

Reaction of $[\text{Mo}_6\text{S}_8(\text{PEt}_3)_6]$ and NOBF_4 : structure and molecular orbital calculation of an octahedral cluster complex $[\text{Mo}_6\text{S}_8(\text{NO})(\text{PEt}_3)_5]^\ddagger$

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An octahedral cluster complex $[\text{Mo}_6\text{S}_8(\text{NO})(\text{PEt}_3)_5]$ **2** and a dodecanuclear cluster complex $[\text{Mo}_{12}\text{S}_{16}(\text{PEt}_3)_{10}]$ have been obtained by the reaction of $[\text{Mo}_6\text{S}_8(\text{PEt}_3)_6]$ with NOBF_4 . A crystallographic study of **2** shows a tetragonal distortion of the cluster core where the nitrosyl-co-ordinated molybdenum atom projects outward. Molecular orbital calculations on **2** indicate that the distortion of the cluster core enhances the π -back donation to the nitrosyl ligand.

The effects of the numbers of cluster valence electrons and the types of ligands on the structures of metal–chalcogenido clusters have attracted much attention in relation to the functions of metalloenzymes and solid-state compounds.¹ We have previously reported that one-electron reduction of an octahedral cluster complex $[\text{Mo}_6\text{S}_8(\text{PEt}_3)_6]$ **1** leads to a slight expansion and distortion of the cluster core.² To investigate the effect of one-electron oxidation on the cluster core, we have carried out the reaction of **1** with NOBF_4 and unexpectedly obtained a novel nitrosyl-co-ordinated octahedral cluster complex $[\text{Mo}_6\text{S}_8(\text{NO})(\text{PEt}_3)_5]$ **2** and a dodecanuclear cluster complex $[\text{Mo}_{12}\text{S}_{16}(\text{PEt}_3)_{10}]$ **3**. Since **2** is the first example of octahedral metal–chalcogenido cluster complexes with a nitrosyl ligand, we investigated its structure and molecular orbitals to evaluate the effect of the nitrosyl ligand on the structure of the cluster core.

Experimental

Preparations

The complex $[\text{Mo}_6\text{S}_8(\text{PEt}_3)_6]$ was prepared according to the literature.² Dichloromethane and hexane were dried with CaCl_2 and distilled from CaH_2 under argon. Acetone was dried and distilled from CaSO_4 under argon. The compound NOBF_4 (Aldrich) was used as received. All the manipulations were performed under inert atmospheres using standard Schlenk techniques. Infrared spectra were recorded with a Hitachi I-3000 spectrometer, UV spectra with a Hitachi U-3500 spectrometer. Elemental analyses were performed by the elemental analysis centre of this department.

$[\text{Mo}_6\text{S}_8(\text{NO})(\text{PEt}_3)_5]$ **2.** A dichloromethane solution (30 cm³) of NOBF_4 (6 mg, 51 μmol) was added to a dichloromethane solution (30 cm³) of $[\text{Mo}_6\text{S}_8(\text{PEt}_3)_6]$ **1** (50 mg, 32 μmol). On stirring for 15 min the mixture changed from red to green-brown. The solvent was removed *in vacuo*, and the resulting green-brown solid extracted with acetone (15 cm³). Standing the solution at -25°C for 3 d afforded green crystals, which were washed with hexane and dried *in vacuo* (10 mg, 21%) (Found: C, 25.2; H, 5.1; N, 0.9. $\text{C}_{30}\text{H}_{75}\text{Mo}_6\text{NOP}_5\text{S}_8$ requires C,

24.8; H, 5.2; N, 1.0%); $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$ (NO) 1634 (KBr); $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{dm}^{-3}\text{mol}^{-1}\text{cm}^{-1}$) (CH_2Cl_2) 362 (3400), 466 (3300), 542 (sh), 622 (860) and 1079 (520).

$[\text{Mo}_{12}\text{S}_{16}(\text{PEt}_3)_{10}]$ **3.** A dichloromethane solution (30 cm³) of NOBF_4 (6 mg, 51 μmol) was added to a dichloromethane solution (30 cm³) of $[\text{Mo}_6\text{S}_8(\text{PEt}_3)_6]$ **1** (50 mg, 32 μmol). Stirring the mixture for 2 d afforded a brown solution. The solvent was removed *in vacuo*, and the resulting brown solid extracted with acetone (15 cm³). Standing the solution at room temperature for 2 d afforded brown crystals, which were dried *in vacuo* (7 mg, 15%) (Found: C, 26.9; H, 5.6. Calc. for $\text{C}_{60}\text{H}_{150}\text{Mo}_{12}\text{P}_{10}\text{S}_{16}$: C, 25.3; H, 5.3%); $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{dm}^{-3}\text{mol}^{-1}\text{cm}^{-1}$) (CH_2Cl_2) 492 (8400), 669 (1900) and 1021 (2200).

Crystallography

A dark green plate crystal of $[\text{Mo}_6\text{S}_8(\text{NO})(\text{PEt}_3)_5]$ **2** with dimensions $0.7 \times 0.4 \times 0.05$ mm was sealed in a glass capillary and mounted on a Rigaku AFC-7R diffractometer equipped with a Rotaflex rotating-anode X-ray generator. Graphite-monochromatised Mo-K α radiation ($\lambda = 0.7107$ Å) was employed. Cell constants and an orientation matrix were determined using 25 reflections in the range $28 < 2\theta < 31^\circ$. The systematic absences uniquely required the space group $P2_1/n$. The intensity data for reflections $+h, +k, \pm l$ were collected at 23°C using ω - 2θ scans to a maximum 2θ value of 55.0° , and an empirical absorption correction using ψ scans³ was applied. The intensities of three standard reflections were monitored every 150, and no decay was observed. All calculations were performed using the TEXSAN crystallographic software package⁴ on a Silicon Graphics Indy workstation. Atomic scattering factors were taken from a standard source,⁵ and anomalous dispersion effects⁶ were included in the calculation. The structure was solved by direct methods using SIR 92,⁷ and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically by full-matrix least squares on F using ORFLS.⁸ Hydrogen atoms were not included in the calculations. Crystallographic parameters are shown in Table 1.

CCDC reference number 186/843.

See <http://www.rsc.org/suppdata/dt/1998/819/> for crystallographic files in .cif format.

Molecular orbital calculations

The molecular orbitals were calculated by the DV-X α method⁹ with the self-consistent charge approximation.¹⁰ Numerical atomic orbitals from atomic Hartree–Fock–Slater calculations

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[‡] Supplementary data available: calculated molecular orbitals. For direct electronic access see <http://www.rsc.org/suppdata/dt/1998/819/>, otherwise available from BLDSC (No. SUP 57339, 22 pp.) or the RSC Library. See Instructions for Authors, 1998, Issue 1 (<http://www.rsc.org/dalton>).

with additional well potential§ were used as basis functions.⁹ The radial functions of the atomic orbitals were calculated at points within 40 (Mo), 30 (S, P, N and O) and 20 au (H) from the nuclei. All the orbitals through 5p were included for Mo, through 3d for S and P, through 2p for N and O, and only 1s was used for H. The number of sampling points for the molecular orbital calculations was 200 000. To attain the self-consistent charge distribution, the process was cycled until the transfer of the electron by Löwdin population analysis¹¹ was less than 0.0001 for all atomic orbitals.

The symmetries of the model compounds were assumed as O_h for $[\text{Mo}_6\text{S}_8(\text{PH}_3)_6]$ and C_{4v} for undistorted and distorted $[\text{Mo}_6\text{S}_8(\text{NO})(\text{PH}_3)_5]$. The geometric parameters for $[\text{Mo}_6\text{S}_8(\text{PH}_3)_6]$ were taken from the averaged values of **1**.² The bond distances for undistorted $[\text{Mo}_6\text{S}_8(\text{NO})(\text{PH}_3)_5]$ were taken from the averaged values of all the corresponding distances in **2** so that the Mo_6S_8 unit has local O_h symmetry, and the P atoms were located on the plane composed of the four equatorial Mo atoms. For distorted $[\text{Mo}_6\text{S}_8(\text{NO})(\text{PH}_3)_5]$, geometric values of **2** were averaged in each group of bonds associated with each other by the virtual C_4 axis. In the PH_3 ligands the P–H distances were set to 1.40 Å and the Mo–P–H angles to 114.63°. Hydrogen atoms which lower the symmetries of the whole structures were treated according to the literature.¹² Spin-restricted calculations were performed for the three models, and a spin-unrestricted calculation only for distorted $[\text{Mo}_6\text{S}_8(\text{NO})(\text{PH}_3)_5]$. The Fermi distribution ($T=0.01$ eV) of electrons was assumed for undistorted $[\text{Mo}_6\text{S}_8(\text{NO})(\text{PH}_3)_5]$ because of the small difference of energy between the HOMO and LUMO.

Results and Discussion

Reaction of $[\text{Mo}_6\text{S}_8(\text{PET}_3)_6]$ **1** with NOBF_4

Addition of a dichloromethane solution of NOBF_4 (1.0–1.8 equivalents) to a dichloromethane solution of $[\text{Mo}_6\text{S}_8(\text{PET}_3)_6]$ **1** gave an immediate change from red to green-brown and further to brown. Depending on the stirring time, two different compounds were isolated. The nitrosyl-co-ordinated cluster complex $[\text{Mo}_6\text{S}_8(\text{NO})(\text{PET}_3)_5]$ **2** was obtained when the reaction was stopped at the green-brown stage (stirring for 5–30 min) by removing the solvent *in vacuo*. From the acetone extract of the resulting brown-green solid green crystals of **2** were obtained. One triethylphosphine ligand in **1** was substituted by a nitrosyl ligand, and the cluster complex has an odd number of electrons, confirmed by a silent ³¹P NMR spectrum. The IR spectrum of **2** shows a strong absorption maximum centred at 1634 cm^{-1} , which is in the range of those assigned for stretching vibrations of N–O ligands.^{13,14} Whereas a number of nitrosyl-co-ordinated cluster complexes are known,¹⁵ octahedral metal–chalcogenido and –halogeno cluster complexes with nitrosyl ligands have not been reported so far.

Most reactions of metal complexes and NOBF_4 lead to a simple oxidation *via* outer-sphere electron transfer or substitution by nitrosyl ligand without a change in the number of electrons on the metal.^{13,16} If the present reaction had led to simple substitution by a nitrosyl ligand without any redox reaction the product would have been the cationic cluster complex $[\text{Mo}_6\text{S}_8(\text{NO})(\text{PET}_3)_5][\text{BF}_4]$. Actually, however, the substitution of a triethylphosphine by a nitrosyl is accompanied by an increase in the number of total electrons of the cluster complex by one, which requires that other species in the reaction mixture must be oxidised. One possibility is that a free triethylphosphine removed by the substitution is oxidised, but we could not detect

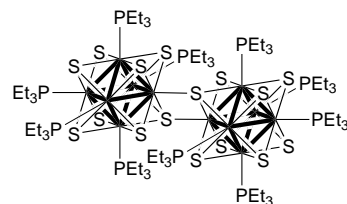


Fig. 1 Schematic representation of the structure of $[\text{Mo}_{12}\text{S}_{16}(\text{PET}_3)_{10}]$ **3**. The molybdenum atom labels are omitted for clarity and only Mo–Mo bonds are shown as thick lines

oxidised phosphorus species. Another is that the disproportionation of **1** occurs, which requires that an oxidised molybdenum compound derived from **1** must exist. The UV spectrum of the acetone extract after the separation of **2** was fairly different from those of **1**, **2** or **3**, which suggests that this species may be the oxidised molybdenum complex, although we have not been able to identify the compound.

From the solution after stirring the reaction mixture of complex **1** and NOBF_4 for several hours (after it had turned brown) brown crystals of a dodecanuclear cluster complex $[\text{Mo}_{12}\text{S}_{16}(\text{PET}_3)_{10}]$ **3** were obtained. We have recently reported the synthesis of **3** by phosphine abstraction from **1** using 1 equivalent of sulfur, and the structure has been determined by single-crystal X-ray analysis.¹⁷ A schematic drawing of the molecular structure is shown in Fig. 1. The complex has two octahedral Mo_6S_8 cores connected to each other by two Mo–(μ_4 -S) bonds, which is a similar connection mode to those found in solid-state Chevrel phases.¹⁸ A few other methods for the syntheses of dimers of octahedral clusters have been reported; $[\text{Co}_{12}\text{S}_{16}(\text{PET}_3)_{10}][\text{TCNQ}]_2$ (TCNQ = tetracyanoquinodimethane) was obtained as a by-product in the synthesis of $[\text{Co}_6\text{S}_8(\text{PET}_3)_6][\text{TCNQ}]$,¹⁹ $[\text{Cr}_{12}\text{S}_{16}(\text{PET}_3)_{10}]$ was synthesized by removal of a triethylphosphine ligand of $[\text{Cr}_6\text{S}_8(\text{PET}_3)_6]$ using sulfur²⁰ and $[\text{Re}_{12}\text{Se}_{16}(\text{PET}_3)_{10}]^{4+}$ by thermal removal of the acetonitrile ligand in $[\text{Re}_6\text{Se}_8(\text{PET}_3)_5(\text{MeCN})]^{2+}$.²¹ The present reaction using NOBF_4 affording **3** is another reaction involving the dimerisation of octahedral cluster cores.

Judging from the change in colour of the reaction solution, the dodecanuclear cluster complex **3** is gradually generated accompanied by a decrease in the amount of the nitrosyl complex **2**. This suggests that **2** plays an important role in the formation of **3**, because the starting compound **1** alone does not dimerise to give **3**. A plausible sequence is that two molecules of **2** lose nitrosyl ligands and dimerise to fill the resulting vacant co-ordination sites. However, we did not observe the formation of **3** in a dichloromethane solution of isolated **2**. Therefore, **2** probably dimerises by the involvement of some other species in the reaction mixture.

Structure of $[\text{Mo}_6\text{S}_8(\text{NO})(\text{PET}_3)_5]$ **2**

Although the structural effects of π -back donation to a nitrosyl ligand on mononuclear complexes have been studied,^{22,23} the effect on the structure of a cluster complex has not been investigated. Since **2** has the molybdenum atoms co-ordinated by σ -donating triethylphosphines and a π -accepting nitrosyl ligand, the structural effect of the π -back donation on the cluster core can be evaluated by comparing the local geometry around each molybdenum atom. Furthermore, the change of the whole structure of the cluster core can be assessed by comparison of the structure between **1** and **2**. To determine the structure of **2**, a single-crystal X-ray analysis was carried out. The molecular structure is shown in Fig. 2 and selected geometric parameters are given in Table 2. Six molybdenum atoms form a distorted octahedral metal core, and eight μ_3 -S ligands cap all the triangular faces of the Mo_6 core, which is topologically the same geometry as found in **1**. One molybdenum atom $[\text{Mo}(1)]$ is co-ordinated by a nitrosyl ligand and the other five by triethylphosphine ligands. All the molybdenum atoms have a

§ The potential used was -0.5 au for $r < r_w$ and proportional to $1/r$ for $r > r_w$; $r_w = 4.5$ (Mo), 4.0 (S and P) and 3.5 au (N, O and H). 1 au = 0.52 918 Å for length and 1 au = 27.211 eV for energy; $eV \approx 1.60 \times 10^{-19}$ J.

Table 1 Crystallographic data of $[\text{Mo}_6\text{S}_8(\text{NO})(\text{PET}_3)_5]_2$

Formula	$\text{C}_{30}\text{H}_{75}\text{Mo}_6\text{NOP}_5\text{S}_8$
<i>M</i>	1452.92
Crystal system	Monoclinic
Space group	$P2_1/n$ (no. 14)
<i>a</i> /Å	15.016(4)
<i>b</i> /Å	16.055(3)
<i>c</i> /Å	23.215(3)
β /°	107.91(1)
<i>U</i> /Å ³	5325(1)
<i>Z</i>	4
<i>D_c</i> /g cm ⁻³	1.812
<i>F</i> (000)	2900
$\mu(\text{Mo-K}\alpha)/\text{cm}^{-1}$	18.57
Transmission factors	0.6579–1.0000
No. unique reflections	12 658
No. observed reflections	5361 [$I > 3.0\sigma(I)$]
No. variables	460
<i>R</i> , <i>R'</i> ^a	0.054, 0.033
Goodness of fit	2.55
Δ/σ ^b	0.03
$\Delta\rho$ ^c /e Å ⁻³	1.18

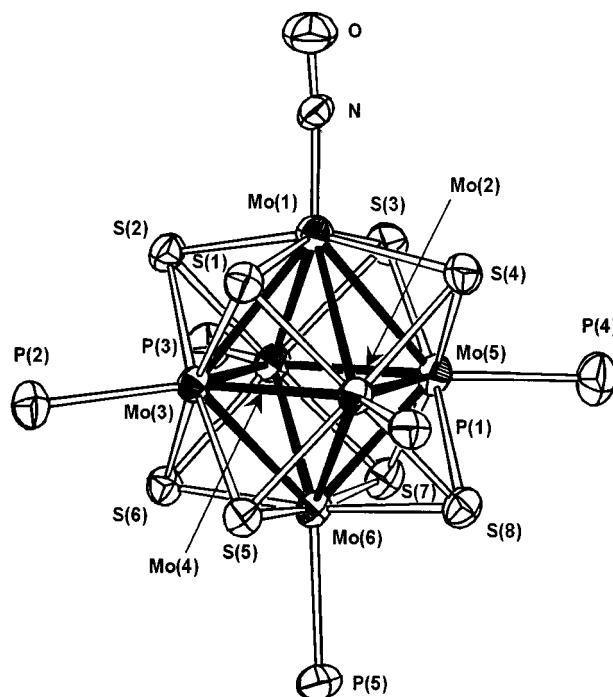
^a $R = \sum |F_o| - |F_c| / \sum |F_o|$; $R' = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$, $w = 1/\sigma^2(F_o)$.

^b Maximum shift/error in the final cycle. ^c The highest residual electron density in the final Fourier-difference map.

Table 2 Selected interatomic distances (Å) in $[\text{Mo}_6\text{S}_8(\text{NO})(\text{PET}_3)_5]_2$

Mo(1)–Mo(2)	2.840(1)	Mo(1)–Mo(3)	2.851(1)
Mo(1)–Mo(4)	2.845(1)	Mo(1)–Mo(5)	2.865(1)
Mo(2)–Mo(3)	2.622(1)	Mo(2)–Mo(5)	2.637(2)
Mo(2)–Mo(6)	2.661(1)	Mo(3)–Mo(4)	2.627(2)
Mo(3)–Mo(6)	2.677(1)	Mo(4)–Mo(5)	2.637(1)
Mo(4)–Mo(6)	2.666(1)	Mo(5)–Mo(6)	2.683(1)
Mo(1)–S(1)	2.456(3)	Mo(1)–S(2)	2.445(3)
Mo(1)–S(3)	2.460(3)	Mo(1)–S(4)	2.459(3)
Mo(2)–S(1)	2.430(3)	Mo(2)–S(4)	2.441(3)
Mo(2)–S(5)	2.451(3)	Mo(2)–S(8)	2.447(3)
Mo(3)–S(1)	2.439(3)	Mo(3)–S(2)	2.420(3)
Mo(3)–S(5)	2.448(3)	Mo(3)–S(6)	2.445(3)
Mo(4)–S(2)	2.424(3)	Mo(4)–S(3)	2.439(3)
Mo(4)–S(6)	2.453(3)	Mo(4)–S(7)	2.458(3)
Mo(5)–S(3)	2.421(3)	Mo(5)–S(4)	2.435(3)
Mo(5)–S(7)	2.462(3)	Mo(5)–S(8)	2.449(3)
Mo(6)–S(5)	2.421(3)	Mo(6)–S(6)	2.436(3)
Mo(6)–S(7)	2.433(3)	Mo(6)–S(8)	2.430(3)
Mo(2)–P(1)	2.540(3)	Mo(3)–P(2)	2.542(3)
Mo(4)–P(3)	2.550(3)	Mo(5)–P(4)	2.546(4)
Mo(6)–P(5)	2.560(3)		
Mo(1)–N	1.795(7)	N–O	1.189(8)

distorted square-pyramidal co-ordination environment if all the Mo–Mo bonds are neglected. The N–O distance is 1.189(8) Å and the angle Mo(1)–N–O is 175.3(8)°, both of which are normal for a linear-type nitrosyl ligand.^{13,23} If the valence-bond scheme is accepted, a linear nitrosyl ligand is monocationic¹³ and the cluster core is reduced from **1** by one electron. This assumption is consistent with the result of the molecular orbital calculations (see below). The Mo(1)–N distance is 1.795(7) Å, which is in the range of those for reported molybdenum nitrosyl complexes.²³ The Mo–S (2.442 Å average) and Mo–P (2.548 Å average) distances are not meaningfully different from those of **1** (2.445 Å average for Mo–S and 2.527 Å for Mo–P).² The Mo–Mo distances in **2** can be classified into the following three ranges: (i) 2.845–2.865 Å (2.850 Å average) for the bonds between the nitrosyl-co-ordinated Mo(1) atom and the ‘equatorial’ molybdenum atoms [Mo(2), Mo(3), Mo(4) and Mo(5)], (ii) 2.622–2.637 Å (2.631 Å average) for those connecting the equatorial molybdenum atoms and (iii) 2.661–2.683 Å (2.672 Å average) for those involving Mo(6). This divergence of Mo–Mo bond distances in **2** (0.243 Å) is notable compared with

**Fig. 2** Molecular structure of $[\text{Mo}_6\text{S}_8(\text{NO})(\text{PET}_3)_5]_2$ with the atom numbering scheme. Ethyl groups are omitted for clarity

those found in previously reported M_6E_8 ($\text{M} = \text{Mo}$ or W ; $\text{E} = \text{S}$, Se or Te) cluster complexes, the maximum value being found in $[\text{W}_6\text{Se}_8(\text{C}_5\text{H}_{10}\text{NH})_6]$ (0.045 Å).²⁴ Compared with the almost regular octahedral Mo_6 core in **1** (Mo–Mo 2.662–2.664 Å),² the Mo_6 core in **2** has a prominent tetragonal distortion owing to the outward projection of Mo(1) by ca. 0.19 Å and the slight contraction of the equatorial square consisting of Mo(2), Mo(3), Mo(4) and Mo(5) by the decrease in the Mo–Mo lengths by ca. 0.03 Å. The larger values of the distances between Mo(1) and the equatorial molybdenum atoms can be qualitatively rationalised in terms of the existence of the π -back donation from Mo(1) to the nitrosyl ligand. Assuming that the d orbitals of Mo(1) which participate in the bonds between it and the equatorial molybdenum atoms are used for the π -back donation to the nitrosyl ligand, the overlaps between the orbitals of Mo(1) and those of the equatorial molybdenum atoms decrease, leading to elongation of the Mo–Mo bonds.

Electronic structure of $[\text{Mo}_6\text{S}_8(\text{NO})(\text{PET}_3)_5]_2$

Whereas several theoretical studies on nitrosyl complexes have been carried out, most of them concentrate on the linear–bent isomerism of the nitrosyl ligand.²⁵ For a detailed theoretical investigation of the effect of the nitrosyl ligand on the cluster core structure in **2**, molecular orbital calculations for a model compound $[\text{Mo}_6\text{S}_8(\text{NO})(\text{PH}_3)_5]$ in the C_{4v} symmetry were performed. The molybdenum atoms are classified into three groups from the requirement of the symmetry: Mo(A) [Mo(1)], Mo(B) [Mo(2), Mo(3), Mo(4) and Mo(5)] and Mo(C) [Mo(6)]. Since **2** has an odd number of electrons a spin-unrestricted calculation was also performed, and the results were not significantly different from those obtained by the spin-restricted calculation. The molybdenum 4d orbitals largely contribute to all the molecular orbitals higher than –12.6 eV as shown in Fig. 3. The orbitals participating in the σ and π donation of the nitrosyl ligand are 53a₁ and 47e, respectively, judging from the large positive overlap populations of Mo(A) 4d–N 2p and N 2p–O 2p and their symmetries. Since these orbitals are mainly composed of Mo(A) 4d, N 2p and O 2p, the donation from the nitrosyl ligand localises at Mo(A). The π -back donation to the nitrosyl ligand is mainly contributed by four e orbitals between

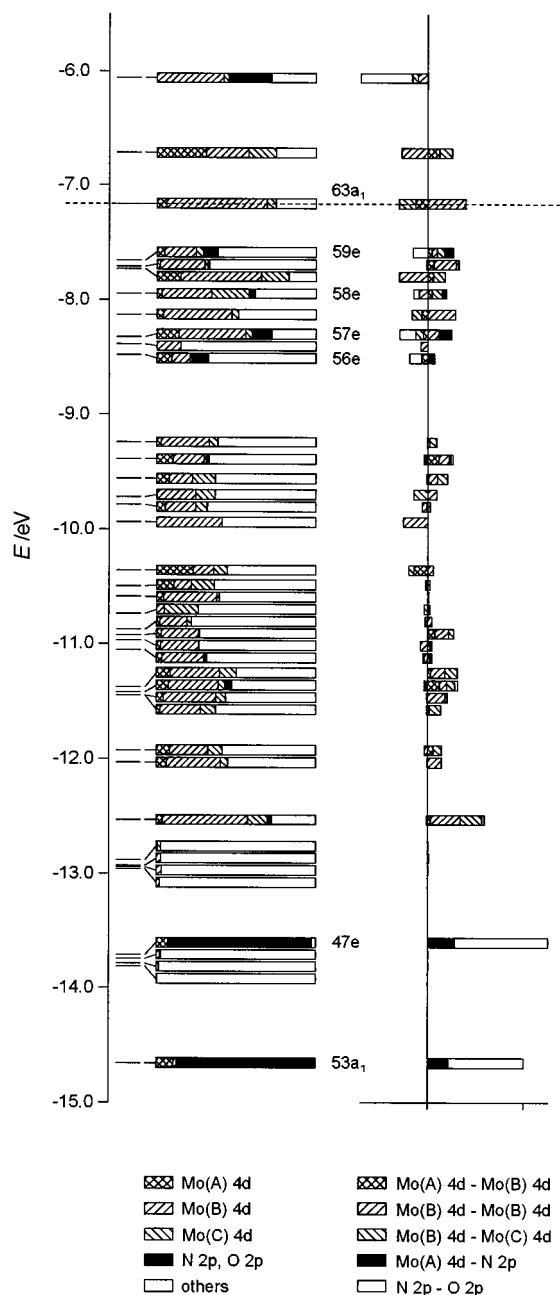


Fig. 3 Electronic levels and overlap populations of $[\text{Mo}_6\text{S}_8(\text{NO})(\text{PH}_3)_5]$ modelled from the crystallographic structure of complex **2**. The orbital on the horizontal broken line is singly occupied and those below the line are completely occupied. The left and the right diagrams show the atomic orbital compositions and the overlap populations, respectively. In the right diagram the strips on the right side of the vertical line indicate positive overlaps and those on the left negative ones. Only the symbols of the orbitals mentioned in the text are shown

–7.5 and –9.0 eV (56e, 57e, 58e and 59e) which have bonding Mo(A) 4d–N 2p overlaps and antibonding N 2p–O 2p overlaps. These orbitals have considerable components of Mo(B) 4d and Mo(C) 4d, which shows that the π -back donation influences the whole cluster core. The $63a_1$ HOMO occupied by a single electron is composed mainly of Mo(B) and the contribution from the nitrosyl ligand is negligible. The spin population on each atom obtained by the spin-unrestricted calculation is shown in Table 3. The spin density concentrates mainly on Mo(B) atoms, which is consistent with the large component of Mo(B) 4d in the singly occupied orbital $63a_1$.

To investigate the change of the electronic structure upon substitution of a phosphine by a nitrosyl ligand, the results of the molecular orbital calculations for the following three model

Table 3 Electron spin populations on the atomic orbitals of distorted $[\text{Mo}_6\text{S}_8(\text{NO})(\text{PH}_3)_5]$ evaluated from the spin-unrestricted molecular orbital calculation

Mo(A) 4d	0.041	Mo(B)* 4d	0.748	Mo(C) 4d	0.015
5s	0.006	5s	0.005	5s	0.003
5p	0.011	5p	0.022	5p	0.007
total	0.058	total	0.776	total	0.026

N –0.006 O –0.010 S and P 0.159

* The values for all the four equivalent Mo(B) atoms are summed.

Table 4 Mulliken overlap populations between atomic orbitals in Mo(A) 4d, N 2p and O 2p the symmetries of which allow the π -back donation* in $[\text{Mo}_6\text{S}_8(\text{NO})(\text{PH}_3)_5]$

MO	Mo(A) 4d–N 2p		N 2p–O 2p	
	Undistorted	Distorted	Undistorted	Distorted
59e	0.001	0.018	–0.003	–0.030
58e	0.000	0.009	–0.000	–0.012
57e	0.015	0.027	–0.015	–0.033
56e	0.045	0.014	–0.069	–0.024
Total	0.124	0.136	–0.176	–0.199

* If the C_4 axis is set parallel to the Cartesian z axis, the symmetry-allowed orbitals are $4d_{xz}$ and $4d_{yz}$ for Mo(A), and $2p_x$ and $2p_y$ for N and O.

compounds were compared: (i) $[\text{Mo}_6\text{S}_8(\text{PH}_3)_6]$ in the O_h symmetry corresponding to **1**,[¶] (ii) ‘undistorted $[\text{Mo}_6\text{S}_8(\text{NO})(\text{PH}_3)_5]$ ’, in which a nitrosyl ligand co-ordinates but the cluster core has still O_h symmetry and (iii) $[\text{Mo}_6\text{S}_8(\text{NO})(\text{PH}_3)_5]$ corresponding to the real structure of **2** the cluster core of which is tetragonally distorted, which is called ‘distorted $[\text{Mo}_6\text{S}_8(\text{NO})(\text{PH}_3)_5]$ ’ from now on. The energy levels of the three models near the HOMO levels are shown in Fig. 4 and the overlap populations relating to the π interaction between Mo(A) and the nitrosyl ligand are given in Table 4.

The substitution of the nitrosyl for a phosphine ligand influences the cluster structure through two electronic effects. The first is the increase of the cluster valence electrons. The discussion based on the valence-bond scheme indicates that the number of cluster valence electrons of complex **2** is larger than that of **1** by one (see above). Consistent with this, the molecular orbital calculations show that one of the orbitals derived from the LUMO of $[\text{Mo}_6\text{S}_8(\text{PH}_3)_6]$ becomes occupied by one electron in $[\text{Mo}_6\text{S}_8(\text{NO})(\text{PH}_3)_5]$. The doubly degenerate LUMO of $[\text{Mo}_6\text{S}_8(\text{PH}_3)_6]$ ($17e_g$) splits into $63a_1$ and $28b_1$ in $[\text{Mo}_6\text{S}_8(\text{NO})(\text{PH}_3)_5]$, and the splitting becomes larger by ca. 0.4 eV as the cluster core is tetragonally distorted. Therefore, the Jahn–Teller effect is one reason for the distortion of the cluster core. The $63a_1$ orbital has negative Mo(A) 4d–Mo(B) 4d overlap populations and positive Mo(B) 4d–Mo(B) 4d ones while $28b_1$ has the opposite overlap populations. Therefore, it is reasonable that $63a_1$ is stabilised by the elongation of the Mo(A)–Mo(B) bonds and the shortening of the Mo(B)–Mo(B) bonds.

The co-ordination of the nitrosyl ligand influences the structure of the cluster core also through the π -back donation to the nitrosyl ligand. The molecular orbitals of $[\text{Mo}_6\text{S}_8(\text{NO})(\text{PH}_3)_5]$ in which the π^* orbitals of the nitrosyl ligand can participate are those with e symmetry. The e orbitals which have suitable energies for the π -back donation are 56e, 57e, 58e and 59e which

[¶] We have previously reported a molecular orbital calculation of $[\text{Mo}_6\text{S}_8(\text{PH}_3)_6]$.¹² In the present work we recalculated the molecular orbitals of $[\text{Mo}_6\text{S}_8(\text{PH}_3)_6]$ using the same conditions (number of sampling points, etc.) as those for $[\text{Mo}_6\text{S}_8(\text{NO})(\text{PH}_3)_5]$, in order to make the calculation consistent with those of $[\text{Mo}_6\text{S}_8(\text{NO})(\text{PH}_3)_5]$. Although the present result for $[\text{Mo}_6\text{S}_8(\text{PH}_3)_6]$ was slightly different from the previously reported one, the difference was too small to affect the following discussion.

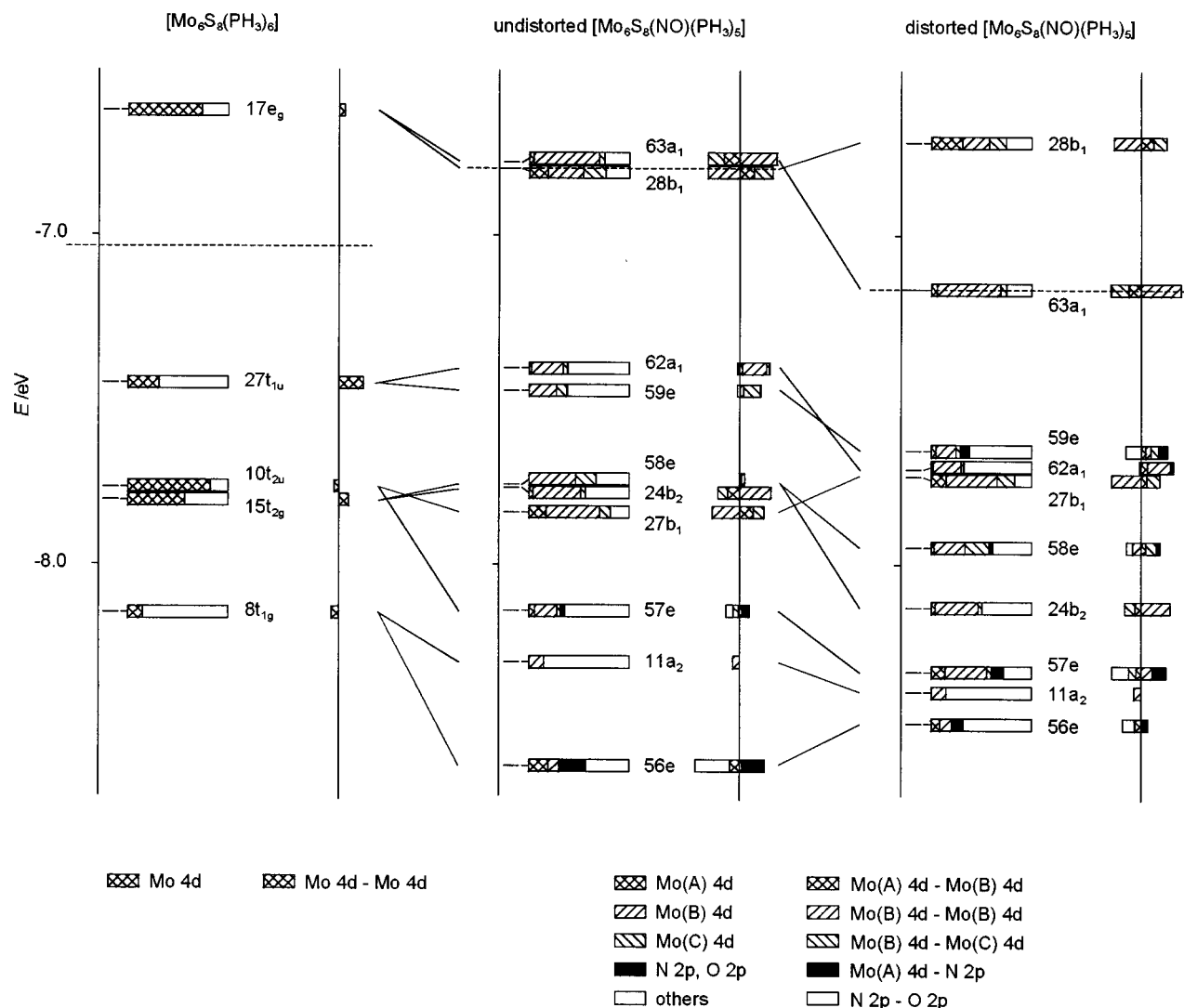


Fig. 4 Energy levels and overlap populations of molecular orbitals of $[\text{Mo}_6\text{S}_8(\text{PH}_3)_6]$, undistorted $[\text{Mo}_6\text{S}_8(\text{NO})(\text{PH}_3)_5]$ and distorted $[\text{Mo}_6\text{S}_8(\text{NO})(\text{PH}_3)_5]$. Related orbitals between the models are connected by lines

are derived from $8t_{1g}$, $10t_{2u}$, $15t_{2g}$ and $27t_{1u}$ of $[\text{Mo}_6\text{S}_8(\text{PH}_3)_6]$, respectively, although these orbitals mix with each other to a certain extent. In undistorted $[\text{Mo}_6\text{S}_8(\text{NO})(\text{PH}_3)_5]$ these four e orbitals are classified into two groups. The orbitals of the first group (56e and 57e) are distributed mainly on Mo(A), Mo(B) and the nitrosyl ligand, and have slightly negative Mo(A) 4d–Mo(B) 4d overlaps. The orbitals of the other group (58e and 59e) are on Mo(B) and Mo(C) with positive Mo(B) 4d–Mo(C) 4d overlaps. Therefore, the upper hemisphere of the cluster core is occupied by the orbitals (56e and 57e) with a weak Mo–Mo antibonding nature while the Mo–Mo bonding orbitals (58e and 59e) distribute in the lower hemisphere. This rehybridisation causes the participation of only orbitals of the first group in the π -back donation to the nitrosyl ligand as indicated by the large positive overlap between Mo(A) 4d and N 2p for the orbitals of the first group (see Table 4). The antibonding nature of the orbitals of the first group is relaxed by elongation of the Mo(A)–Mo(B) bonds as observed in the real structure. Upon distortion of the cluster core, the e orbitals mix with each other again and the orbitals of the second group gain the Mo(A) component. As a result, the orbitals in the second group also contribute to the π -back donation to the nitrosyl ligand (see Table 4). This leads to an increase in the sum of the overlaps between Mo(A) 4d and N 2p in the four e orbitals and to a decrease in that between N 2p and O 2p (see Table 4). Concurrently, the total electron population of N 2p + O 2p increases from 7.72 to 7.83 (calculated by Löwdin population analysis¹¹)

and that of the Mo_6S_8 core (Mo 4d + S 3p) decreases from 62.30 to 62.19. These changes show that the total π -back donation from Mo(A) to the nitrosyl ligand is enhanced by the rehybridisation of the four e orbitals. Therefore, the distortion of the cluster core is also aided by enhancement of the π -back donation from the cluster core to the nitrosyl ligand. The stability of the nitrosyl complex **2** is perhaps due to the flexibility of the cluster core structure which allows the large π -back donation to the nitrosyl ligand and the stabilisation of the orbital occupied by the additional electron.

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