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Transition metal complexes with sulfur ligands Part CVII[☆]. Complexes of the [Mo(NO)('S_4')] fragment with 16, 17 and 18 valence electrons ('S_4'$^{2-}$ = 1,2-bis(2-mercaptophenylthio)ethane(2−))

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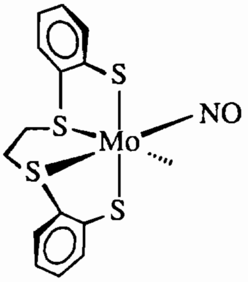
Abstract

Redox-substitution reactions of [Mo^{III}(SPh)(NO)('S_4')] (**4**) with phosphines yielded the mononuclear and paramagnetic 17-electron complexes [Mo^{II}(PR_3)(NO)('S_4')] (PR_3 = PMe_3 (**5**), PEt_3 (**6**), PPr_3 (**7**) and PMe_2Ph (**8**)), exhibiting well resolved EPR spectra. The molecular structure of **5** was determined by X-ray structure analysis. **5** crystallizes in space group $R\bar{3}$ with $a = 2586.6(5)$, $c = 1756.4(4)$ pm, $Z = 18$, shows pseudo-octahedral coordination of the Mo center, and exhibits no anomalies in distances and angles in comparison with other [Mo(L)(NO)('S_4')] complexes. The ability of all 17-electron [Mo(PR_3)(NO)('S_4')] complexes to take up or release one electron to give 18- or 16-electron species was proved by cyclovoltammetry. Attempts to generate the resulting [Mo(PMe_3)(NO)('S_4')]$^{-/+}$ anions or cations by chemical redox reagents led to products which could not be characterized unambiguously. Isolable 16-electron species which could be fully characterized were obtained by oxidation of **5** with Cl_2, Br_2 and I_2 yielding [Mo^{III}(X)(NO)('S_4')] (X = Cl (**3**), Br (**10**), I (**11**)). **10** and **11** were also obtained by treatment of either the chloro complex [Mo(Cl)(NO)('S_4')] (**3**) or the hydroxylaminyl complex [Mo(NH_2O)(NO)('S_4')] (**2**) with HBr and HI. Reaction of **5** with NO gave the 18-electron complex [Mo$(NO)_2$('S_4')] (**1**).

Keywords: Crystal structures; Redox reactions; Molybdenum complexes; Nitrosyl complexes; Polydentate sulfur ligand complexes

1. Introduction

Electron transfer is essential for reactions catalyzed by oxidoreductases. In search of model compounds for oxidoreductases containing molybdenum sulfur centers [2] we have been investigating complexes with [Mo('S_4')] fragments. They coordinate a wide variety of small molecules or ions as coligands, e.g. CO, PMe_3, NO, NH_2O, halides, NH_2^-, SR^-, S^{2-}, forming complexes with six- or seven-coordinate Mo centers in oxidation states II, III or IV. Particularly versatile is the 15-electron [Mo(NO)('S_4')] fragment, which catalyzes the transformation of NO into NH_2OH [3].



[Mo(NO)('S_4')]

This reduction comprises three steps and intermediates showing that the molybdenum center can assume coordination numbers of six or seven and oxidation states of II or III. (In assigning oxidation states, 'S_4' and NO are regarded as dianionic and neutral ligands, respectively.) Isolable intermediates are the six-coordinate [$Mo^{II}$$(NO)_2$('$S_4$')] (**1**), the seven-coordinate [Mo^{II}(NH_2O)(NO)('S_4')] (**2**) and the six-coordinate [Mo^{III}(Cl)(NO)('S_4')] (**3**) which are either 18-electron or 16-electron species. Assignments of oxidation states are supported by ^{95}Mo NMR spectroscopy showing that

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the ^{95}Mo NMR shift is nearly identical for **1** and **2**. ^{95}Mo NMR spectroscopy also indicates a change in oxidation state of molybdenum from +II to +III when **1** reacts with phosphines to give the phosphineiminato complexes [Mo(NPR$_3$)(NO)('S$_4$')] [4]. This reaction probably proceeds via an associative mechanism including a seven-coordinate [Mo(PR$_3$)(NO)$_2$('S$_4$')] intermediate.

Associative mechanisms can also be assumed for the substitution reactions according to Eq. (1) [5], because **3** easily forms seven-coordinate adducts when

$$\underset{\mathbf{3}}{[\mathrm{Mo(Cl)(NO)('S_4')}]} + \mathrm{RS^-} \longrightarrow [\mathrm{Mo(SR)(NO)('S_4')}] + \mathrm{Cl^-} \qquad (1)$$

reacted with nucleophiles such as PMe$_3$ [5] according to Eq. (2).

$$[\mathrm{Mo(Cl)(NO)('S_4')}] + \mathrm{PMe_3} \longrightarrow [\mathrm{Mo(Cl)(PMe_3)(NO)('S_4')}] \qquad (2)$$

When we tried to carry out the analogous reaction with the thiolate derivative [Mo(SPh)(NO)('S$_4$')] (**4**), we observed a redox coupled substitution of the PhS ligand and formation of the 17-electron species [Mo(PMe$_3$)(NO)('S$_4$')] (**5**). It completes the series of 16-, 17- and 18-electron complexes which can be generated from the 15-electron fragment [Mo(NO)('S$_4$')].

2. Experimental

2.1. General

Unless otherwise noted all synthetic procedures were carried out under nitrogen atmosphere at room temperature using standard Schlenk techniques. Solvents were dried and distilled before use. As far as possible the reactions were monitored by IR spectroscopy. Spectra were recorded on the following instruments: IR: Perkin-Elmer 1620 FT IR (KBr discs or CaF$_2$ cuvettes, solvent bands were compensated). NMR: Jeol FT NMR spectrometer JNM-GX 270 and EX 270 (^{14}N chemical shifts were referred to ext. NH$_4$NO$_3$, ^{31}P shifts to ext. H$_3$PO$_4$). EPR: Bruker ESP 300. Mass spectra: Varian MAT 212. Magnetic moments were determined with a Johnson Matthey susceptibility balance. Cyclic voltammetry (CV) experiments were carried out with a PAR 264A potentiostat, ROTEL A glassy carbon working electrode, Ag/AgCl reference and Pt counter electrodes. Potentials were measured versus internal ferrocene and referred to NHE.

[Mo(SPh)(NO)('S$_4$')] [5], [Mo(Cl)(NO)('S$_4$')] [6], [Mo(η^2-NH$_2$O)(NO)('S$_4$')] [3] and [Cp$_2$Fe]PF$_6$ [7] were prepared by literature methods.

2.2. Synthesis and reactions

2.2.1. [Mo(PMe$_3$)(NO)('S$_4$')] (5)

A dark purple suspension of [Mo(SPh)(NO)('S$_4$')]·0.5CH$_2$Cl$_2$ (1.48 g, 2.5 mmol) and PMe$_3$ (2.5 ml, 24 mmol) in 30 ml of THF was stirred for 3 days at 40 °C yielding a deep red solution. It was evaporated to dryness and the resulting residue was dissolved in 20 ml of CH$_2$Cl$_2$. The solution was layered with 20 ml of MeOH and cooled to −35 °C. Precipitated black–red crystals were separated after 10 days, washed with 10 ml of MeOH, and dried in vacuo. Yield 970 mg (70%).

Anal. Calc. for C$_{17}$H$_{21}$MoNOPS$_4$·0.5CH$_2$Cl$_2$ (552.97) = [Mo(PMe$_3$)(NO)('S$_4$')]·0.5CH$_2$Cl$_2$: C, 38.01; H, 4.01; N, 2.53; S, 23.19. Found: C, 38.34; H, 4.02; N, 2.59; S, 23.31%.

IR (KBr): ν(NO) = 1603 cm^{-1}, δ(PCH) = 952 cm^{-1}.

EI mass spectrum (^{98}Mo (*m/z*): 512 ([Mo(PMe$_3$)(NO)('S$_4$')]$^+$), 454 ([Mo(PMe$_3$)('S$_2$')$_2$]$^+$), 378 ([Mo('S$_2$')$_2$]$^+$); ('S$_2$'$^{2-}$ = 1,2-benzenedithiolate(2−)).

2.2.2. [Mo(PEt$_3$)(NO)('S$_4$')] (6)

A dark purple suspension of [Mo(SPh)(NO)('S$_4$')]·0.5CH$_2$Cl$_2$ (410 mg, 0.7 mmol) and PEt$_3$ (0.7 ml, 4.7 mmol) in 40 ml of THF was refluxed for 3 days yielding a deep red solution. Volatile components were removed in vacuo and the remaining tarry residue was stirred with 50 ml of pentane for 3 days. The resulting red powder was separated, washed with 20 ml of pentane, and dried in vacuo. Yield 360 mg (93%).

Anal. Calc. for C$_{20}$H$_{27}$MoNOPS$_4$ (552.59) = [Mo(PEt$_3$)(NO)('S$_4$')]: C, 43.47; H, 4.92; N, 2.53. Found: C, 44.01; H, 5.07; N, 2.40%.

IR (KBr): ν(NO) = 1603 cm^{-1}.

FD mass spectrum (CH$_2$Cl$_2$, ^{98}Mo (*m/z*)): 554 ([Mo(PEt$_3$)(NO)('S$_4$')]$^+$).

2.2.3. [Mo(PPr$_3$)(NO)('S$_4$')] (7)

A dark purple suspension of [Mo(SPh)(NO)('S$_4$')]·0.5CH$_2$Cl$_2$ (270 mg, 0.46 mmol) and PPr$_3$ (1.0 ml, 5.0 mmol) in 25 ml of THF was refluxed for 3 days yielding a deep red solution. Volatile components were removed in vacuo and the remaining tarry residue was stirred with 30 ml of pentane for 3 days. The resulting red powder was separated, washed with 20 ml of pentane, and dried in vacuo. Yield 220 mg (80%).

Anal. Calc. for C$_{23}$H$_{33}$MoNOPS$_4$ (594.67) = [Mo(PPr$_3$)(NO)('S$_4$')]: C, 46.45; H, 5.59; N, 2.36; S, 21.56. Found: C, 46.15; H, 5.46; N, 2.23; S, 21.46%.

IR (KBr): ν(NO) = 1600 cm^{-1}.

FD mass spectrum (CH$_2$Cl$_2$, ^{98}Mo (*m/z*)): 596 ([Mo(PPr$_3$)(NO)('S$_4$')]$^+$).

2.2.4. [Mo(PMe$_2$Ph)(NO)('S$_4$')] (8)

A dark purple suspension of [Mo(SPh)(NO)('S$_4$')]·0.5CH$_2$Cl$_2$ (200 mg, 0.34 mmol) and PMe$_2$Ph (0.5 ml, 3.5 mmol) in 15 ml of THF was refluxed for 3 days yielding a deep red solution. Volatile components were removed in vacuo and the remaining tarry residue was stirred with 30 ml of pentane for 1 day. The resulting red powder was separated, washed with 15 ml of pentane, dissolved in 6 ml of CH_2Cl_2, layered with 6 ml of MeOH, and cooled to −35 °C. Precipitated black–red crystals were separated after 6 days, washed with 4 ml of MeOH, and dried in vacuo. Yield 100 mg (51%).

Anal. Calc. for $C_{22}H_{23}MoNOPS_4$ (572.58) = [Mo(PMe_2Ph)(NO)('S_4')]: C, 46.15; H, 4.05; N, 2.45. Found: C, 46.02; H, 4.02; N, 2.46%.

IR (KBr): ν(NO) = 1608 cm^{-1}.

FD mass spectrum (CH_2Cl_2, ^{98}Mo (*m/z*)): 574 ([Mo(PMe_2Ph)(NO)('S_4')]$^+$).

2.2.5. Reaction of [Mo(PMe$_3$)(NO)('S$_4$')] (5) with O$_2$

Oxygen gas (10 ml, 0.45 mmol) was injected by means of a syringe into the atmosphere above a deep red solution of [Mo(PMe_3)(NO)('S_4')]·0.5CH_2Cl_2 (110 mg, 0.2 mmol) in 10 ml of CH_2Cl_2. After 3 h of stirring at room temperature, the color of the solution had darkened and black microcrystals precipitated. The mixture was evaporated to dryness. [μ-O{Mo(NO)('S_4')}$_2$] and $OPMe_3$ were identified by IR, NMR and FD mass spectroscopy in the resulting residue.

IR (KBr): ν(NO) = 1654, 1634 cm^{-1}.

FD mass spectrum (CH_2Cl_2, $^{98/96}$Mo (*m/z*)): 886 [μ-O{Mo(NO)('S_4')}$_2$]$^+$).

^{1}H NMR (269.6 MHz, CD_2Cl_2, δ (ppm)): 7.7–6.8 (m, 16H, C_6H_4), 3.5–2.4 (m, 8H, C_2H_4), 1.5 (d, $^3J(^{31}P–^1H)$ = 13 Hz, $OP(CH_3)_3$).

$^{31}P\{^1H\}$ NMR (109.38 MHz, CD_2Cl_2, δ (ppm)): 35 (s, $OPMe_3$).

2.2.6. [Mo(PMe$_3$)(NO)('S$_4$')]PF$_6$·CH$_2$Cl$_2$ (9)

[Cp_2Fe]PF_6 (220 mg, 0.66 mmol) was added to a deep red solution of [Mo(PMe_3)(NO)('S_4')]·0.5CH_2Cl_2 (360 mg, 0.67 mmol) in 20 ml of CH_2Cl_2 at −78 °C. The mixture was slowly warmed up to room temperature and stirred for ~10 h. Black–red microcrystals precipitated which were separated, washed with 4 ml of CH_2Cl_2, and dried in vacuo. Yield 270 mg (54%).

Anal. Calc. for $C_{17}H_{21}F_6MoNOP_2S_4 \cdot CH_2Cl_2$ (740.39) = [Mo(PMe_3)(NO)('S_4')]PF_6·CH_2Cl_2: C, 29.20; H, 3.13; N, 1.89; S, 17.32. Found: C, 29.21, H, 3.34; N, 1.88; S, 17.41%.

IR (KBr): ν(NO) = 1653, 1635 cm^{-1} (superimposed).

^{1}H NMR (269.6 MHz, DMF-d_7, δ (ppm)): 7.75–6.85 (m, 8H, C_6H_4), 5.75 (s, CH_2Cl_2), 3.80–2.80 (m, 4H, C_2H_4), 1.98 (d, $^3J(^{31}P–^1H)$ = 16 Hz, 4.5H, $P(CH_3)_3$), 1.97 (d, $^3J(^{31}P–^1H)$ = 16 Hz, 4.5H, $P(CH_3)_3$).

$^{31}P\{^1H\}$ NMR (109.38 MHz, DMF-d_7, δ (ppm)): −1.5 (s, PMe_3), −145 (septet, $^1J(^{19}F–^{31}P)$ = 710 Hz, PF_6).

$^{13}C\{^1H\}$ NMR (67.7 MHz, DMF-d_7, δ (ppm)): 156.4, 155.2, 152.8, 151.8, 134.6–123.6 (C_6H_4), 55.2, 44.0, 41.2, 41.0 (C_2H_4), 5.0 (d, $^1J(^{31}P–^{13}C)$ = 56 Hz, $P(CH_3)_3$).

2.2.7. Reaction of [Mo(PMe$_3$)(NO)('S$_4$')] (5) with Cl$_2$

Chlorine gas (4 ml, 0.18 mmol) was injected by means of a syringe into the atmosphere above a deep red solution of [Mo(PMe_3)(NO)('S_4')]·0.5CH_2Cl_2 (100 mg, 0.18 mmol) in 10 ml of CH_2Cl_2. After 4 h of stirring at room temperature the resulting purple–red solution was evaporated to dryness. In the residue, [Mo(Cl)(NO)('S_4')] was identified by IR and FD mass spectroscopy.

IR (KBr): ν(NO) = 1670 cm^{-1}.

FD mass spectrum (CH_2Cl_2, ^{98}Mo (*m/z*)): 471 ([Mo(Cl)(NO)('S_4')]$^+$).

2.2.8. Reaction of [Mo(PMe$_3$)(NO)('S$_4$')] (5) with Br$_2$

A solution of bromine (16 μl, 0.31 mmol) in 5 ml of CH_2Cl_2 was added to a solution of [Mo(PMe_3)(NO)('S_4')]·0.5CH_2Cl_2 (160 mg, 0.29 mmol) in 10 ml of CH_2Cl_2. The reaction mixture was evaporated to dryness. In the resulting residue, [Mo(Br)(NO)('S_4')] was identified by IR and FD mass spectroscopy.

IR (KBr): ν(NO) = 1672 cm^{-1}.

FD mass spectrum (CH_2Cl_2, ^{98}Mo (*m/z*)): 515 ([Mo(Br)(NO)('S_4')]$^+$).

2.2.9. Reaction of [Mo(PMe$_3$)(NO)('S$_4$')] (5) with I$_2$

Iodine (110 mg, 0.43 mmol) was added to a solution of [Mo(PMe_3)(NO)('S_4')]·0.5CH_2Cl_2 (240 mg, 0.43 mmol) in 20 ml of CH_2Cl_2, in the course of which the color of the solution changed from deep red to blue–violet and microcrystals of [Mo(I)(NO)('S_4')] precipitated. They were separated and identified by IR and FD mass spectroscopy.

IR (KBr): ν(NO) = 1670 cm^{-1}.

FD mass spectrum (CH_2Cl_2, ^{98}Mo (*m/z*)): 563 ([Mo(I)(NO)('S_4')]$^+$).

2.2.10. [Mo(Br)(NO)('S$_4$')] (10) from [Mo(Cl)(NO)('S$_4$')] (3)

1 ml of HBr (~50% in H_2O) was added to a suspension of [Mo(Cl)(NO)('S_4')] (1.1 g, 2.34 mmol) in 50 ml of THF. The reaction mixture was stirred for 1 h and evaporated to dryness. The resulting microcrystals of [Mo(Br)(NO)('S_4')] were washed with 40 ml of MeOH and dried in vacuo. Yield 1.15 g (96%).

Anal. Calc. for $C_{14}H_{12}BrMoNOS_4$ (514.34) = [Mo(Br)(NO)('S_4')]: C, 32.69; H, 2.35; N, 2.72; S, 24.94. Found: C, 32.99; H, 2.38; N, 2.11; S, 25.11%.

IR (KBr): ν(NO) = 1672 cm^{-1}.

^{1}H NMR (269.6 MHz, CD_2Cl_2, δ (ppm)): 7.80–7.00 (m, 8H, C_6H_4), 3.45–2.45 (m, 4H, C_2H_4).

$^{13}C\{^1H\}$ NMR (67.94 MHz, CD_2Cl_2, δ (ppm)): 157.2, 156.6, 134.4–124.4 (C_6H_4); 45.5, 41.2 (C_2H_4).

^{14}N NMR (19.53 MHz, CD_2Cl_2, δ (ppm)): +41 (*N*O).

FD/EI mass spectrum (^{98}Mo (*m/z*)): 515 ([Mo(Br)(NO)('S_4')]$^+$).

2.2.11. [Mo(Br)(NO)('S$_4$')] (10) from [Mo(η^2-NH$_2$O)(NO)('S$_4$')] (2)

1.5 ml of HBr (~50% in H_2O) were added to a yellow suspension of [Mo(η^2-NH_2O)(NO)('S$_4$')]·THF (315 mg, 0.59 mmol) in 35 ml of MeOH, whereupon the color changed to red–violet. After 2 h of stirring at room temperature, the resulting microcrystals of [Mo(Br)(NO)('S$_4$')] were separated, washed with 40 ml of MeOH and 10 ml of Et_2O, and dried in vacuo. Yield 255 mg (85%).

Anal. Calc. for $C_{14}H_{12}BrMoNOS_4$ (514.34) = [Mo(Br)(NO)('S$_4$')]: C, 32.69; H, 2.35; N, 2.72. Found: C, 33.12; H, 2.28; N, 2.38%.

2.2.12. [Mo(I)(NO)('S$_4$')] (11) from [Mo(Cl)(NO)('S$_4$')] (3)

1 ml of HI (~57% in H_2O) was added to a suspension of [Mo(Cl)(NO)('S$_4$')] (600 mg, 1.28 mmol) in 30 ml of THF, whereupon the color changed from red–violet to blue–violet. After 1 h of stirring at room temperature the reaction mixture was evaporated to dryness. The resulting microcrystals of [Mo(I)(NO)('S$_4$')] were washed with 20 ml of MeOH and 10 ml of Et_2O, and dried in vacuo. Yield 660 mg (92%).

Anal. Calc. for $C_{14}H_{12}IMoNOS_4$ (561.33) = [Mo(I)(NO)('S$_4$')]: C, 29.96; H, 2.15; N, 2.49. Found: C, 30.89; H, 2.07; N, 2.14%.

IR (KBr): ν(NO) = 1670 cm^{-1}.

^{1}H NMR (269.6 MHz, CD_2Cl_2, δ (ppm)): 7.85–7.00 (m, 8H, C_6H_4), 3.50–2.40 (m, 4H, C_2H_4).

^{13}C{^{1}H} NMR (67.94 MHz, CD_2Cl_2, δ (ppm)): 143.8, 141.4, 120.3–110.2 (C_6H_4); 31.1, 28.3 (C_2H_4).

^{14}N NMR (19.53 MHz, CD_2Cl_2, δ (ppm)): +43.5 (*N*O).

FD/EI mass spectrum (^{98}Mo (*m*/*z*)): 563 ([Mo(I)(NO)('S$_4$')]$^+$).

2.2.13. [Mo(I)(NO)('S$_4$')] (11) from [Mo(η^2-NH$_2$O)(NO)('S$_4$')] (2)

0.13 ml of HI (~57% in H_2O) was added to a yellow suspension of [Mo(η^2-NH_2O)(NO)('S$_4$')]·THF (270 mg, 0.50 mmol) in 30 ml of MeOH, whereupon the color changed to blue–violet. After 3 h of stirring at room temperature, the resulting black lustrous microcrystals of [Mo(I)(NO)('S$_4$')] were separated, washed with 40 ml of MeOH and 20 ml of Et_2O, and dried in vacuo. Yield 250 mg (89%).

Anal. Calc. for $C_{14}H_{12}IMoNOS_4$ (561.33) = [Mo(I)(NO)('S$_4$')]: C, 29.96; H, 2.15; N, 2.49. Found: C, 29.86; H, 1.87; N, 2.21%.

2.2.14. Reaction of [Mo(PMe$_3$)(NO)('S$_4$')] (5) with Na

A solution of [Mo(PMe_3)(NO)('S$_4$')]·0.5CH_2Cl_2 (160 mg, 0.29 mmol) in 15 ml of THF was stirred at −78 °C with sodium powder for 5 h, in the course of which the color changed from deep red to orange–brown. The resulting species, presumably Na[Mo(PMe_3)(NO)('S$_4$')], was too unstable to be isolated.

2.2.15. Reaction of [Mo(PMe$_3$)(NO)('S$_4$')] (5) with NO

NO gas (14 ml, 0.6 mmol) was injected by means of a syringe into the atmosphere above a deep red solution of [Mo(PMe_3)(NO)('S$_4$')]·0.5CH_2Cl_2 (160 mg, 0.29 mmol) in 15 ml of CH_2Cl_2. After 3 h of stirring at room temperature, the resulting orange–brown solution was evaporated to dryness. In the resulting residue, [Mo$(NO)_2$('S$_4$')] and $OPMe_3$ were identified by IR, NMR and FD mass spectroscopy.

IR (KBr): ν(NO) = 1760, 1665 cm^{-1}.

^{1}H NMR (269.6 MHz, $CDCl_3$, δ (ppm)): 7.7–6.9 (m, C_6H_4), 3.5–2.9 (m, C_2H_4), 1.55 (d, OP$(CH_3)_3$).

^{31}P{^{1}H} NMR (109.38 MHz, $CDCl_3$, δ (ppm)): 37.5 (s, O*P*Me$_3$).

FD mass spectrum (CH_2Cl_2, ^{98}Mo (*m*/*z*)): 466 [(Mo$(NO)_2$('S$_4$')]$^+$).

2.3. X-ray structure analysis of [Mo(PMe$_3$)(NO)('S$_4$')]

Single crystals of **5** were obtained from a CH_2Cl_2 solution which was layered with MeOH and cooled to −35 °C. A suitable crystal was sealed in a glass capillary under N_2. The structure was solved by direct methods. Non-hydrogen atoms were refined anisotropically, the positions of the hydrogen atoms were taken from difference Fourier syntheses and restricted during refinement. Hydrogen atoms were refined with common isotropic temperature factors. High residual electron density at $x = 0$, $y = 0$, $z = 0.6$ indicated residual and disordered CH_2Cl_2 whose atomic coordinates could not be determined. Table 1 summarizes crystallographic data for **5**; the fractional atomic coordinates are listed in Table 2.

3. Results and discussion

3.1. Syntheses of [Mo(PR$_3$)(NO)('S$_4$')] complexes

The reaction of PMe_3 with the chloro complex [Mo(Cl)(NO)('S$_4$')] (**3**) yielding [Mo(Cl)(PMe_3)(NO)('S$_4$')] takes place in solution at ambient temperature [5]. In contrast, the reaction solution had to be heated in order to observe a reaction between PMe_3 and the thiolato complex [Mo(SPh)(NO)('S$_4$')] (**4**). It yielded, however, no simple PMe_3 adduct but the 17-electron complex [Mo(PMe_3)(NO)('S$_4$')] (**5**) according to Eq. (3).

Table 1
Summary of crystallographic data and data collection procedures for **5**

Formula	$C_{17}H_{21}MoNOPS_4$
Molecular weight	510.51
Crystal size (mm^3)	$0.6 \times 0.5 \times 0.5$
Colour, habit	black, cubes
Space group	$R\bar{3}$
Crystal system	rhombohedral
a (pm)	2586.6(5)
c (pm)	1756.4(4)
V (nm^3)	10.179(4)
Z	18
ρ_{calc} (g/cm^3)	1.499
μ (mm^{-1})	1.026
Diffractometer	Siemens P4
Radiation (pm)	Mo Kα, 71.073
Temperature of measurement (K)	293
Scan technique	ω scan
Scan range	$3.0 < 2\Theta < 54.0$
Scan speed (°/min)	3–29.3
Reflections measured	11868
Independent reflections	4978
Observed reflections	3570
σ Criterion	$F > 4\sigma(F)$
Program	SHELXTL-PLUS
R; R_w (%)	4.2; 4.1
Parameters refined	226

Table 2
Fractional atomic coordinates ($\times 10^4$) and isotropic thermal parameters (pm$^2 \times 10^{-1}$) of the non-hydrogen atoms of **5**

	x	y	z	U_{eq}[a]
Mo(1)	1567(1)	3659(1)	403(1)	36(1)
N(1)	1024(3)	3741(3)	936(4)	45(3)
O(1)	655(3)	3804(3)	1267(4)	73(4)
S(1)	2430(1)	4528(1)	926(1)	51(1)
S(2)	2375(1)	3589(1)	−371(1)	39(1)
S(3)	1711(1)	2986(1)	1311(1)	41(1)
S(4)	890(1)	2694(1)	−236(1)	47(1)
P(1)	1478(1)	4282(1)	−603(1)	52(1)
C(1)	834(6)	3938(6)	−1190(7)	98(9)
C(2)	2092(6)	4633(6)	−1277(7)	95(8)
C(3)	1423(7)	4886(5)	−193(7)	94(9)
C(15)	3059(3)	4167(3)	−27(5)	38(4)
C(14)	3585(4)	4208(4)	−294(5)	49(4)
C(13)	4129(4)	4640(5)	−3(6)	62(5)
C(12)	4150(4)	5038(4)	545(6)	58(4)
C(11)	3634(4)	5016(4)	801(5)	50(4)
C(10)	3067(3)	4565(4)	528(5)	41(4)
C(25)	1137(4)	2238(4)	1076(5)	43(4)
C(24)	1055(4)	1781(4)	1558(5)	55(5)
C(23)	616(5)	1207(4)	1379(7)	66(5)
C(22)	266(4)	1094(4)	764(7)	60(5)
C(21)	345(4)	1534(4)	293(6)	55(4)
C(20)	787(3)	2134(4)	411(5)	43(4)
C(16)	2375(3)	2959(3)	80(5)	40(4)
C(26)	2369(3)	2988(3)	929(5)	44(4)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensors.

$$\underset{\mathbf{4}}{[Mo(SPh)(NO)(\text{'}S_4\text{'})]} + PMe_3 \text{ (excess)} \xrightarrow[3 \text{ days}]{\text{THF, 40 °C}}$$

$$\underset{\mathbf{5}}{[Mo(PMe_3)(NO)(\text{'}S_4\text{'})]} + \tfrac{1}{2}\, PhS\text{–}SPh \quad (3)$$

The thiolate ligand was oxidized and released as disulfide PhSSPh that was identified by mass spectroscopy. The reaction could conveniently be monitored by IR spectroscopy (Fig. 1). Analogous reactions took place with bulkier phosphines such as PEt_3, PPr_3 and PMe_2Ph yielding [Mo(PEt$_3$)(NO)('S$_4$')] (**6**), [Mo(PPr$_3$)(NO)('S$_4$')] (**7**) and [Mo(PMe$_2$Ph)(NO)('S$_4$')] (**8**). Phosphines with even larger cone angles [8], e.g. $PMePh_2$, PPh_3 and PCy_3, did not react with [Mo(SPh)(NO)('S$_4$')].

The resulting dark red complexes are soluble in CH_2Cl_2, $CHCl_3$ or THF and were characterized by elemental analysis and spectroscopy. They exhibit characteristic ν(NO) bands at ~1605 cm^{-1} in their IR (KBr) spectra (Table 3), **5** additionally shows the typical δ(PCH) of PMe_3 at 952 cm^{-1}. In the FD mass spectra, the molecular ions could be observed, the EI mass spectrum of **5** additionally showed the fragment ions [Mo(PMe$_3$)('S$_2$')$_2$]$^+$ and [Mo('S$_2$')$_2$]$^+$ ('S$_2$'$^{2-}$ = 1,2-benzenedithiolate(2−)). The paramagnetism was only determined for **5** whose $\mu_{eff} = 1.55$ BM corresponds to one unpaired electron. All 17-electron complexes

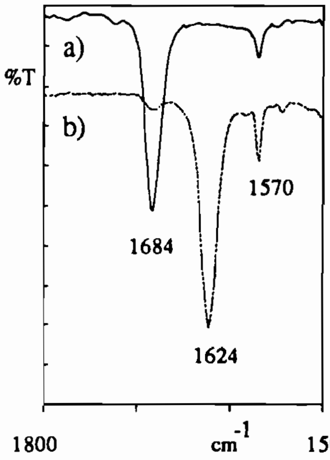


Fig. 1. ν(NO) IR spectra of a THF solution of: (a) [Mo(SPh)(NO)('S$_4$')], (b) after reaction with PMe_3 for 3 days at 40 °C.

Table 3
ν(NO) frequencies and EPR data of **5**, **6**, **7** and **8**

	ν(NO) (KBr) (cm^{-1})	g	a(N) (G)	a(P) (G)
[Mo(PMe$_3$)(NO)('S$_4$')] (**5**)	1603	2.009	2.7	23.1
[Mo(PEt$_3$)(NO)('S$_4$')] (**6**)	1603	2.007	2.9	23.5
[Mo(PPr$_3$)(NO)('S$_4$')] (**7**)	1600	2.007	2.8	23.7
[Mo(PMe$_2$Ph)(NO)('S$_4$')] (**8**)	1608	2.007	2.6	23.3

yielded well resolved EPR spectra exhibiting very similar g values and coupling constants (Table 3).

Fig. 2 shows the observed and simulated EPR spectra of [Mo(PMe$_3$)(NO)('S$_4$')] (**5**). The spectrum exhibits a signal at $g_{iso} = 2.009$ with hyperfine coupling due to the nitrogen (^{14}N, $I = 1$, $a = 2.7$ G), phosphorus (^{31}P, $I = 1/2$, $a = 23.1$ G) and molybdenum nuclei (^{95}Mo (15.9%), $I = 5/2$, $a \approx 30.5$ G and ^{97}Mo (9.6%), $I = 5/2$, $a \approx 32.2$ G). The data are consistent with delocalization of the unpaired electron over at least the [N–Mo–P] core of **5**.

3.2. Molecular structure of [Mo(PMe$_3$)(NO)('S$_4$')] (5)

5 was also characterized by X-ray structure determination. Fig. 3 shows the molecular structure of **5**, Table 4 lists selected distances and angles. The molybdenum center of **5** is pseudo-octahedrally surrounded by one N, one P and four S atoms. Nitrosyl and phosphine ligands occupy *cis* positions. The thiolate S donors are *trans* to each other, as in most [Mo('S$_4$')] complexes. Distances and angles show no anomalies and lie in the range of other [Mo(L)(NO)('S$_4$')] complexes such as [Mo(Cl)(NO)('S$_4$')] [6], [Mo(NMe$_2$)(NO)('S$_4$')] [6], [Mo(NPMePh$_2$)(NO)('S$_4$')] [9] and [Mo(NO)$_2$('S$_4$')] [4]. Although these complexes possess different valence electron numbers, Mo oxidation states and ν(NO) frequencies, they exhibit very similar Mo–S distances (Table 5).

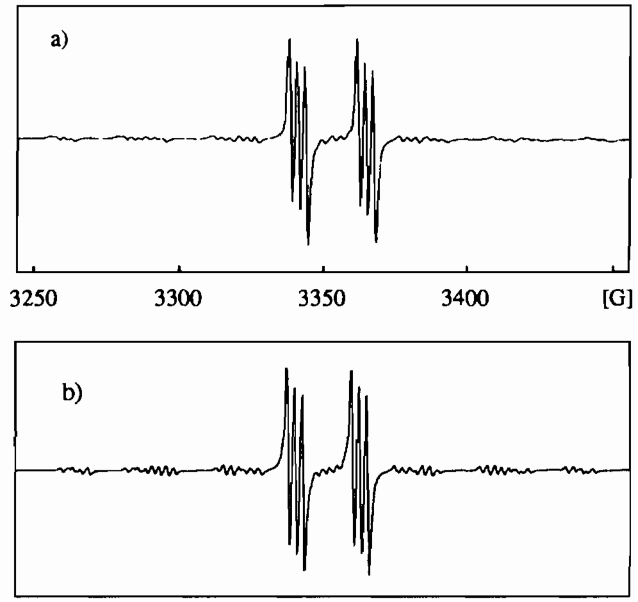


Fig. 2. (a) Observed and (b) simulated EPR spectra of [Mo(PMe$_3$)(NO)('S$_4$')] (5).

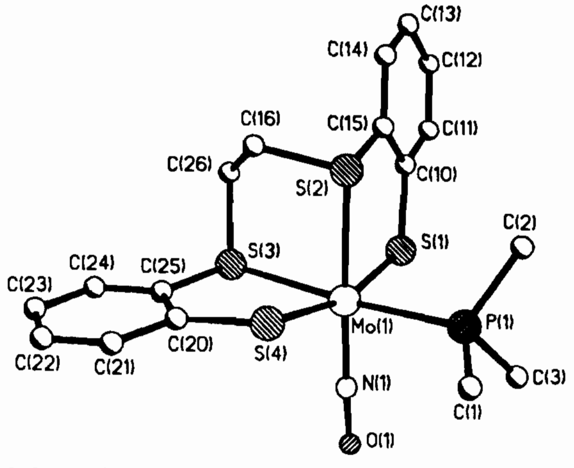


Fig. 3. Molecular structure of [Mo(PMe$_3$)(NO)('S$_4$')] (5) (H atoms omitted).

Table 4
Selected distances (pm) and angles (°) of [Mo(PMe$_3$)(NO)('S$_4$')] (5)

Mo(1)–N(1)	178.6(9)	N(1)–Mo(1)–S(2)	177.6(2)
Mo(1)–S(1)	242.1(2)	N(1)–Mo(1)–S(3)	98.4(3)
Mo(1)–S(2)	257.4(3)	S(1)–Mo(1)–S(2)	82.1(1)
Mo(1)–S(3)	252.0(3)	S(1)–Mo(1)–S(3)	90.8(1)
Mo(1)–S(4)	248.6(2)	S(1)–Mo(1)–S(4)	164.3(1)
Mo(1)–P(1)	247.9(3)	S(2)–Mo(1)–S(3)	83.1(1)
N(1)–O(1)	119.8(12)	N(1)–Mo(1)–P(1)	87.9(3)
S(1)–C(10)	174.7(10)	S(1)–Mo(1)–P(1)	90.5(1)
S(2)–C(15)	175.8(7)	S(3)–Mo(1)–P(1)	173.4(1)
S(2)–C(16)	181.0(10)	Mo(1)–N(1)–O(1)	177.3(7)

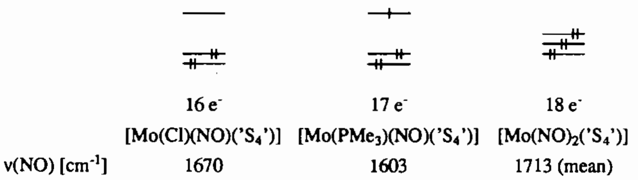
With standard deviations taken into account, Mo–S(thiolate) or Mo–S(thioether) distances only show a small or no elongation when going from [Mo(Cl)(NO)('S$_4$')] via [Mo(PMe$_3$)(NO)('S$_4$')] to [Mo(NO)$_2$('S$_4$')]. In contrast, the ν(NO) frequencies of these complexes vary significantly by more than 100 cm^{-1}, when 1713 cm^{-1} is taken as a mean ν(NO) value of [Mo(NO)$_2$('S$_4$')] (ν(NO) = 1760, 1665 cm^{-1}). This indicates that changes in electron density are restricted to π type molecular orbitals involving mainly the [Mo(X)(NO)] unit and that the Mo–S bonds predominantly have σ character. In terms of MO theory, the t_{2g} frontier orbitals of pseudo-octahedral [Mo(X)(NO)('S$_4$')] complexes can be assumed to have π character and the approximate splittings and occupancies according to Scheme 1 [10].

5 versus 4 electrons in these orbitals explain the ν(NO) decrease when comparing [Mo(Cl)(NO)('S$_4$')] with [Mo(PMe$_3$)(NO)('S$_4$')]. The high ν(NO) in [Mo(NO)$_2$('S$_4$')] is certainly due to the second NO ligand. Although the orbitals are now fully occupied, four π*(NO) orbitals compete for the six molybdenum centered electrons, when going from [Mo(PMe$_3$)(NO)('S$_4$')] to [Mo(NO)$_2$('S$_4$')] and replacing the weak π acceptor PMe$_3$ by the very strong π acceptor NO.

Scheme 1 also explains the different ν(NO)s in the 16-electron species [Mo(X)(NO)('S$_4$')], X = Cl, NMe$_2$, NPMePh$_2$. The LUMOs of these complexes are empty but suitable to interact with lone pairs of X. As expected

Table 5
Molybdenum oxidation states, valence electron numbers, ν(NO) frequencies and selected distances and angles of [Mo(L)(NO)('S_4')] complexes

	[Mo(L)(NO)('S_4')], L=				
	Cl	PMe_3	NO	NMe_2	$NPMePh_2$
Mo oxidation state	III	II	II	III	III
Valence electrons	16	17	18	16	16
ν(NO) (KBr) (cm^{-1})	1670	1603	1713	1642	1605
$\bar{d}$(Mo–S(thiolate)) (pm)	239.7(2)	242.5(2)	245.1(3)	244.1(3)	243.4(2)
$\bar{d}$(Mo–S(thioether)) (pm)	253.8(2)	254.7(3)	253.6(3)	259.8(3)	263.7(2)
∢ Mo–N–O (°)	172.7(8)	177.3(7)	177.1(5)	174.7(8)	175.3(6)
Reference	[6]	this work	[4]	[6]	[9]



Scheme 1. Splittings and occupancies of frontier orbitals in 16-, 17- and 18-electron [Mo(X)(NO)('S_4')] complexes.

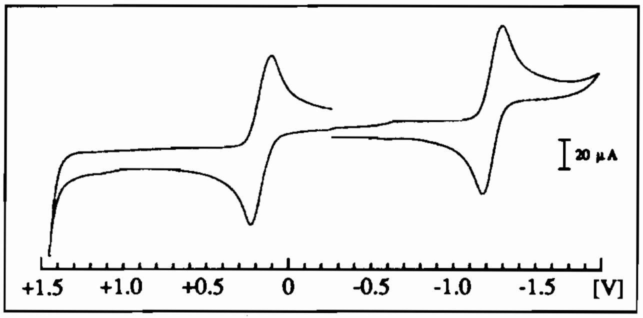


Fig. 4. Cyclic voltammogram of [Mo(PPr_3)(NO)('S_4')] (7) (10^{-3} M in CH_2Cl_2, $v=100$ mV s^{-1}, $T=20$ °C, potentials vs. NHE).

and shown by the ν(NO)s, the π donating ability of X increases in the series $Cl^- < NMe_2^- < NPMePh_2^-$.

3.3. Cyclovoltammetry

Due to their 17-electron molybdenum centers all [Mo(PR_3)(NO)('S_4')] complexes were expected to convert to either 18- or 16-electron species by take-up or loss of one electron. Such electron transfer reactions could be observed in cyclic voltammograms. Fig. 4 shows the cyclic voltammogram of [Mo(PPr_3)(NO)('S_4')] (7) as an example. It exhibits one cathodic and one anodic redox wave which are both reversible and can be assigned to the redox couples [7]/$[7]^-$ and [7]/$[7]^+$.

The cyclic voltammograms of all four [Mo(PR_3)(NO)('S_4')] complexes were nearly identical indicating that the influence of the PR_3 ligands upon the redox behavior is negligible. Selected electrochemical data are summarized in Table 6.

The low oxidation potentials of ~ +0.2 V indicate a very facile oxidation of [Mo(PR_3)(NO)('S_4')] complexes. This was confirmed by their high sensitivity towards air. Upon exposure to air, solutions of [Mo(PR_3)(NO)('S_4')] complexes immediately reacted according to Eq. (4) yielding the corresponding

$$[Mo(PR_3)(NO)('S_4')] \xrightarrow{O_2} [\mu\text{-}O\{Mo(NO)('S_4')\}_2] + OPR_3 \quad (4)$$

μ-oxo complexes [μ-O{Mo(NO)('S_4')}$_2$] [11] and phosphine oxides. The μ-oxo complexes could be identified by their characteristic ν(NO) bands at ~1650 cm^{-1} in the IR spectra, and additionally by a small redox wave at ~ −0.63 V in the cyclic voltammograms [11].

The very negative potentials of the cathodic redox waves around −1.2 V indicate a low tendency of the 17-electron complexes to form the closed shell 18-electron anions $[Mo(PR_3)(NO)('S_4')]^-$. They also explain the easy formation of the neutral [Mo(PR_3)(NO)('S_4')] complexes in the reaction according to Eq. (3).

3.4. Redox reactions of [Mo(PMe_3)(NO)('S_4')] (5)

In order to isolate and characterize the redox products indicated by the cyclic voltammograms, 5 was reacted with various oxidizing and reducing reagents. $[Cp_2Fe]PF_6$ was used for the oxidation of [Mo(PMe_3)(NO)('S_4')], because the PF_6^- anion shows negligible coordinating properties and the oxidation potential of the Fc/Fc^+ couple (+0.4 V) [12] lies well above that of the molybdenum complexes. When a CH_2Cl_2 solution of 5 was treated with $[Cp_2Fe]PF_6$ according to Eq. (5), a reaction took place immedi-

$$\underset{\mathbf{5}}{[Mo(PMe_3)(NO)('S_4')]} + [Cp_2Fe]PF_6 \xrightarrow[-[Cp_2Fe]]{CH_2Cl_2} \underset{\mathbf{9}}{[Mo(PMe_3)(NO)('S_4')]PF_6} \quad (5)$$

Table 6
Selected electrochemical data of the [Mo(PR$_3$)(NO)('S$_4$')] complexes[a]

Complex	$E_{p,c}$ (V)	$E_{p,a}$ (V)	$E°$ (V)	$I_{p,c}/I_{p,a}$	Redox process
[Mo(PMe$_3$)(NO)('S$_4$')] (**5**)	−1.23	−1.11	−1.17	1.1	[**5**]/[**5**]$^-$
	+0.13	+0.26	+0.20	1.0	[**5**]/[**5**]$^+$
[Mo(PEt$_3$)(NO)('S$_4$')] (**6**)	−1.27	−1.14	−1.21	1.1	[**6**]/[**6**]$^-$
	+0.11	+0.25	+0.18	1.0	[**6**]/[**6**]$^+$
[Mo(PPr$_3$)(NO)('S$_4$')] (**7**)	−1.29	−1.16	−1.22	1.0	[**7**]/[**7**]$^-$
	+0.10	+0.23	+0.17	1.0	[**7**]/[**7**]$^+$
[Mo(PMe$_2$Ph)(NO)('S$_4$')] (**8**)	−1.18	−0.97	−1.08	1.0	[**8**]/[**8**]$^-$
	+0.15	+0.29	+0.22	1.0	[**8**]/[**8**]$^+$

[a] $E_{p,c}$ = cathodic peak potential, $E_{p,a}$ = anodic peak potential; $E°$ = redox potential, $I_{p,c}/I_{p,a}$ = peak current ratio.

ately. The color of the solution turned from deep red to red–brown and black lustrous microcrystals started precipitating. They analyzed for [Mo(PMe$_3$)(NO)('S$_4$')]PF$_6$·CH$_2$Cl$_2$ (**9**) but could not be characterized unambiguously. **9** is only soluble in DMF and DMSO, but decomposes in DMSO yielding OPMe$_3$ among other unidentifiable products. Characteristic bands in the IR (KBr) spectrum of **9** are the typical 'S$_4$' absorptions, a splitted ν(NO) band at 1653/1635 cm^{-1} and δ(PCH) and ν(PF$_6$) bands at 968 and 835 cm^{-1}. ^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR spectra also exhibited the typical signals of the ligands and the CH$_2$Cl$_2$ molecule, but allowed no conclusive proposal for the structure of **9**. Solubility and NMR spectra could indicate, however, that **9** is a binuclear complex formed by dimerization of [Mo(PMe$_3$)(NO)('S$_4$')]$^+$ cations. This assumption is supported by the cyclic voltammogram of **9** which completely differs from that of **5**.

Complexes which could be fully characterized were obtained when [Mo(PMe$_3$)(NO)('S$_4$')] (**5**) was oxidized by chlorine, bromine and iodine according to Eq. (6).

$$\underset{\mathbf{5}}{[\mathrm{Mo(PMe_3)(NO)(`S_4')}]} + \mathrm{X_2} \xrightarrow{\mathrm{CH_2Cl_2}} [\mathrm{Mo(X)(NO)(`S_4')}] + \text{other products} \quad (6)$$

X = Cl (**3**), Br (**10**), I (**11**)

One equivalent of X$_2$ was necessary to complete the reactions, but the fate of the removed PMe$_3$ and formal excess of halogen remained incomprehensible. The resulting halide complexes were easily identified by comparison with authentic samples. The bromo and iodo complexes **10** and **11** were alternatively and more easily obtained in high yields by treatment of either the chloro complex **3** or the hydroxylaminyl complex **2** with an excess of HX according to Eqs. 7(a) and (b).

$$\underset{\mathbf{3}}{[\mathrm{Mo(Cl)(NO)(`S_4')}]} + \mathrm{HX(excess)} \xrightarrow{\mathrm{THF}} [\mathrm{Mo(X)(NO)(`S_4')}] + \mathrm{HCl} \quad (7a)$$

$$\underset{\mathbf{2}}{[\mathrm{Mo(NH_2O)(NO)(`S_4')}]} + \mathrm{HX(excess)} \xrightarrow{\mathrm{MeOH}} [\mathrm{Mo(X)(NO)(`S_4')}] + [\mathrm{NH_3OH}]\mathrm{X} \quad (7b)$$

X = Br (**10**), I (**11**)

10 and **11** are sparingly soluble in CH$_2$Cl$_2$, THF and DMF, and exhibit IR and NMR spectra which are very similar to those of **3** [6].

Attempts to isolate salts containing the [Mo(PMe$_3$)(NO)('S$_4$')]$^-$ anion remained unsuccessful. IR spectroscopy showed a shift of the ν(NO) band from 1624 to 1520 cm^{-1} (Fig. 5), and the color of the reaction solution visibly changed from red to orange, when **5** was reacted with sodium powder in THF at −78 °C.

These results could indicate a reaction according to Eq. (8). Working up the solution, however, either

$$\mathbf{5} + \mathrm{Na} \xrightarrow[-78\ °\mathrm{C}]{\mathrm{THF}} \mathrm{Na}^+[\mathbf{5}]^- \quad (8)$$

yielded again the starting complex **5** or decomposition products which no longer contained 'S$_4$' but benz-

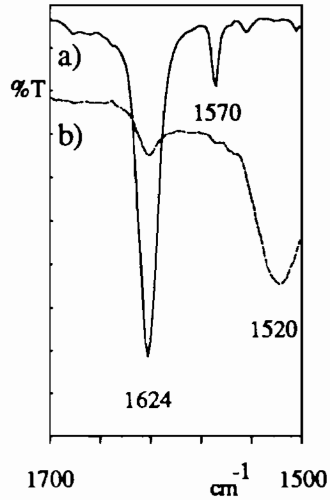


Fig. 5. ν(NO) IR spectra of the THF solution of (a) [Mo(PMe$_3$)(NO)('S$_4$')], (b) after reaction with Na for 5 h at −78 °C.

enedithiolate ligands resulting from elimination of the C_2H_4 bridge of the 'S$_4$' ligand.

Similar results were obtained when **5** was reacted with $LiBEt_3H$, metallic lithium in TMEDA or sodium in liquid ammonia. It was not possible to trap the $[\mathbf{5}]^-$ anion, which presumably formed in reaction (8), by reacting it with H^+ ions or Me_3OBF_4.

The 18-electron complex $[Mo(NO)_2(\text{'S}_4\text{'})]$ (**1**) formed in nearly quantitative yields, when **5** was reacted with NO gas (Eq. (9)). Two equivalents of NO were necessary to complete the formation of **1** via formal substitution of the two-electron donor PMe_3 by the three-electron donor NO. $OPMe_3$, which forms simultaneously, was identified spectroscopically. The fact that 2 equiv. of NO are needed corresponds with the oxidation reactions according to Eq. (6) in which twice as much halogen as formally necessary is required. This might indicate that both types of reactions comprise several steps of substitution and redox processes.

$$\underset{\mathbf{5}}{[Mo(PMe_3)(NO)(\text{'S}_4\text{'})]} + 2NO \longrightarrow \underset{\mathbf{1}}{[Mo(NO)_2(\text{'S}_4\text{'})]} + OPMe_3 + \{\tfrac{1}{2}N_2\} \quad (9)$$

4. Conclusions

Paramagnetic $[Mo(PR_3)(NO)(\text{'S}_4\text{'})]$ complexes formed in redox-substitution reactions from $[Mo(SPh)(NO)(\text{'S}_4\text{'})]$ and phosphines. The 17-electron $[Mo(PR_3)(NO)(\text{'S}_4\text{'})]$ complexes are redox active and can be oxidized or reduced by cyclic voltammetry to give 16-electron $[Mo(PR_3)(NO)(\text{'S}_4\text{'})]^+$ cations or 18-electron $[Mo(PR_3)(NO)(\text{'S}_4\text{'})]^-$ anions. Attempts to isolate salts containing these ions remained unsuccessful or yielded products which could not be characterized unambiguously. Upon reaction of $[Mo(PMe_3)(NO)(\text{'S}_4\text{'})]$ with halogens or NO, however, $[Mo(X)(NO)(\text{'S}_4\text{'})]$ (X = Cl, Br, I) and $[Mo(NO)_2(\text{'S}_4\text{'})]$ were obtained, which can be considered as either 16-electron Mo(III) or 18-electron Mo(II) complexes.

The Mo–S distances in 16-, 17- and 18-electron $[Mo(X)(NO)(\text{'S}_4\text{'})]$ complexes remain nearly invariant although the respective ν(NO) frequencies vary significantly. This indicates that uptake and release of electrons concerns π type molecular orbitals localized in the [Mo(X)(NO)] units. In this respect, the complexes described here resemble trispyrazolylborato (tpb) complexes of the type [Mo(NO)(X)(Y)(tpb)] (X = Y = Cl, Br, I; X = Cl, Y = NO) [13]. These complexes are either 16- or 18-electron species, but can also exist as 17-electron derivatives such as [Mo(NO)(Cl)(3,5-dimethylpyrazole)(tpb)] [14].

5. Supplementary material

Further details of the X-ray structure analysis have been deposited and can be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Informationen mbH, D-76344 Eggenstein-Leopoldshafen by citing the deposition No. CSD-400712, the authors and reference.

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