

Preparation and X-Ray Crystal Structure Analysis of a Novel, Trinuclear Nitrido Complex $[\{Et_2NCS_2\}_3MoN\}_2Mo(S_2CNEt_2)_3]^{3+}[PF_6^-]_3$

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Summary The reaction of $[MoN(S_2CNEt_2)_3]$ with hydroxylamine-*O*-sulphonic acid and $NaBF_4$ in methanol gives the title compound, the structure of which has been determined by X-ray diffraction.

THE nitride ligand of the complex $[MoN(S_2CNEt_2)_3]^1$ is sufficiently nucleophilic to cleave elemental sulphur to give the thionitrosyl complex $[Mo(NS)(S_2CNEt_2)_3]^2$. An attempt to prepare a hydrazido(2-) complex by reaction of the nitrido-complex with hydroxylamine-*O*-sulphonic acid and $NaBF_4$ in methanol gave a brown diamagnetic, crystalline product. The ionic character of this species (a 3:1 electrolyte in nitrobenzene) precluded a molecular weight determination, so its structure was determined by X-ray diffraction techniques.

Crystal data: $[C_{45}H_{90}N_{11}S_{18}Mo_3][PF_6]_3$, mol. wt. = 2082.22. Triclinic, $a = 17.960$, $b = 17.341$, $c = 16.109$ Å, $\alpha = 105.6$, $\beta = 102.8$, $\gamma = 102.0^\circ$, $D_m = 1.53$, $Z = 2$, $D_c = 1.52$, $\mu(Cu-K\alpha) = 81.2$ cm⁻¹, and space group $P\bar{1}$. Intensity data were recorded on a Nonius CAD4R computer controlled diffractometer, using an $\omega/2\theta$ scan and $Cu-K\alpha$ radiation. Of the 6516 reflections measured in the range $1.5 < \theta < 42.5^\circ$, 3995 had significant ($I > 3\sigma$) intensities. The structure was solved using the automatic direct methods link in the SHELX³ program and refined by a blocked full-matrix least-squares method. R is currently 0.10 and although the ethyl groups of the dtc (dtc = diethyldithiocarbamate) ligands and the PF_6^- ions (of which only two of the three present in the asymmetric unit have been identified) show severe positional disorder, the structure of the cation is well defined.

It is best described as two tris(diethyldithiocarbamato)molybdenum nitride molecules, with pentagonal bipyra-

midal geometry, co-ordinating to a central [tris(diethyldithiocarbamato)molybdenum] group, in which the metal atom has dodecahedral geometry (see Figure). The two nitride components co-ordinate at the B sites of one dodecahedral trapezium with a dtc ligand occupying the *a* edge; the

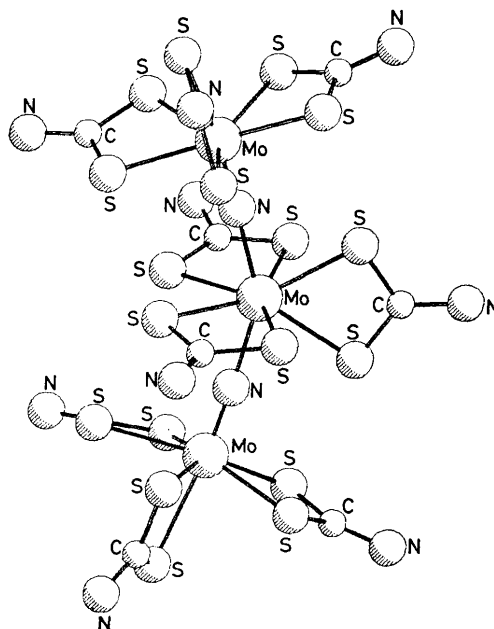


FIGURE. A view of the cation structure, $[\{Et_2NCS_2\}_3Mo=N\}_2Mo(S_2CNEt_2)_3]^{3+}$ (carbon atoms of the ethyl groups are omitted for clarity).

second trapezium is formed from two *m* edge chelating dtc ligands.

The MoN distances in the nitride portion are 1.65 and 1.66(1) Å, very similar to the value found in the isolated [(Me₂NCS₂)₃MoN] molecule,⁴ whilst the N → Mo distances are 2.12 and 2.14 Å. This asymmetric nitride bridging mode is very similar to that found in the tetrameric solid state structure of [MoNCl₃]₄⁵ and supports the formulation

of the cation as [(dtc)₃Mo^{VI}≡N→Mo^{VI}(dtc)₃←N≡Mo^{VI}-(dtc)₃]³⁺. The Mo-S distances are in the usual range, 2.49–2.74 Å with those *trans* to the nitride being the longest.

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¹ J. Chatt and J. R. Dilworth, *J.C.S. Chem. Comm.*, 1974, 517.

² J. Chatt and J. R. Dilworth, *J.C.S. Chem. Comm.*, 1974, 508.

³ The SHELX crystal structure calculations program: G. M. Sheldrick, University of Cambridge.

⁴ M. B. Hursthouse and M. Motevalli, unpublished work.

⁵ J. Strahle, *Angew. Chem. Internat. Edn.*, 1969, 925.