide gives the cubane compound $[Mo(\eta\text{-}C_5H_4Pr^i)(\mu^3\text{-}S)]_4$ (**2**) in good yield. Treatment of (**2**) with dilute aqueous acid causes oxidation to the cation $\{[Mo(\eta\text{-}C_5H_4Pr^i)(\mu^3\text{-}S)]_4\}^+$ (**3**) which was isolated as the tetrafluoroborate salt. Addition of iodine to a toluene solution of (**2**) results in a two-electron oxidation giving $\{[Mo(\eta\text{-}C_5H_4Pr^i)(\mu^3\text{-}S)]_4\}^{2+}$, (**4**), as the bis(tri-iodide) salt.

$[Mo(\eta\text{-}C_5H_4Pr^i)(\mu\text{-}Cl)_2]_2$
(**1**)

$[Mo(\eta\text{-}C_5H_4Pr^i)(\mu^3\text{-}S)]_4{}^{n+}$
(**2**) $n = 0$
(**3**) $n = 1$, $BF_4{}^-$ salt
(**4**) $n = 2$, $(I_3{}^-)_2$ salt

Reduction of (**4**) *via* (**3**) to (**2**) can be achieved using sodium amalgam.

Cyclic voltammetry studies on solutions in dimethylformamide using Et_4NClO_4 as the electrolyte show that the oxidations of (**2**) to (**3**) and then (**4**) are fully reversible; the data are given in Table 1.

The crystal structures of (**2**)—(**4**) have been determined. *Crystal data:* (**2**), $C_{32}H_{44}Mo_4S_4$, $M = 940.7$, monoclinic, space group $I2/c$, $a = 17.764(3)$, $b = 8.580(1)$, $c = 23.103(2)$ Å, $\beta = 107.72(1)°$, $U = 3354.3$ Å^3, $D_c = 1.86$ g cm^{-3}, $Z = 4$ (dimers), $R = 3.18\%$ ($R_w = 4.03\%$) for 5218 observed

Table 1. Cyclic voltammetric data for the compounds (**2**)—(**4**).[a]

Oxidation	$E^{1/2}$/V	E_p/mV	i_{p2}/I_{pc}
(**2**) → (**3**)	−0.33	60	1.0
(**3**) → (**4**)	0.32	60	1.0
[b]	0.43	65	1.0

[a] Millimolar solution of (**2**) in dimethylformamide–0.1 M Et_4NClO_4 oxidised at a Pt gauze electrode. Scan rate = 100 mV s^{-1}. [b] Data shown for ferrocene–ferrocinium redox couple *vs.* standard calomel electrode in accordance with 'Recommendations on Reporting Electrode Potentials in Non-aqueous Solvents,' ref. 3.

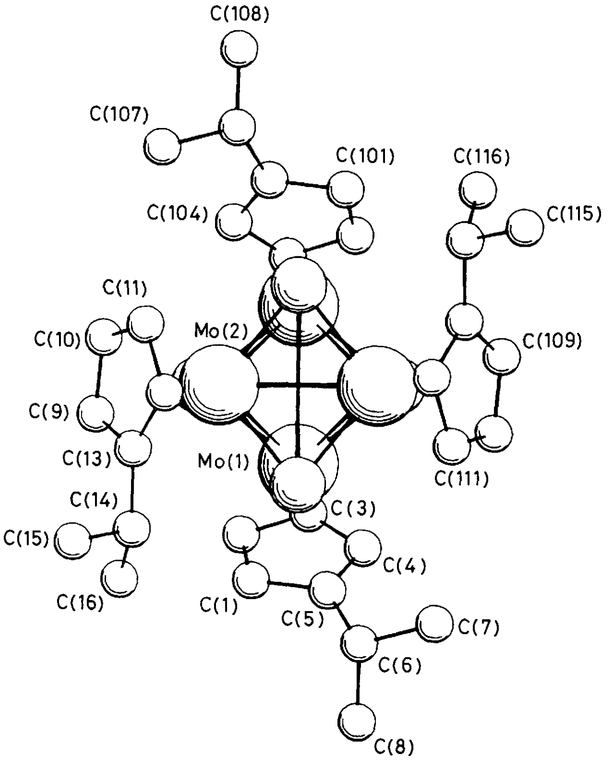

Figure 1. The crystal structure of (**2**).

reflections [$I > 3\sigma(I)$]. (**3**), $C_{32}H_{44}BF_4Mo_4S_4$, M = 1027.5, monoclinic, space group $P2_1/n$, a = 14.985(2), b = 12.612(2), c = 19.355(3) Å, β = 95.71(1)°, U = 3639.8 Å^3, D_c = 1.88 g cm^{-3}, Z = 4, R = 2.12% (R_w = 2.40%) for 5524 observed reflections. (**4**), $C_{32}H_{44}Mo_4S_4I_6$, M = 1702.1, monoclinic, space group $P2_1/n$, a = 10.971(2), b = 19.495(3), c = 21.927(8) Å, β = 101.78(2)°, U = 4590.8 Å^3, D_c = 2.46 g cm^{-3}, Z = 4, R = 3.65% (R_w = 4.67%) for 4589 observed reflections.† Data were collected on an Enraf-Nonius CAD-4F diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.71069 Å). The structures were solved using Patterson and direct methods and were refined, first isotropically and then anisotropically for all non-hydrogen atoms, by blocked full-matrix least squares. Hydrogen atoms were located but included in calculated positions which were modified between successive cycles of refinement.‡

The structure of (**2**) is shown in Figure 1. The Mo_4S_4 core in compounds (**2**)—(**4**) may be considered as a Mo_4 tetrahedron, each face being triply-bridged by sulphur. The S···S distances are non-bonding but each molybdenum atom takes part in three intermetallic bonds. The neutral cluster possesses a crystallographic two-fold axis which is not present in either of the cations. (Atoms generated by this two-fold axis are labelled by adding 100 to the corresponding atom number.) The cubane compound [$Mo(\eta\text{-}C_5H_5)(\mu^3\text{-}S)]_4$ has been described previously and the crystal structure has been reported.[4] However, it appears that a reliable synthesis has not been developed.

Important distances and angles are given in Table 2. These show that the removal of the two electrons causes only very slight and irregular decreases in the Mo–Mo distances and this is reflected in the volumes of the Mo_4 tetrahedra of (**2**)—(**4**) which are (**2**) 2.887, (**3**) 2.856, and (**4**) 2.749 Å^3 (e.s.d. 0.007 Å^3). In contrast, the related [$Fe(\eta\text{-}C_5H_5)(\mu^3\text{-}S)]_4^{n+}$ cubane systems, n = 0, 1, or 2, show regular changes.[5]

The photoelectron spectrum of (**2**) has been determined (Figure 2) and may be interpreted in terms of the M.O. scheme devised by Dahl *et al.* for $Fe_4(\eta\text{-}C_5H_5)S_4$.[5] In addition to the electrons used in binding the cyclopentadienyl rings (4 × 6 = 24) and forming Mo–S bonds (12 × 2 = 24) and sulphur 'lone-pair' electrons (4 × 2 = 8), there remain 12 excess electrons for metal cluster formation. Dahl's model assigns these twelve electrons to a_1, e, and t_2 bonding M.O.'s, though a calculation by Bottomley on the related cluster $Cr_4(\eta\text{-}C_5H_5)_4O_4$[6] suggests that the occupation in this case differs. The spectrum of (**2**) shows three ionisation bands with ionisation energy (I.E.) below 7.5 eV, with He-II/He-I intensity characteristics of ionisation from orbitals localised

Table 2. Important interatomic distances (Å) and angles (°).† Cp = cyclopentadienyl.

Compound[a]	(**1**)		(**2**)	(**3**)
Mo(1)–Mo(2)	2.912(1)[b] ×2	Mo(1)–Mo(2)	2.893(1)	2.861(1)
Mo(1)–Mo(101)	2.892(1)	Mo(1)–Mo(3)	2.887(1)	2.902(1)
Mo(1)–Mo(102)	2.902(1) ×2	Mo(1)–Mo(4)	2.860(1)	2.897(1)
Mo(2)–Mo(102)	2.905(1)	Mo(2)–Mo(3)	2.900(1)	2.820(1)
		Mo(2)–Mo(4)	2.901(1)	2.790(1)
		Mo(3)–Mo(4)	2.923(1)	2.879(1)
Mean bond distances and angles:				
Mo–Mo	2.904(3)		2.894(8)	2.858(18)
Mo–S	2.344 (2)		2.343(3)	2.343(2)
Mo–Mo–Mo	60.0(1)		60.0 (2)	60.0 (4)
Mo–S–Mo	76.56(9)		76.3 (2)	75.2 (4)
S–Mo–S	101.98(12)		102.2(3)	103.0(5)
Mo(1)–Cp	2.357(8)		2.360(12)	2.335(13)
Mo(2)–Cp	2.355(7)		2.346(9)	2.340(12)
Mo(3)–Cp			2.339(7)	2.319(18)
Mo(4)–Cp			2.346(9)	2.329(12)

[a] The numbering scheme does not imply that atoms with the same number in different clusters are equivalent. [b] E.s.d.s of means are calculated as $[\Sigma\Delta^2/n(n-1)]^{\frac{1}{2}}$ where Δ is the difference between each observed value and the mean, and n is the number of observations.

---

† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

‡ Crystallographic calculations were performed on the VAX 11/750 computer of the Chemical Crystallograhy Laboratory, Oxford, using the Oxford CRYSTALS pakage (ref. 7).

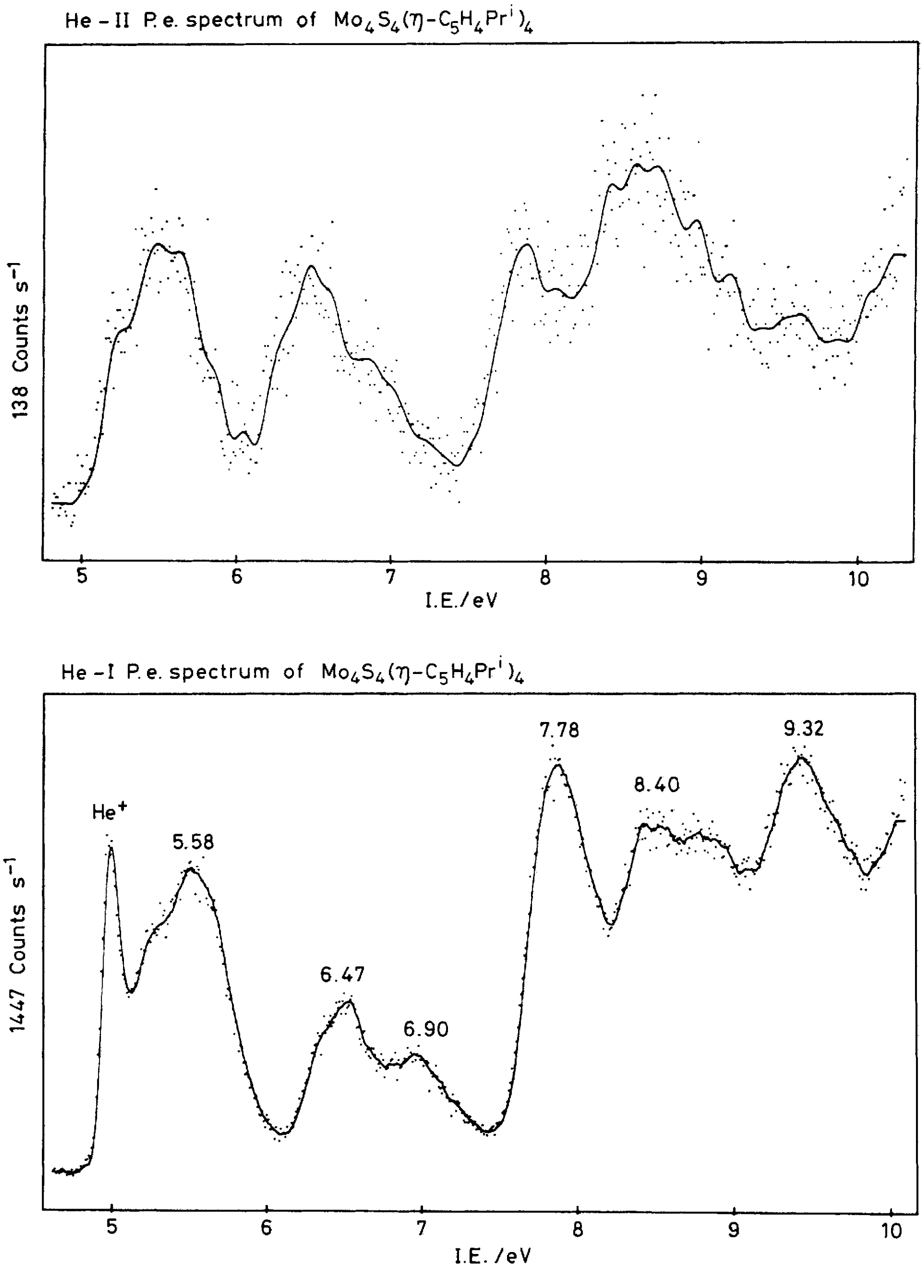

Figure 2. The photoelectron (p.e.) spectrum of (**2**).

on the metal atom. The relative band areas and band profiles strongly suggest an assignment of $^2T_2$ (split into ^2B and ^2E) (5.58 eV), ^2E (6.47 eV), and $^2A_1$ (6.90 eV) ion states consistent with a ground state configuration of $a_1^2\ e^4\ t_2^6$.

The substantial separation of the bands suggests that the e and a_1 orbitals are strongly bonding. The t_2 orbitals appear comparatively less stable, the first ionisation energy being rather low [5.0 (adiabatic), 5.2 (shoulder), 5.58 eV (vertical)] showing the cluster (**2**) to be extremely electron rich, correlating with the ease of oxidation. Attempts to reduce (**2**) with, for example, potassium metal, or electrochemically were unsuccessful. However (**2**) will reduce dilute aqueous acid giving (**3**) and in strong aqueous acid will oxidise (**3**) to (**4**).

In conclusion, the Mo_4S_4 cubane system of (**2**) is a thermally very stable, highly electron-rich cluster which will readily and reversibly lose two electrons and remarkably small structural changes occur with the oxidations.

We thank the Climax Molybdenum Company for the generous gift of chemicals and the S.E.R.C. for support (to D. P. S. R.).

Received, 27th July 1983; Com. 1008

References

1 E. T. Admen, L. C. Sieker, and L. H. Jensen, *J. Biol. Chem.*, 1973, **248**, 3987 and references therein.
2 B. K. Burgess, D. B. Jacobs, and E. I. Steifel, *Biochim. Biophys. Acta*, 1980, **614**, 196.
3 G. Gritzner and J. Kuta, *Pure Appl. Chem.*, 1982, **54**, 1527.
4 L. F. Dahl, presented at the VIth International Conference on Organometallic Chemistry, Amherst, Massachusetts, U.S.A., August, 1973.
5 T. Toan, B. K. Teo, J. A. Ferguson, T. J. Meyer, and L. F. Dahl, *J. Am. Chem. Soc.*, 1977, **99**, 409.
6 F. Bottomley and F. Grein, *Inorg. Chem.*, 1982, **21**, 4170.
7 J. R. Carruthers and D. J. Watkin, CRYSTALS User Manual, Oxford University Computing Laboratory, Oxford, 1981.