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Bonding in Nitrosylated Molybdenum–Sulphur Clusters

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Abstract

The bonding in a range of nitrosylated molybdenum–sulphur clusters, and in the fundamental fragments from which they are built up, has been analysed by the use of extended Hückel calculations. While the deep valence levels in nitrosylated molybdenum sulphur clusters are very similar to those in nitrosylated iron sulphur clusters the frontier orbitals are entirely different These differences in frontier orbitals are used to discuss and predict differences in the patterns of reactivity between the molybdenum–sulphur systems and the iron sulphur systems

Introduction

We recently reported extended Hückel calculations on the nitrosylated iron- sulphur clusters $Fe_4S_4(NO)_4$, $[Fe_4S_3(NO)_7]^-$ $[Fe_2S_2(NO)_4]^{2-}$, and $Fe_2(SH)_2(NO)_4$ [1]. The calculations show that in every case, the frontier orbitals are concentrated in the Fe_2 or Fe_4 framework, and that the LUMO is always antibonding. Hence the calculations shed light on the propensity [2] of both the dinuclear and the tetranuclear nitrosylated iron–sulphur clusters to undergo fragmentation, forming mononuclear complexes, upon electron addition. Because of the value of these calculations in the interpretation of chemical behaviour in the iron–sulphur systems, we have now made a similar study of the analogous molybdenum–sulphur system.

Although the structurallly characterised nitrosylated molybdenum–sulphur cluster anions, $[Mo_2(NO)_2(S_2)_3(S_5)OH]^{3-}$ [3, 4], $[Mo_3(NO)_3S_2(S_2)_4(S_3NO)]^{4-}$ [5], $[Mo_4(NO)_4(S_2)_6O]^{2-}$ [6, 7], and $[Mo_4(NO)_4S_3(S_2)_5]^{4-}$ [8, 9], are stoichiometrically all apparently quite different, they exhibit several common features. First, all are built up from $[Mo(NO)]^{3+}$ fragments, whose electronic configuration may be described [10] as $\{MoNO\}^4$: always the Mo–N–O fragment is essentially linear, so that it may be regarded as a d^4 Mo(II) atom bonded to the ligand $(NO)^+$. Second, the coordination about molybdenum is always approximately pentagonal bipyramidal, with the nitrosyl ligand occupying one of the axial sites, and either a sulphide (S^{2-}) or an oxide ligand occupying the other: the five equatorial sites are always occupied by sulphurs, either two disulphide $(S_2{}^{2-})$ ligands and one further sulphur, as in $[Mo_2(NO)_2(S_2)_3(S_5)OH]^{3-}$ and $[Mo_4(NO)_4(S_2)_6O]^{2-}$, or one disulphide and three further sulphurs, as in $[Mo_3(NO)_3S_2(S_2)_4(S_3NO)]^{4-}$ and $[Mo_4(NO)_4S_3(S_2)_5]^{4-}$. Third, the anions $[Mo_2(NO)_2(S_2)_3(S_5)OH]^{3-}$, $[Mo_4(NO)_4(S_2)_6O]^{2-}$, and $[Mo_4(NO)_4S_3(S_2)_5]^{4-}$ are all reported [3, 6, 8] to be diamagnetic, despite the presence of molybdenum(II).

The exception to these generalisations is found [11] in the octacyano anion $[Mo_4(NO)_4S_4(CN)_8]^{8-}$ in which linear $[Mo(NO)]^{2+}$, *i.e.* $\{MoNO\}^5$, groups and sulphide ligands form a distorted cubane-type framework, with each molybdenum octahedrally coordinated by one pendant nitrosyl and two pendant cyano ligands, and by three *fac* μ_3-sulphurs which are within the Mo_4S_4 cage: again the system is diamagnetic, and but for the cyano ligands bears a stoichiometric resemblance to the iron–sulphur cubane-type cluster $Fe_4S_4(NO)_4$.

The present paper presents the results of a study of the foregoing nitrosylated molybdenum–sulphur clusters and some of the fundamental fragments of which they are composed, with especial emphasis on a comparison of their properties and behaviour with those of the nitrosylated iron–sulphur clusters discussed earlier [1].

Calculations

Extended Hückel calculations [12, 13] employed parameters previously published [14]: the values used are summarised in Table I. Geometries were derived from published X-ray data [3–7, 9, 11], with fractional atomic coordinates transformed into orthogonal Ångstrom coordinates such that both the location of the origin and the orientation of the axes could be varied as required. MNDO calculations [15] on $[S_3NO]^-$ and $[S_3SH]^-$ were made using the

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TABLE I. Parameters Used in Extended Hückel Calculations

Orbital	H_{ii} (eV)	ξ_1	ξ_2	C_1[a]	C_2[a]
N 2s	−26.0	1.950			
2p	−13.4	1.950			
O 2s	−32.3	2.275			
2p	−14.8	2.275			
S 3s	−20.0	1.817			
3p	−13.3	1.817			
3d	−8.0	1.500			
Mo4d	−11.06	4.540	1.900	0.5899	0.5899
5s	−8.77	1.960			
5p	−5.60	1.960			

[a] Coefficients in double-ξ expansion.

MOPAC system [16], with atomic parameters as previously published [15, 17].

Results

It is convenient to deal firstly with the fundamental fragments which form the common building blocks for these nitrosylated molybdenum–sulphur clusters, and then to discuss the large cluster anions themselves.

Fundamental Fragments

$[Mo(NO)]^{3+}$

This linear fragment is common to all of the clusters considered here, with the exception of $[Mo_4(NO)_4S_4(CN)_8]^{8-}$ [11]. In this ion, the three lowest valence-shell energy levels, corresponding to the 2s levels of the nitrosyl ligand, and its pπ level are essentially unchanged from those in $(NO)^+$. The σ interaction, between the molybdenum d_{z^2} orbital at −11.06 eV and the $3A_1$ level of $(NO)^+$ at −14.82 eV, gives two levels at −15.56 eV (occupied) and −10.40 eV (unoccupied); the π interaction, between molybdenum d_{yz} and d_{zx} at −11.06 eV, and the $2E_1$ level (pπ^*) of $(NO)^+$ gives two new pairs of orbitals at −12.52 eV ($2E_1$, occupied by the four d electrons of the Mo(II) atom) and −9.70 eV ($3E_1$, unoccupied). The molybdenum d orbitals of δ symmetry, $1E_2$, (d_{xy} and $d_{x^2-y^2}$) are strictly unchanged at −11.06 eV. Because of the very intense axial ligand field induced by the strong π-acceptor ligand $(NO)^+$, the HOMO–LUMO gap between $2E_1$ and $1E_2$ is 1.46 eV: hence this axial field is sufficient to maintain spin pairing independent of the rest of the molybdenum coordination.

Unlike the analogous iron–sulphur nitrosyls [1, 2] therefore, fragmentation of oligonuclear clusters to form mononuclear complexes, would not be expected, in the absence of redox changes, to be detectable by EPR spectroscopy.

$[Mo(NO)S]^+$

In this linear fragment, also common to several of the clusters considered in this work, the major orbital interaction is again that of the π^*(NO) levels with the d_{yz} and d_{zx} orbitals of molybdenum to give $3E_1$ (occupied by d^4) at −12.39 eV and $4E_1$ (unoccupied) at −9.92 eV. The δ orbitals, $1E_2$, are at −11.08 eV, giving a HOMO–LUMO gap of 1.31 eV, so that again such a fragment is expected always to be diamagnetic.

$\{[Mo(NO)]_2O\}^{4+}$ and $\{[Mo(NO)]_4O\}^{10+}$

These fragments form the central cores of the clusters $[Mo_2(NO)_2(S_2)_3(S_5)OH]^{3-}$ [3, 4] and $[Mo_4(NO)_4(S_2)_6O]^{2-}$ [6, 7] respectively. In neither of these fragments is the central molybdenum oxygen interaction strong. The oxygen 2p levels are very little perturbed upon binding to $[Mo(NO)]^{3+}$ fragments, and the molybdenum oxygen overlap populations are only *ca.* 0.20 in each case. The Mo–O bond energy term in these fragments is around 60 kJ mol^{-1}

$\{[Mo(NO)]_4S\}^{10+}$

This fragment is the central core of the cluster $[Mo_4(NO)_4(S)_3(S_2)_5]^{4-}$ [8, 9]. Here the central sulphur interacts much more strongly with its four molybdenum neighbours than the central oxygen in $\{[Mo(NO)_3]_4O\}^{10+}$ does. The sulphur 3p levels are lowered by almost 1 eV on binding to the molybdenums, and the molybdenum–sulphur overlap populations range from 0.35 to 0.43. The Mo–S bond energy term in this fragment is around 150 kJ mol^{-1}, very much higher than the 60 kJ mol^{-1} found above for Mo–O.

$[Mo(NO)(S_2)_2(S)_2]^{5-}$ and $[Mo(NO)(S)_6]^{9-}$

These two stoichiometries represent the two extreme forms of the approximate pentagonal bipyramidal coordination of molybdenum in these clusters, the first containing two μ_2-$(S_2)^{2-}$ and two S^{2-} ligands and the second containing six sulphide ligands. For each formulation, two isomeric forms were investigated, having the nitrosyl ligand either axial or equatorial, but with all other geometric parameters identical.

In $[Mo(NO)(S_2)_2(S)_2]^{5-}$, the isomer having axial NO is the more stable by 102 kJ mol^{-1}, while in $[Mo(NO)(S)_6]^{9-}$ the axial nitrosyl isomer is the more stable by 162 kJ mol^{-1}. In a pentagonal bipyramid, with z oriented along the major axis of the polyhedron, the two occupied d orbitals in a d^4 system are d_{yz} and d_{zx}. If a nitrosyl ligand is in an axial site, it can engage in π bonding with both of these occupied d orbitals, but with only one if it is in an equatorial site: this is confirmed by comparison of the molybdenum–nitrogen overlap populations for the various isomers.

Nitrosylated Molybdenum–Sulphur Clusters

In all of the nitrosylated molybdenum–sulphur clusters studied here, the general pattern of the deep, occupied, valence-level molecular orbitals is very similar, and resembles the general pattern found earlier [1] in the analogous iron–sulphur systems. Thus the σ(NO) levels are found in two groups around −23 eV and −35 eV, corresponding to essentially pσ and sσ levels respectively, and the π(NO) levels are at about −16 eV. The sulphur 3s combinations fall in the range −17 eV to −25 eV, with the Mo-S(3p) levels in the range −14 eV to −16 eV. In both $[Mo_2(NO)_2(S_2)_3(S_5)O]^{4-}$ and $[Mo_4(NO)_4(S_2)_6O]^{2-}$, the oxygen 2s level is virtually unperturbed at −32.4 eV. We discuss the frontier orbitals of each cluster individually below.

In all of these anionic clusters, the nitrogen atoms of the nitrosyl groups bound to molybdenum bear the least negative charge, ranging from −0.14 in $[Mo_2(NO)_2(S_2)_3(S_5)O]^{4-}$ to −0.38 for two of the nitrosyl ligands in $[Mo_3(NO)_3(S)_2(S_2)_4(S_3NO)]^{4-}$: hence attack by nucleophiles should be at this site. The most negatively charged atoms (excepting the sterically inaccessible μ_2- or μ_4-oxo ligands in $[Mo_2(NO)_2(S_2)_3(S_5)O]^{4-}$ and $[Mo_4(NO)_4(S_2)_6O]^{2-}$ respectively) are the oxygens of the nitrosyl ligands, which bear charges in the range −0.92 to −1.05, so that attack by electrophiles is expected to be at this site. Thus in terms of reactions with electrophiles and nucleophiles, the nitrosyl ligands in these clusters are expected to show behaviour similar to that of nitrosyl ligands bound, for example, to iron [18, 19].

$[Mo_2(NO)_2(S_2)_3(S_5)O]^{4-}$

The anion $[Mo_2(NO)_2(S_2)_3(S_5)OH]^{3-}$ was described by Müller, and was characterised crystallographically as its ammonium salt [3]. Wu described a structurally identical anion, characterised crystallographically as the salt with two Me_4N^+ and one potassium ion as counter ions [4], as $[Mo_2(NO)_2(S_2)_3(S_5)O]^{3-}$, *i.e.* with a μ_2-oxo ligand in stead of the μ-hydroxo described earlier [3]. Although no hydrogen was located in that anion by X-ray methods, ν(OH) was observed at 3580 cm^{-1} in the infra-red spectrum, and the complex was found to be diamagnetic [3]: Wu's formulation requires an odd number of electrons, and hence paramagnetism, and we conclude that the hydroxo formulation is correct but that these two structure analyses [3, 4] involve identically the same anion. Since the hydrogen position was not identified, our calculations refer, for the sake of simplicity, to the deprotonated anion $[Mo_2(NO)_2(S_2)_3(S_5)O]^{4-}$.

In sharp contrast to the dinuclear nitrosylated iron–sulphur species $[Fe_2S_2(NO)_4]^{2-}$ and $Fe_2(SH)_2(NO)_4$ [1], the frontier orbitals of $[Mo_2(NO)_2(S_2)_3(S_5)O]^{4-}$ are not concentrated in the molecular core, MoOMo: rather, the HOMO and the neighbouring occupied orbitals are concentrated primarily in the Mo–NO π interactions, while the LUMO and the neighbouring unoccupied orbitals consist primarily of anti-bonding combinations of sulphur 3p orbitals. Apart from the nitrosyl ligands, where the Mo–N overlap population is 0.81, the principal interactions of each molybdenum are with the terminal sulphur atoms of the S_5 ligand (overlap 0.46). There is no significant difference between the overlap populations between molybdenum and the sulphurs of the bridging S_2 ligand (0.27) and the terminal S_2 ligands (0.28). The Mo–O overlap is much lower (0.17), but the Mo–Mo interaction is negligible.

$[Mo_3(NO)_3(S)_2(S_2)_4(S_3NO)]^{4-}$

Mixtures of ammonium molybdate (containing $[Mo_7O_{24}]^{6-}$), hydroxylamine, and ammonium thiocyanate yield with polysulphide not only $[Mo_2(NO)_2(S_2)_3(S_5)OH]^{3-}$ [3, 4], but under slightly different experimental conditions, an anion described as $[Mo_3(NO)_3(S)_2(S_2)_4(S_3NO)]^{4-}$, and characterised thus by X-ray crystallography [5]. One unusual feature of the reported structure is the existence of the ligand $[S_3NO]^-$: this bridges two molybdenum atoms with the terminal sulphur, and has an NO function at the other end of the tri-sulphur chain. The geometrical details of this ligand summarised in Table II, (especially the S–N and N–O distances, and the SNO angle), raise doubts about the assignment of the atomic identities in the structural analysis, and lead us to suggest an alternative. Comparison with MNDO calculations of the geometry for the two isolated ligands $(S_3NO)^-$ and $(S_3SH)^-$ (Table II), immediately suggests a reformulation of

TABLE II. Geometric Comparison of the Ligands $[S_3NO]^-$ and $[S_3SH]^-$

	Distances (Å)			Angles (°)	
	(S_2-S_3)	(S_3-X)	$(X-Y)$	(S_2S_3X)	(S_3XY)
$[S_3NO]^-$	1.958	1.665	1.163	104.4	117.4
$[S_3SH]^-$	1.938	1.919	1.307	110.4	101.0
Experimental [5]	1.945	1.827	1.340	122.5	94.9

this anion, as $[Mo_3(NO)_3(S)_2(S_2)_4(S_4H)]^{4-}$: it should be noted that no independent evidence, either analytical or spectroscopic, was provided [5] to support the assignment of this ligand as $[S_3NO]^-$, rather than as $[S_3SH]^-$. Inspection of the reported [5] isotropic temperature factors for the atoms in this ligand also suggests that the assignments of the two terminal atoms may be incorrect: in particular that for the atom assigned as nitrogen appears to be far too small, indicative of too low an assigned atomic number. The present calculations were performed for both variants, using the atomic positions reported [5] on the basis of a bridging ligand $[S_3NO]^-$.

As in $[Mo_2(NO)_2(S_2)_3(S_5)O]^{4-}$, the frontier orbitals in $[Mo_3(NO)_3(S)_2(S_2)_4(S_3XY)]^{4-}$ (XY = NO or SH) do not involve the Mo_3S_2 core of the anion: the HOMO is again concentrated in the Mo–NO π orbitals, and the LUMO is composed of sulphur 3p orbitals in antibonding combinations. The overlap populations between molybdenum and the various types of sulphur ligand in the structure vary considerably, thus: S^{2-} in an axial site (about a pentagonal bipyramidal molybdenum), 0.35; S^{2-} in an equatorial site, 0.44 for one Mo and 0.38 for the other two; 0.36 for the terminal sulphur of the $[S_3XY]^-$ ligand (regardless of whether XY represents NO or SH), 0.35 for $(S_2)^{2-}$ acting as a monodentate ligand, and 0.22–0.25 for $(S_2)^{2-}$ acting as a bidentate ligand. As in the previously discussed dinuclear complex, the direct interactions between the molybdenum centres are negligible.

$[Mo_4(NO)_4(S_2)_6O]^{2-}$

Crystals of $(NH_4)K[Mo_4(NO)_4(S_2)_6O]\cdot 2H_2O$ are tetragonal, and their structure was solved [6] in space group $I4_1/a$: the anion has crystallographic S_4 symmetry, and the diammonium salt is isostructural. On the other hand, the structure of $Na_2[Mo_4(NO)_4(S_2)_6O]\cdot 3H_2O$ was solved [7] in the monoclinic space group *Ic*, although the authors did consider, and reject, $I4_1/a$. However the structure of the anion is essentially the same as that in the tetragonal case. The present calculations used the coordinates from the tetragonal structure [6], giving the anion S_4 symmetry.

The two highest occupied molecular orbitals, at −11.93 eV (HOMO) and −11.95 eV respectively, belong to the symmetry classes B and A respectively in S_4 symmetry, and both are of π^* (S–S) type, concentrated in the two-fold disulphide ligands, described by Müller [6] as 'handle-shaped'. The next eight occupied orbitals, in the energy range −12.10 to −12.57 eV, of symmetry classes 2A + 2B + 2E, are the Mo–NO π orbitals. The LUMO and the neighbouring unoccupied orbitals are, like the HOMO, of π^* (S–S) type, but now concentrated in the four-fold disulphide ligands, those described by Müller [6] as 'roof-shaped'. None of the orbitals in the frontier region contains any significant contribution from the μ_4-oxo ligand.

The strongest interaction, as measured by the overlap population, is as before, the Mo–N interaction (overlap 0.80): the Mo–S overlap populations again vary widely; 0.52 for the 'handle' type sulphur, and values in the range 0.31–0.25 for the four distinct Mo–S interactions involving the 'roof' type sulphurs. There is a monotonic inverse relationship between the Mo–S distances and the Mo–S overlap populations.

$[Mo_4(NO)_4(S)_3(S_2)_5]^{4-}$

This cluster anion [8, 9] is remarkable chiefly for the wide variety of different types of sulphur environments, five in all, which it exhibits. The core of the structure consists of a roughly trigonal bipyramidal SMo_4 cluster, having the sulphur in an equatorial site bonded to all four molybdenum atoms, with a μ_3-sulphur capping each triangular Mo_3 face. As in previous clusters, the frontier orbitals do not involve the molecular core: the HOMO, and the neighbouring occupied orbitals are primarily Mo–NO π-orbitals, while the LUMO and the neighbouring virtual orbitals are π^* orbitals of the S_2 ligands. As in $[Mo_4(NO)_4(S_2)_6O]^{2-}$, the Mo–S overlap populations vary widely: those involving the μ_4-sulphide range from 0.24 to 0.34, considerably less than in the core fragment $\{[Mo(NO)]_4S\}^{10+}$; those involving the μ_3-sulphide ligands are in the range 0.37 to 0.45 (*cf.* 0.42 to 0.56 in the fragment $\{[Mo(NO)_4(S)_3]\}^{6+}$), those of the symmetric μ_2-$(S_2)^{2-}$ ligand are 0.28, while those involving the asymmetrically bond disulphide ligands range from 0.24 to 0.38.

$[Mo_4(NO)_4S_4(CN)_8]^{8-}$ and $Mo_4(NO)_4S_4$

The octacyano cluster $[Mo_4(NO)_4S_4(CN)_8]^{8-}$ was isolated in low yield from the reaction of $[Mo_4(NO)_4(S_2)_6O]^{2-}$ with an excess of cyanide [11]. The crystal structure of $K_8[Mo_4(NO)_4S_4(CN)_8]\cdot 4H_2O$ is complex, having only two formula unit in space-group $P4_2/nmc$, in which there are sixteen general positions. Since there are only eight each of molybdenum, sulphur, and nitrosyl groups in the unit cell, either all of these atoms must lie on symmetry elements, or this must be accompanied by orientational disorder within the cluster, giving an apparently higher site symmetry. The anions lie on sites of D_{2d} symmetry, with three different orientations, of which two are crystallographically distinct, and the detailed structures of the two distinct types of anion are markedly different [11]. Both can however be regarded as rather loose aggregates of two $[Mo_2(NO)_2S_2(CN)_4]^{4-}$ species coupled by very long (2.76 Å) Mo–S interactions.

The fundamental fragment of this cubane-type cluster is the neutral dinuclear species $Mo_2(NO)_2S_2$, which occurs [11] in masked form in the dinuclear anion $[Mo_2(NO)_2S_2(CN)_6]^{6-}$. In contrast to all other molybdenum–sulphur nitrosyl species so far considered, in $Mo_2(NO)_2S_2$ the HOMO, at −11.44 eV is concentrated in the Mo_2 fragment, where it is strongly bonding: with the Mo_2S_2 group in the xy plane, this orbital is primarily the in-phase σ combination of $d_{x^2-y^2}$. The next four occupied orbitals, in the range −11.66 to −12.70 eV are the Mo–NO π orbitals. The LUMO at −10.49 eV is likewise concentrated in the Mo_2 fragment, where it is a π^* orbital, made up of the in-phase combination of d_{xy}: the next virtual orbital is a similar π^* combination of d_{yz}. Coordination by cyano ligands effects a reorganisation of the orbitals in the frontier region so that the HOMO in $[Mo_2(NO)_2S_2(CN)_4]^{4-}$ at −11.47 eV is an Mo–NO π orbital and the LUMO is an Mo–NO π^* orbital: the next occupied orbital at −11.52 eV is however a strongly bonding Mo–Mo σ orbital comprised of the in-phase combination of $d_{x^2-y^2}$. Entirely analogous frontier orbitals occur in the tetranuclear species $Mo_4(NO)_4S_4$ and $[Mo_4(NO)_4S_4(CN)_8]^{8-}$.

Two measures of the interactions between the pairs of dinuclear fragments in $Mo_4(NO)_4S_4$ and $[Mo_4(NO)_4S_4(CN)_8]^{8-}$ are the Mo–S overlap populations, and the dimerisation energies. In the cyanide free system, the Mo–S overlap population in $Mo_2(NO)_2S_2$ is 0.84: in the dimer, $Mo_4(NO)_4S_4$, the Mo–S overlap is essentially the same, 0.79, within the $Mo_2(NO)_2S_2$ units, but only 0.29 between the units. In the cyano-complexes, the Mo–S overlap population in $[Mo_2(NO)_2S_2(CN)_4]^{4-}$ is 0.80, whereas in $[Mo_4(NO)_4S_4(CN)_8]^{8-}$ it is 0.76 within the units but only 0.28 between them. For dimerisation of $Mo_2(NO)_2S_2$ the inter-unit Mo–S bond energy is calculated to be 71 kJ (mol Mo–S)$^{-1}$ and for dimerisation of $[Mo_2(NO)_2S_2(CN)_4]^{4-}$ it is 75 kJ (mol Mo–S)$^{-1}$: these are weak bonds.

Discussion

The results outlined above point up a number of generalisations wherein nitrosylated molybdenum–sulphur clusters may be contrasted with nitrosylated iron–sulphur clusters.

First, the general forms of the frontier orbitals are entirely different for the two classes of clusters. In the iron systems, the frontier orbitals are concentrated in the Fe_x cage which is electron precise, so that addition or removal of electrons is expected to weaken the cage bonding, but to leave all other bonds essentially unaltered. In contrast, the frontier orbitals of the molybdenum cluster are not concentrated on the metal centres: rather the HOMO is always concentrated in the bonding Mo–NO interaction, so that oxidation is expected to liberate NO, while leaving the cluster core unaltered; the LUMO is generally antibonding and concentrated in the S_2 ligands, so that further reduction of these anionic clusters is expected to effect cleavage of at least some of the S_2 ligands.

Secondly, the intense axial ligand field of the nitrosyl ligand is sufficient always to impose diamagnetism on Mo(II): in the corresponding iron–sulphur systems which contain d^7 and/or d^9 metal centres, there is evidence from Mössbauer spectroscopy [20] that although $Fe_4S_4(NO)_4$ has a diamagnetic ground state, there is some paramagnetism (although with an effective magnetic moment of less than 1 BM per iron). Hence, although the coupling between the individual paramagnetic centres in the nitrosylated iron–sulphur clusters is strong, it may in some instances be incomplete, and it is possible that as further physical data become available for such species, more sophisticated theoretical models than employed hitherto [1] will be required. On the other hand, in the d^4 molybdenum case, no paramagnetic behaviour is to be expected from any $[Mo(NO)]^{3+}$ fragment: hence, in the absence of redox changes, even if a process were to lead to fragmentation of a nitrosylated molybdenum–sulphur cluster this would, unlike the fragmentation of a nitrosylated iron–sulphur cluster [2] remain undetectable by EPR spectroscopy.

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