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Synthesis and structural characterization of some molybdenum carbonyl nitrosyl complexes of diethyldithiocarbamate ☆

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Abstract

Ten complexes, M'[Mo(Et_2NCS_2)$(CO)_2$(NO)X] (M'^+ = PPN^+ or Et_4N^+; X^- = NCS^- (**1**), NO_3^- (**2**), N_3^- (**3**), Br^- (**4**) or Cl^- (**5**)) and [Mo(Et_2NCS_2)(CO)(NO)L_2] (L_2 = py and CO (**6**); dppe (**7**); 2PPh_3 (**8**); 2PMe_3 (**9**); 2$P(OMe)_3$ (**10**)), have been prepared. Crystal structures of **1**, **3**, **4**, **6**, **7**, **8** and **10** were determined from single crystal X-ray data. The structures show clearly that the stronger electron-withdrawing NO, compared with CO, prefers the location *trans* to the better electron donor such as NCS^- in **1**, N_3^- in **3** and Br^- in **4**, unless some other apparent counteracting factors are also involved. The two bulky phosphine ligands are as expected *trans* to each other in **8** and **10** and a chelate dppe is found in **7**. Although the structure of **6** has NO *trans* to py, the spectral data of **6** (and **7**), both in solution and in the solid state, reveal the presence of two different structures. Crystal data: **1**, space group $P2_1/n$, $a = 9.879(2)$, $b = 30.302(3)$, $c = 14.858(4)$ Å, $\beta = 97.00(2)°$, $Z = 4$; **3**, space group $P2_1/c$, $a = 16.806(5)$, $b = 16.128(3)$, $c = 18.025(4)$ Å, $\beta = 116.94(2)°$, $Z = 4$; **4**, space group Ia, $a = 14.773(8)$, $b = 8.982(2)$, $c = 17.748(5)$ Å, $\beta = 96.49(5)°$, $Z = 4$; **6**, space group $P2_1/c$, $a = 13.499(4)$, $b = 10.033(5)$, $c = 12.962(2)$ Å, $\beta = 91.66(2)°$, $Z = 4$; **7**, space group $P2_1/n$, $a = 11.634(3)$, $b = 19.881(4)$, $c = 15.225(4)$ Å, $\beta = 111.10(2)°$, $Z = 4$; **8**, space group $P2_1/n$, $a = 11.767(2)$, $b = 18.851(4)$, $c = 19.436(4)$ Å, $\beta = 107.12(2)°$, $Z = 4$; **10**, space group $P2_1/n$, $a = 8.732(2)$, $b = 23.98(3)$, $c = 11.303(3)$ Å, $\beta = 97.66(2)°$, $Z = 4$.

Keywords: Crystal structures; Molybdenum complexes; Carbonyl complexes; Nitrosyl complexes; Dithiocarbamate complexes

1. Introduction

Following the discovery of the symmetrical and asymmetrical orientations of the allyl group with respect to the neutral pyrazole-derived tridentate ligand (N-N-N) in cations, [M(N-N-N)$(CO)_2$(η^3-allyl)]$^+$ (M = Cr, Mo and W) [1,2], we were interested in examining the structure predictability from the electronic and steric property of the associated ligands. In this paper we report some related results from the syntheses and structures of a number of six-coordinate complexes of molybdenum, [Mo(Et_2NCS_2)(NO)(CO)L_2]$^{m-}$ (m = 0 or 1; L_2 = 1,2-bis(diphenylphosphino)ethane (dppe) or L = PPh_3, PMe_3, $P(OMe)_3$, Br^-, Cl^-, N_3^-, NO_3^-, NCS^- or pyridine (py)).

2. Experimental

All manipulations were carried out under an atmosphere of prepurified nitrogen by using conventional Schlenk-tube techniques. Solvents were purified by distillation from an appropriate drying agent (ethers, paraffins and arenes from potassium with benzophenone as indicator; halocarbons and acetonitrile from CaH_2 and alcohols from the corresponding alkoxide).

^1H and ^{13}C NMR spectra were recorded on a Bruker AM-200 (^1H, 200 MHz; ^{13}C, 50 MHz) or AMC-400 (^1H, 400 MHz) NMR spectrometer and chemical shifts (δ ppm, J Hz) are positive downfield relative to internal $MeSi_4$ (TMS) or the deuterated solvent (s, singlet; d, doublet; m, multiplet; br, broad). ^{31}P NMR spectra were recorded on a Bruker AMC-400 (^{31}P, 162 MHz) NMR spectrometer and the chemical shifts (δ ppm) are defined as positive downfield relative to external 85% H_3PO_4. IR spectra were recorded by using a Hitachi 270-30 instrument (vs, very strong; s, strong; m, medium; w, weak; br, broad; sh, shoulder). Elemental

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☆ Dedicated to Professor F. Albert Cotton on the occasion of his 65th birthday and the graduation of his 100th Ph.D. student.

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analysis results were obtained by the staff of the Microanalytical Service of the Department of Chemistry, National Cheng Kung University. $[Mo(Et_2NCS_2)(CO)_2(NO)]_2$ was prepared by the published procedure [3].

2.1. Synthesis of $[PPN][Mo(Et_2NCS_2)(CO)_2(NO)(NCS)]$ (1)

To a 50 ml round-bottom flask containing a magnetic bar, 0.099 g of $[Mo(Et_2NCS_2)(CO)_2(NO)]_2$ (0.15 mmol) and 0.18 g of PPN^+SCN^- (0.30 mmol) (PPN^+ = bis(triphenylphosphino)iminium (1+) cation) were added to 15 ml of CH_2Cl_2. The resulting solution was stirred for 15 min at 28 °C and its color changed from orange–red to orange–yellow. The solvent was then removed under vacuum. Recrystallization from CH_2Cl_2/MeOH gave a yellow product (0.24 g, 86%). *Anal.* Calc. for $C_{44}H_{40}MoN_4O_3P_2S_3$: C, 57.02; H, 4.35; N, 6.04. Found: C, 56.89; H, 4.35; N, 6.00%. ^1H NMR (23 °C, acetone-d_6, 200 MHz); δ, phenyl protons 7.70 (m, 30H); ethyl protons, 3.81 (q, 2H), 3.84 (q, 2H), 1.24 (t, 6H, $^3J(H,H)=7.1$). IR (KBr, cm^{-1}): ν(CO) 2012s, 1926s; ν(NO) 1628s; ν(CN) of $Et_2NCS_2^-$, 1496s; ν(CN) of NCS^-, 2076s. IR (CH_2Cl_2, cm^{-1}): ν(CO) 2016s, 1924s; ν(NO) 1626s; ν(CN) of $Et_2NCS_2^-$, 1492s; ν(CN) of SCN^-, 2076s.

2.2. Synthesis of $[PPN][Mo(Et_2NCS_2)(CO)_2(NO)(\eta^1\text{-}NO_3)]$ (2)

This yellow compound was prepared in a yield of 71% by a procedure similar to that used for **1**, using $PPN^+NO_3^-$. *Anal.* Calc. for $C_{43}H_{40}MoN_4O_6P_2S_2$: C, 55.49; H, 4.33; N, 6.02. Found: C, 55.27; H, 4.33; N, 5.76%. ^1H NMR (23 °C, acetone-d_6, 200 MHz): δ, phenyl protons 7.70 (m, 30H); ethyl protons 3.85 (q, 2H, $^3J(H,H)=7.1$), 3.80 (q, 2H, $^3J(H,H)=7.1$), 1.23 (t, 3H), 1.22 (t, 3H). IR (KBr, cm^{-1}): ν(CO) 2016s, 1930s; ν(NO) 1626s; ν(CN) 1496s. IR (CH_2Cl_2, cm^{-1}): ν(CO) 2020s, 1926s; ν(NO) 1616s; ν(CN) 1486s.

2.3. Synthesis of $[PPN][Mo(Et_2NCS_2)(CO)_2(NO)(\eta^1\text{-}N_3)]$ (3)

This yellow compound was prepared in a yield of 88% by a procedure similar to that used for **1**, using $PPN^+N_3^-$. *Anal.* Calc. for $C_{43}H_{40}MoN_6O_3P_2S_2$: C, 56.70; H, 4.43; N, 9.23. Found: C, 56.48; H, 4.43; N, 8.97%. ^1H NMR (23 °C, acetone-d_6, 200 MHz): δ, phenyl protons 7.70 (m, 30H); ethyl protons 3.80 (q, 2H, $^3J(H,H)=7.1$), 3.78 (q, 2H, $^3J(H,H)=7.1$), 1.24 (t, 3H), 1.23 (t, 3H). $^{13}C\{^1H\}$ NMR (23 °C, $CDCl_3$, 50 MHz): δ, carbonyls 223.52; CN, 214.52; phenyl carbons 133.91, 133.88, 132.24, 132.18, 132.07, 131.95, 131.88, 129.77, 129.71, 129.58, 129.44, 129.40, 128.00, 125.85; ethyl carbons 44.90, 12.38. IR (KBr, cm^{-1}): $\nu(N_3)$ 2060s; ν(CO) 2000s, 1914s; ν(NO) 1596s; ν(CN) 1506. IR (CH_2Cl_2, cm^{-1}): $\nu(N_3)$ 2064s; ν(CO) 2008s, 1920s; ν(NO) 1608s; ν(CN) 1494s.

2.4. Synthesis of $[Et_4N][Mo(Et_2NCS_2)(CO)_2(NO)(Br)]$ (4)

This yellow compound was prepared in a yield of 92% by a procedure similar to that used for **1**, using $Et_4N^+Br^-$. *Anal.* Calc. for $C_{15}H_{30}BrMoN_3O_3S_2$: C, 33.34; H, 5.60; N, 7.78. Found: C, 33.35; H, 5.62; N, 7.76%. ^1H NMR (23 °C, acetone-d_6, 200 MHz): δ, Et_4N^+ 1.39 (tt, 12H, $^3J(H,H)=7.25$, $^3J(N,H)=1.86$), 3.50 (q, 8H); $Et_2NCS_2^-$ 1.23 (t, 6H, $^3J(H,H)=7.1$), 3.80 (q, 2H), 3.79 (q, 2H). IR (KBr, cm^{-1}): ν(CO) 2012s, 1908s; ν(NO) 1608s; ν(CN) 1502s. IR (CH_2Cl_2, cm^{-1}): ν(CO) 2012s, 1920s; ν(NO) 1610s; ν(CN) 1486s.

2.5. Synthesis of $[PPN][Mo(Et_2NCS_2)(CO)_2(NO)(Cl)]$ (5)

This yellow compound was prepared in a yield of 95% by a procedure similar to that used for **1**, using PPN^+Cl^-. *Anal.* Calc. for $C_{43}H_{40}ClMoN_3O_3P_2S_2$: C, 57.11; H, 4.46; N, 4.65. Found: C, 57.07; H, 4.50; N, 4.72%. ^1H NMR (23 °C, acetone-d_6, 200 MHz): δ, phenyl protons 7.70 (m, 30H); $Et_2NCS_2^-$ 1.24 (t, 6H, $^3J(H,H)=7.2$), 3.85 (q, 2H), 3.81 (q, 2H). IR (KBr, cm^{-1}): ν(CO) 2000s, 1912s; ν(NO) 1608s; ν(CN) 1502s. IR (CH_2Cl_2, cm^{-1}): ν(CO) 2016s, 1922s; ν(NO) 1604s; ν(CN) 1488s.

2.6. Synthesis of $[Mo(Et_2NCS_2)(CO)_2(NO)(py)]$ (6)

To a 50 ml round-bottom flask containing a magnetic bar, 0.16 g of $[Mo(Et_2NCS_2)(CO)_2(NO)]_2$ (0.24 mmol) and 15 ml of CH_2Cl_2, 0.5 ml of py was added and the resulting solution stirred for 15 min at room temperature. The solvents were then removed under vacuum. Recrystallization from CH_2Cl_2/hexane gave an orange–red product (0.17 g, 87%). *Anal.* Calc. for $C_{12}H_{16}MoN_3O_3S_2$: C, 35.21; H, 3.69; N, 10.27. Found: C, 35.07; H, 3.73; N, 10.33%. ^1H NMR (23 °C, acetone-d_6, 200 MHz): δ, py 7.45 (m, 2H), 8.03 (m, 2H), 8.78 (m, 1H); $Et_2NCS_2^-$ 1.23 (m, 6H), 3.86 (m, 2H). IR (KBr, cm^{-1}): ν(CO) 2012s, 1916s; ν(NO) 1644s, 1602m; ν(CN) 1504s. IR (CH_2Cl_2, cm^{-1}): ν(CO) 2020s, 1924s; ν(NO) 1646s, 1602m; ν(CN) 1498s.

2.7. Synthesis of $[Mo(Et_2NCS_2)(CO)(NO)(dppe)]$ (7)

To a 50 ml round-bottom flask containing a magnetic bar, 0.16 g of $[Mo(Et_2NCS_2)(CO)_2(NO)]_2$ (0.24 mmol) and 0.96 g of dppe (0.24 mmol) were added to 15 ml of CH_2Cl_2. The resulting solution was stirred for 30 min at room temperature. The solvent was then removed under vacuum. Recrystallization from CH_2Cl_2/Et_2O gave a red product (0.28 g, 83%). *Anal.* Calc. for $C_{32}H_{34}MoN_2O_2P_2S_2$: C, 54.86; H, 4.89; N, 4.00. Found: C, 54.85; H, 4.91; N, 3.99%. $^1H\{^{31}P\}$ NMR (27 °C, acetone-d_6, 400 MHz): δ, dppe 7.55 (m, 40H), 2.66 (m, 8H); $Et_2NCS_2^-$ 1.08 (t, 3H, ^3J(H,H) = 7.2), 1.00 (t, 3H, ^3J(H,H) = 7.2), 0.88 (t, 3H, ^3J(H,H) = 7.2), 0.75 (t, 3H, ^3J(H,H) = 7.2), 3.55 (m, 4H), 3.23 (m, 4H). $^{31}P\{^1H\}$ NMR (27 °C, acetone-d_6, 162 MHz): δ, dppe 67.76, 64.22, 41.10, 23.07. IR (KBr, cm^{-1}): ν(CO) 1898s, 1872s; ν(NO) 1602s, 1580m; ν(CN) 1488s. IR (CH_2Cl_2, cm^{-1}): ν(CO) 1912 (s, br); ν(NO) 1600 (s, br); ν(CN) 1488 s.

2.8. Synthesis of [Mo(Et_2NCS_2)(CO)(NO)(PPh_3)$_2$] (8)

This red compound was prepared in a yield of 85% by a procedure similar to that used for **1**, using 4 equiv. of PPh_3. *Anal.* Calc. for $C_{42}H_{40}MoN_2O_2P_2S_2$: C, 61.01; H, 4.88; N, 3.39. Found: C, 60.87; H, 4.86; N, 3.34%. ^1H NMR (27 °C, $CDCl_3$, 200 MHz): δ, PPh_3 7.45 (m, 30H); $Et_2NCS_2^-$ 0.62 (t, 3H, ^3J(H,H) = 7.1), 0.49 (t, 3H, ^3J(H,H) = 7.1), 2.97 (q, 2H), 2.76 (q, 2H). $^{31}P\{^1H\}$ NMR (27 °C, $CDCl_3$, 162 MHz): δ, PPh_3 43.08. IR (KBr, cm^{-1}): ν(CO) 1888s; ν(NO) 1604s; ν(CN) 1484s. IR (CH_2Cl_2, cm^{-1}): ν(CO) 1904s; ν(NO) 1606s; ν(CN) 1486s.

2.9. Synthesis of [Mo(Et_2NCS_2)(CO)(NO)(PMe_3)$_2$] (9)

This red compound was prepared in a yield of 75% by a procedure similar to that used for **1**, using 1.5 ml of PMe_3 (1.0 M solution in toluene). *Anal.* Calc. for $C_{12}H_{28}MoN_2O_2P_2S_2$: C, 31.72; H, 6.21; N, 6.17. Found: C, 31.70; H, 6.19; N, 6.25%. ^1H NMR (27 °C, acetone-d_6, 200 MHz): δ, PMe_3 1.45 (t, 18H, ^2J(P,H) = ^4J(P,H) = 3.3); $Et_2NCS_2^-$ 1.25 (t, 3H, ^3J(H,H) = 7.1), 1.78 (t, 3H, ^3J(H,H) = 7.1), 3.89 (q, 2H), 3.76 (q, 2H). $^{31}P\{^1H\}$ NMR (27 °C, $CDCl_3$, 162 MHz): δ, PMe_3 −6.62. IR (KBr, cm^{-1}): ν(CO) 1874s; ν(NO) 1596s; ν(CN) 1496s. IR (CH_2Cl_2, cm^{-1}): ν(CO) 1874s; ν(NO) 1600s; ν(CN) 1488s.

2.10. Synthesis of [Mo(Et_2NCS_2)(CO)(NO){P(OMe)$_3$}$_2$] (10)

This red compound was prepared in a yield of 75% by a procedure similar to that used for **1**, using 0.5 ml of P(OMe)$_3$. *Anal.* Calc. for $C_{12}H_{28}MoN_2O_8P_2S_2$: C, 26.19; H, 5.13; N, 5.09. Found: C, 26.13; H, 5.13; N, 5.18%. ^1H NMR (27 °C, $CDCl_3$, 200 MHz): δ, P(OMe)$_3$ 3.72 (t, 18H, ^3J(P,H) = ^5J(P,H) = 2.7); $Et_2NCS_2^-$, 1.17 (t, 3H, ^3J(H,H) = 7.1), 1.25 (t, 3H, ^3J(H,H) = 7.1), 3.81 (q, 2H), 3.67 (q, 2H). $^{31}P\{^1H\}$ NMR (27 °C, $CDCl_3$, 162 MHz): δ, P(OMe)$_3$ 159.30. IR (KBr, cm^{-1}): ν(CO) 1924s; ν(NO) 1626s; ν(CN) 1502s. IR (CH_2Cl_2, cm^{-1}): ν(CO) 1922s; ν(NO) 1626s; ν(CN) 1494s.

2.11. X-ray diffraction study

Single crystals were grown by the liquid diffusion method from CH_2Cl_2/hexane at room temperature. The intensity data for suitable crystals of the complexes were collected at room temperature on a CAD-4 diffractometer using monochromated Mo Kα radiation ($\lambda = 0.710930$ Å). The unit-cell constants were derived from a least-squares refinement of 24 setting reflections. The θ–2θ scan technique and a variable scan speed were used to obtain the integrated intensities. Three reference reflections were monitored throughout the measurement and the variation of the intensities was a total decay of less than 2% in any complex. Absorption corrections were applied for each structure according to experimental ψ rotation curves. The structural analyses were carried out on Microvax III using NRCVAX programs [4]. Atomic scattering factors were taken from the literature [5].

The metal atom position in any of the seven structures reported here was first determined by the heavy atom method. The remaining non-hydrogen atoms were subsequently located from the Fourier difference maps and all atoms except the disordered atom were then refined anisotropically (C(12) and C(12′) each with occupancy = 0.50 in structure **10** were found disordered). We have checked the transformed cells of both **3** and **8** crystals, by transformation matrix 1 0 0 1 0 2 0 −1 0 and 1 0 0 1 0 2 0 1 0, respectively, and found that they are not satisfactory. First, the γ angles deviate from 90.0°. Second, the intensities of *hkl* do not equal to those of $h\bar{k}l$. The ambiguities of locating NO and CO positions, if there are any, were solved according to the chemical and crystallographical meaningfulness of thermal displacement coefficients. A more restricted N atomic peak with a lower thermal parameter, *U*, than the neighboring O atomic peak [6] confirmed the successful assignment of the NO positions. Accordingly, only one nitrosyl position was found for any of the seven structures described here. The positions of all hydrogen atoms were calculated and refined isotropically to give residual *R* and R_w values shown in Table 1 with other crystallographic information.

In the asymmetric unit of the crystal used for **8**, there is a half molecule of CH_2Cl_2. The ORTEP plots for anions of **1** (Fig. 1), **3** (Fig. 2) and **4** (Fig. 3), and neutral molecules of **6** (Fig. 4), **7** (Fig. 5), **8** (Fig. 6) and **10** (Fig. 7) are shown with 50% probability thermal ellipsoids. The numbering schemes in the figures correspond to the atomic positions (Table 2). Some selected bond lengths and angles are collected in Table 3. See also Section 4.

Table 1
Crystal data for diethyldithiocarbamate complexes of molybdenum(0)

	1	**3**	**4**	**6**	**7**	**8**	**10**
Formula	$C_{44}H_{40}MoN_4O_3P_2S_3$	$C_{43}H_{40}MoN_6O_3P_2S_2$	$C_{15}H_{30}BrMoN_3O_3S_2$	$C_{12}H_{15}MoN_3O_3S_2$	$C_{32}H_{34}MoN_2O_2P_2S_2$	$C_{42.5}H_{40}ClMoN_2O_2P_2S_2$	$C_{12}H_{28}MoN_2O_8P_2S_2$
Formula weight	926.89	910.84	540.38	409.44	700.64	868.25	550.37
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$	Ia	$P2_1/c$	$P2_1/n$	$P2_1/n$	$P2_1/n$
Cell parameters							
a (Å)	9.879(2)	16.806(5)	14.773(8)	13.499(4)	11.634(3)	11.767(2)	8.732(2)
b (Å)	30.302(3)	16.128(3)	8.982(2)	10.033(5)	19.881(4)	18.851(4)	23.98(3)
c (Å)	14.858(4)	18.025(4)	17.748(5)	12.962(2)	15.225(4)	19.436(4)	11.303(3)
β (°)	97.00(2)	116.94(2)	96.49(5)	91.66(2)	111.10(2)	107.12(2)	97.66(2)
V (Å^3)	4415(2)	4355(2)	2340(2)	1755(1)	3285(1)	4120(1)	2346(3)
Z	4	4	4	4	4	4	4
D_{calc} (g cm^{-3})	1.395	1.389	1.534	1.549	1.417	1.400	1.545
$F(000)$	1904	1872	1096	824	1440	1784	1128
λ (Mo Kα) (Å)	0.70930	0.70930	0.70930	0.70930	0.70930	0.70930	0.70930
μ (mm^{-1})	0.539	0.501	2.43	0.968	0.637	0.586	0.879
T_{min}–T_{max}	0.855–1.000	0.961–1.000	0.937–0.997	0.936–1.000	0.856–1.000	0.958–0.998	0.766–1.000
2θ Limits (°)	$0<\theta<45$	$0<\theta<45$	$0<\theta<50$	$0<\theta<45$	$0<\theta<45$	$0<\theta<50$	$0<\theta<45$
Total data	5741	5676	2059	2285	4284	7231	3065
Data used	4050 ($>2.0\sigma(I)$)	3688 ($>2.0\sigma(I)$)	1822 ($>2.0\sigma(I)$)	1708 ($>2.0\sigma(I)$)	3321 ($>2.0\sigma(I)$)	4798 ($>2.0\sigma(I)$)	1977 ($>2.0\sigma(I)$)
Parameters used	514	515	225	191	370	479	243
R, R_w [a]	0.038, 0.038	0.038, 0.027	0.024, 0.022	0.038, 0.035	0.032, 0.028	0.043, 0.034	0.059, 0.057
S [a]	2.05	1.60	1.73	2.54	1.88	2.09	2.75
Weighting factor [b]	0.000020	0	0.000020	0.000020	0.000020	0	0.000050
Residual peak/hole	0.28/−0.33	0.25/−0.29	0.35/−0.49	0.40/−0.36	0.45/−0.35	1.16 [c]/−0.62	1.03 [c]/−0.68
Max. shift/error	0.35	0.73	0.043	0.17	1.03	0.23	0.40

[a] $R=\Sigma\|F_o|-|F_c\|/\Sigma|F_o|$; $R_w=[\Sigma w(|F_o|-|F_c|)^2/\Sigma wF_o^2]^{1/2}$; $S=[\Sigma w\|F_o|-|F_c\|^2/(N_o-N_v)]^{1/2}$, where N_o is the number of the data used and N_v is the number of the parameters used.

[b] $w^{-1}=\sigma^2(F_o)+g(F_o)^2$, where g is the weighting factor.

[c] Ghost peak.

Table 2
Fractional atomic coordinates and B_{eq} values

Atom	x	y	z	B_{eq} [a]
(a) $[PPN][Mo(Et_2NCS_2)(CO)_2(NO)(NCS)]$ (**1**)				
Mo	0.13725(5)	0.11904(2)	0.13528(3)	3.52(3)
S1	0.2655(2)	0.19142(5)	0.1642(1)	3.96(8)
S2	0.3820(2)	0.10506(5)	0.2030(1)	4.14(8)
S3	0.0230(2)	0.11011(6)	0.4495(1)	4.77(9)
C1	0.0592(5)	0.1163(2)	0.3470(4)	3.2(3)
N1	0.0865(5)	0.1204(2)	0.2740(3)	4.0(3)
C2	0.4083(6)	0.1609(2)	0.2017(4)	3.5(3)
N2	0.5287(5)	0.1790(2)	0.2287(3)	3.7(2)
C3	0.6453(6)	0.1523(2)	0.2675(5)	5.1(4)
C4	0.6449(7)	0.1445(3)	0.3674(5)	6.7(4)
C5	0.5522(6)	0.2264(2)	0.2234(5)	4.8(4)
C6	0.6246(7)	0.2388(2)	0.1433(5)	6.5(4)
N3	0.1625(4)	0.1130(2)	0.0192(3)	3.9(3)
O1	0.1706(4)	0.1072(2)	−0.0599(3)	5.9(3)
C7	0.0689(7)	0.0569(2)	0.1256(4)	4.3(3)
O2	0.0319(5)	0.0214(2)	0.1132(3)	6.6(3)
C8	−0.0506(7)	0.1413(2)	0.0972(4)	4.4(3)
O3	−0.1586(5)	0.1535(2)	0.0735(4)	7.1(3)
P1	0.9722(1)	0.43299(5)	0.2227(1)	2.66(6)
P2	1.0119(1)	0.33664(5)	0.1964(1)	2.68(6)
N4	0.9421(4)	0.3834(1)	0.1951(3)	3.0(2)
C11A	0.8098(5)	0.4609(2)	0.2128(3)	2.6(3)
C12A	0.6930(6)	0.4387(2)	0.1791(4)	3.6(3)
C13A	0.5695(6)	0.4611(2)	0.1659(4)	4.4(3)
C14A	0.5634(6)	0.5050(2)	0.1871(4)	4.3(3)
C15A	0.6792(6)	0.5268(2)	0.2222(4)	4.2(3)
C16A	0.8026(6)	0.5054(2)	0.2344(4)	3.6(3)
C11B	1.0523(6)	0.4411(2)	0.3377(4)	3.1(3)
C12B	0.9731(7)	0.4387(2)	0.4071(4)	4.8(3)
C13B	1.0344(9)	0.4407(3)	0.4959(5)	6.6(5)
C14B	1.173(1)	0.4442(3)	0.5136(5)	7.2(5)
C15B	1.2530(7)	0.4467(3)	0.4450(5)	6.0(4)
C16B	1.1926(6)	0.4445(2)	0.3561(4)	4.4(3)
C11C	1.0762(5)	0.4604(2)	0.1491(3)	2.7(3)
C12C	1.1246(6)	0.5029(2)	0.1691(4)	3.6(3)
C13C	1.1989(6)	0.5245(2)	0.1100(5)	4.4(3)
C14C	1.2260(6)	0.5044(3)	0.0322(4)	4.9(4)
C15C	1.1787(7)	0.4625(3)	0.0112(4)	5.4(4)
C16C	1.1021(6)	0.4412(2)	0.0691(4)	3.9(3)
C21A	1.1953(5)	0.3374(2)	0.2163(4)	2.9(3)
C22A	1.2576(6)	0.3388(2)	0.3060(4)	3.7(3)
C23A	1.3978(6)	0.3441(2)	0.3230(4)	4.5(3)
C24A	1.4751(6)	0.3468(2)	0.2539(5)	5.1(4)
C25A	1.4142(6)	0.3446(2)	0.1652(4)	5.1(4)
C26A	1.2750(6)	0.3401(2)	0.1472(4)	3.7(3)
C21B	0.9634(5)	0.3104(2)	0.0895(3)	2.8(3)
C22B	1.0251(6)	0.2713(2)	0.0658(4)	4.1(3)
C23B	0.9805(7)	0.2507(2)	−0.0149(4)	4.6(3)
C24B	0.8767(7)	0.2688(2)	−0.0735(4)	4.7(3)
C25B	0.8183(6)	0.3076(2)	−0.0530(4)	4.9(4)
C26B	0.8582(6)	0.3286(2)	0.0294(4)	4.0(3)
C21C	0.9544(5)	0.3025(2)	0.2845(4)	2.8(3)
C22C	0.9943(6)	0.2590(2)	0.2954(4)	4.3(3)
C23C	0.9518(7)	0.2340(2)	0.3638(5)	5.2(4)
C24C	0.8717(7)	0.2522(2)	0.4227(4)	5.0(4)
C25C	0.8332(7)	0.2955(3)	0.4124(5)	5.7(4)
C26C	0.8732(6)	0.3207(2)	0.3433(4)	4.1(3)
(b) $[PPN][Mo(Et_2NCS_2)(CO)_2(NO)(\eta^1\text{-}N_3)]$ (**3**)				
Mo	0.22821(4)	0.19321(3)	0.24184(3)	3.30(3)
S1	0.3126(1)	0.1142(1)	0.3759(1)	4.0(1)
S2	0.2366(1)	0.2781(1)	0.3630(1)	4.2(1)
N1	0.3542(3)	0.2512(3)	0.2611(3)	4.5(3)
N2	0.4124(4)	0.2755(3)	0.3222(4)	4.7(4)
N3	0.4720(4)	0.3003(4)	0.3811(4)	7.6(4)
N4	0.1237(3)	0.1421(3)	0.2147(3)	3.6(3)
O4	0.0556(3)	0.1054(3)	0.1958(3)	5.1(3)
C1	0.2443(4)	0.1140(4)	0.1641(4)	4.1(4)
O1	0.2502(3)	0.0664(3)	0.1200(3)	6.1(3)
C2	0.1717(4)	0.2817(4)	0.1556(4)	4.3(4)
O2	0.1405(3)	0.3347(3)	0.1092(3)	6.6(3)
C3	0.2982(3)	0.1987(4)	0.4256(3)	3.3(3)
N5	0.3328(3)	0.2019(3)	0.5084(3)	3.7(3)
C4	0.3766(4)	0.1292(4)	0.5605(4)	5.0(4)
C5	0.3103(5)	0.0730(5)	0.5695(4)	6.9(5)
C6	0.3288(4)	0.2768(4)	0.5521(4)	4.5(4)
C7	0.4109(5)	0.3288(4)	0.5766(4)	6.5(5)
P1	0.2801(1)	0.6990(1)	0.18466(9)	2.87(8)
P2	0.1875(1)	0.78094(9)	0.02154(9)	2.83(8)
N6	0.2670(3)	0.7447(3)	0.1030(3)	3.2(3)
C11A	0.3192(4)	0.7695(4)	0.2712(4)	2.9(3)
C12A	0.3200(4)	0.8539(4)	0.2583(4)	4.1(4)
C13A	0.3522(5)	0.9077(4)	0.3241(5)	5.6(5)
C14A	0.3850(5)	0.8785(5)	0.4031(5)	5.8(5)
C15A	0.3854(4)	0.7956(5)	0.4187(4)	5.3(5)
C16A	0.3521(4)	0.7403(4)	0.3520(4)	4.5(4)
C11B	0.1809(4)	0.6484(4)	0.1768(3)	3.1(3)
C12B	0.1301(4)	0.6853(4)	0.2106(3)	4.2(4)
C13B	0.0489(5)	0.6500(5)	0.1952(4)	5.9(5)
C14B	0.0199(5)	0.5796(5)	0.1475(5)	6.8(6)
C15B	0.0707(5)	0.5422(4)	0.1155(5)	6.4(5)
C16B	0.1511(4)	0.5771(4)	0.1302(4)	4.9(5)
C11C	0.3651(4)	0.6209(3)	0.2100(3)	2.8(3)
C12C	0.3698(4)	0.5534(4)	0.2591(4)	3.9(4)
C13C	0.4387(5)	0.4963(4)	0.2813(4)	5.0(5)
C14C	0.5015(5)	0.5085(5)	0.2544(5)	5.4(4)
C15C	0.4981(4)	0.5751(5)	0.2071(4)	4.9(5)
C16C	0.4302(4)	0.6318(4)	0.1844(4)	3.8(4)
C21A	0.0961(3)	0.8220(4)	0.0359(3)	2.8(3)
C22A	0.0989(4)	0.9017(4)	0.0633(4)	3.9(4)
C23A	0.0332(5)	0.9316(4)	0.0812(4)	5.3(5)
C24A	−0.0374(5)	0.8827(5)	0.0701(4)	5.5(5)
C25A	−0.0411(4)	0.8036(5)	0.0440(4)	5.2(5)
C26A	0.0252(4)	0.7716(4)	0.0263(3)	3.8(4)
C21B	0.1437(4)	0.7050(3)	−0.0604(3)	2.9(3)
C22B	0.1955(4)	0.6364(4)	−0.0570(4)	3.8(4)
C23B	0.1651(5)	0.5814(4)	−0.1229(5)	5.2(5)
C24B	0.0845(5)	0.5935(4)	−0.1911(4)	5.1(5)
C25B	0.0325(4)	0.6597(4)	−0.1947(4)	4.9(4)
C26B	0.0614(4)	0.7158(4)	−0.1302(4)	4.0(4)
C21C	0.2314(4)	0.8644(3)	−0.0147(3)	2.9(3)
C22C	0.1757(4)	0.9119(4)	−0.0826(4)	3.9(4)
C23C	0.2099(4)	0.9751(4)	−0.1104(4)	4.3(4)
C24C	0.3001(5)	0.9917(4)	−0.0711(4)	4.3(4)
C25C	0.3554(4)	0.9451(4)	−0.0052(4)	4.7(4)
C26C	0.3222(4)	0.8809(4)	0.0237(3)	3.7(4)
(c) $[Et_4N][Mo(Et_2NCS_2)(CO)_2(NO)(Br)]$ (**4**)				
Mo	0.30830	0.99507(5)	0.15025	2.85(2)
Br	0.30139(7)	0.70062(6)	0.13508(6)	4.08(3)
S1	0.3999(1)	1.0082(2)	0.03845(9)	3.61(7)
S2	0.2028(1)	1.0211(2)	0.0270(1)	4.04(8)
C	0.2984(4)	1.0219(7)	−0.0190(3)	3.6(3)
N1	0.2953(4)	1.0329(6)	−0.0938(3)	4.7(3)
C1	0.3781(6)	1.0342(9)	−0.1330(4)	6.6(4)
C2	0.4028(9)	0.884(1)	−0.1547(6)	10.6(7)
C3	0.2079(6)	1.047(1)	−0.1436(5)	6.0(4)
C4	0.1807(6)	1.210(1)	−0.1506(5)	7.3(5)

(continued)

Table 2 (*continued*)

Atom	x	y	z	B_{eq} [a]
C5	0.4105(5)	0.9627(7)	0.2329(4)	4.2(3)
O5	0.4681(4)	0.9485(7)	0.2814(3)	7.3(3)
C6	0.2211(5)	0.9548(7)	0.2265(4)	4.0(3)
O6	0.1753(4)	0.9333(7)	0.2727(3)	7.3(3)
N7	0.3079(3)	1.1890(6)	0.1725(3)	3.0(2)
O7	0.3055(3)	1.3148(5)	0.1914(3)	5.1(3)
N3	0.5284(3)	0.4698(5)	0.0514(3)	3.2(2)
C8	0.4804(4)	0.4024(7)	0.1139(3)	3.6(3)
C9	0.5412(6)	0.3324(9)	0.1782(5)	6.3(5)
C10	0.6004(4)	0.5823(7)	0.0831(4)	4.2(3)
C11	0.5676(6)	0.703(1)	0.1311(5)	5.6(5)
C12	0.4601(4)	0.5495(7)	−0.0041(4)	4.3(3)
C13	0.3840(6)	0.451(1)	−0.0427(5)	6.3(4)
C14	0.5757(4)	0.3450(7)	0.0132(4)	4.1(3)
C15	0.6187(6)	0.3859(9)	−0.0555(4)	6.5(4)
(d) $[Mo(Et_2NCS_2)(CO)_2(NO)(py)]$ (**6**)				
Mo	0.30211(4)	0.18907(6)	0.07959(4)	5.84(3)
S1	0.1313(1)	0.2206(2)	−0.0008(1)	6.51(9)
S2	0.1896(1)	0.2920(2)	0.2091(1)	7.0(1)
C1	0.0981(4)	0.2819(6)	0.1162(4)	6.6(3)
N1	0.0064(3)	0.3168(7)	0.1348(4)	9.5(4)
C2	−0.0727(6)	0.331(1)	0.0439(8)	17.2(8)
C3	−0.1175(7)	0.213(1)	0.0547(7)	18.1(8)
C4	−0.0283(5)	0.3505(9)	0.2434(6)	10.9(5)
C5	−0.0251(7)	0.4846(9)	0.2488(7)	14.9(7)
N2	0.2872(4)	0.0168(6)	0.1183(4)	8.6(4)
O2	0.2812(4)	−0.0972(5)	0.1443(4)	12.4(4)
C6	0.3744(4)	0.1234(6)	−0.0423(5)	7.3(4)
O6	0.4155(4)	0.0818(5)	−0.1113(4)	11.3(3)
C7	0.4259(4)	0.1882(7)	0.1636(4)	6.9(3)
O7	0.4966(3)	0.1830(5)	0.2145(3)	10.1(3)
N8	0.3334(3)	0.4017(5)	0.0278(3)	5.4(4)
C9	0.3223(4)	0.4399(6)	−0.0700(4)	6.4(4)
C10	0.3430(4)	0.5662(7)	−0.1031(4)	7.5(4)
C11	0.3754(4)	0.6601(7)	−0.0330(5)	7.9(4)
C12	0.3863(5)	0.6217(7)	0.0673(5)	7.8(4)
C13	0.3657(4)	0.4931(7)	0.0962(4)	6.8(3)
(e) $[Mo(Et_2NCS_2)(CO)(NO)(dppe)]$ (7)				
Mo	0.08472(3)	0.22115(2)	0.06342(3)	2.86(2)
P1	0.2405(1)	0.26312(5)	0.20842(8)	3.02(6)
P2	−0.0545(1)	0.27263(6)	0.14857(8)	3.26(6)
S1	0.0453(1)	0.11248(6)	0.13693(8)	3.83(6)
S2	−0.1002(1)	0.15963(6)	−0.04975(8)	3.90(6)
O1	0.2920(3)	0.1590(2)	0.0112(2)	5.1(2)
O2	0.0981(3)	0.3436(2)	−0.0510(2)	5.8(2)
N1	0.2085(4)	0.1820(2)	0.0283(3)	4.3(2)
N2	−0.1460(4)	0.0424(2)	0.0196(3)	4.8(2)
C1	0.0913(4)	0.2974(2)	−0.0051(3)	2.7(2)
C2	−0.0756(4)	0.0983(2)	0.0341(3)	3.7(3)
C3	−0.2454(5)	0.0281(3)	−0.0702(4)	6.3(3)
C4	−0.3671(6)	0.0256(4)	−0.0633(5)	9.5(5)
C5	−0.1171(5)	−0.0089(3)	0.0941(5)	6.5(4)
C6	−0.1705(6)	0.0059(3)	0.1679(5)	8.1(4)
C7	0.1674(4)	0.3144(2)	0.2729(3)	3.9(2)
C8	0.0498(4)	0.2799(2)	0.2712(3)	3.8(2)
C11	0.3264(4)	0.1995(2)	0.2926(3)	3.1(2)
C12	0.3584(4)	0.1405(2)	0.2600(3)	4.4(3)
C13	0.4312(5)	0.0938(3)	0.3221(4)	5.8(3)
C14	0.4709(5)	0.1040(3)	0.4164(4)	6.0(3)
C15	0.4384(6)	0.1615(3)	0.4499(4)	7.2(4)
C16	0.3673(5)	0.2089(3)	0.3886(3)	5.5(3)
C21	0.3614(4)	0.3191(2)	0.2012(3)	3.3(2)
C22	0.4834(5)	0.3020(2)	0.2354(4)	4.5(3)
C23	0.5722(4)	0.3455(3)	0.2262(4)	5.6(3)
C24	0.5383(5)	0.4059(3)	0.1840(4)	5.5(3)
C25	0.4174(5)	0.4240(2)	0.1501(4)	5.7(3)
C26	0.3291(4)	0.3810(2)	0.1572(3)	4.7(3)
C31	−0.1091(4)	0.3592(2)	0.1190(3)	3.6(2)
C32	−0.1301(5)	0.4018(3)	0.1831(3)	4.9(3)
C33	−0.1639(5)	0.4682(3)	0.1602(4)	6.2(3)
C34	−0.1790(6)	0.4914(3)	0.0735(5)	7.3(5)
C35	−0.1610(7)	0.4500(4)	0.0087(5)	10.0(5)
C36	−0.1273(6)	0.3833(3)	0.0311(4)	7.4(4)
C41	−0.1879(4)	0.2280(2)	0.1548(3)	3.7(2)
C42	−0.2908(5)	0.2218(3)	0.0737(4)	5.2(3)
C43	−0.3924(5)	0.1861(3)	0.0739(4)	6.2(4)
C44	−0.3928(6)	0.1577(3)	0.1546(6)	7.2(5)
C45	−0.2931(6)	0.1642(3)	0.2354(5)	7.0(4)
C46	−0.1909(5)	0.1993(3)	0.2362(4)	5.3(3)
(f) $[Mo(Et_2NCS_2)(CO)(NO)(PPh_3)_2]$ (**8**)				
Mo	0.05515(4)	0.16060(2)	0.20113(2)	2.58(2)
S1	0.2547(1)	0.19704(7)	0.28992(7)	3.71(6)
S2	0.1633(1)	0.05317(7)	0.27322(7)	3.49(6)
P1	−0.0458(1)	0.15938(7)	0.29858(7)	2.81(6)
P2	0.1808(1)	0.15413(7)	0.11556(7)	2.86(6)
O1	−0.1585(3)	0.0983(2)	0.0900(2)	5.1(2)
O2	−0.0368(3)	0.3107(2)	0.1567(2)	6.2(3)
N2	0.3671(5)	0.0895(3)	0.3682(3)	10.4(4)
N1	−0.0742(4)	0.1219(2)	0.1351(2)	3.9(2)
C2	−0.0007(4)	0.2531(2)	0.1724(3)	3.1(2)
C3	0.2744(4)	0.1104(3)	0.3161(3)	4.7(3)
C4	0.3691(6)	0.0148(4)	0.4070(4)	9.9(5)
C5	0.4289(7)	−0.0248(5)	0.3703(5)	12.7(7)
C6	0.4588(8)	0.1423(4)	0.4203(5)	13.0(7)
C7	0.5553(8)	0.1335(5)	0.4110(7)	20(1)
C11	0.0501(4)	0.1900(3)	0.3851(2)	3.0(2)
C12	0.0663(5)	0.2619(3)	0.3981(3)	4.1(3)
C13	0.1467(5)	0.2875(3)	0.4602(3)	5.2(3)
C14	0.2127(5)	0.2402(3)	0.5093(3)	5.5(3)
C15	0.2010(5)	0.1693(3)	0.4972(3)	5.5(3)
C16	0.1192(5)	0.1436(3)	0.4353(3)	4.2(3)
C21	−0.1052(4)	0.0745(3)	0.3182(2)	3.0(2)
C22	−0.1374(5)	0.0628(3)	0.3804(3)	5.1(3)
C23	−0.1892(6)	0.0000(3)	0.3910(3)	6.5(4)
C24	−0.2150(5)	−0.0517(3)	0.3392(3)	5.6(3)
C25	−0.1846(5)	−0.0409(3)	0.2774(3)	4.9(3)
C26	−0.1300(4)	0.0215(3)	0.2671(3)	3.8(3)
C31	−0.1800(4)	0.2130(3)	0.2840(2)	3.0(2)
C32	−0.2179(5)	0.2402(3)	0.3396(3)	4.9(3)
C33	−0.3251(5)	0.2743(3)	0.3267(3)	5.8(4)
C34	−0.3977(5)	0.2818(3)	0.2579(3)	5.5(3)
C35	−0.3633(5)	0.2554(3)	0.2025(3)	5.1(3)
C36	−0.2554(4)	0.2208(3)	0.2150(3)	4.2(3)
C41	0.2985(4)	0.0878(3)	0.1403(3)	3.3(3)
C42	0.4164(5)	0.1064(3)	0.1741(3)	4.9(3)
C43	0.5016(5)	0.0545(4)	0.1982(4)	7.0(4)
C44	0.4713(5)	−0.0157(3)	0.1897(4)	7.0(4)
C45	0.3551(5)	−0.0349(3)	0.1582(3)	5.7(4)
C46	0.2703(4)	0.0166(3)	0.1342(3)	4.3(3)
C51	0.2610(4)	0.2341(3)	0.1024(2)	3.1(2)
C52	0.2611(4)	0.2954(3)	0.1417(3)	3.7(3)
C53	0.3243(5)	0.3552(3)	0.1326(3)	4.5(3)
C54	0.3872(5)	0.3540(3)	0.0834(3)	5.1(3)
C55	0.3883(4)	0.2941(3)	0.0435(3)	4.5(3)
C56	0.3248(4)	0.2343(3)	0.0520(3)	3.8(3)
C61	0.0972(4)	0.1332(2)	0.0223(2)	3.0(2)
C62	0.1304(5)	0.0830(3)	−0.0195(3)	4.8(3)

(*continued*)

Table 2 (*continued*)

Atom	x	y	z	B_{eq} [a]
C63	0.0624(6)	0.0718(3)	−0.0900(3)	5.8(4)
C64	−0.0378(5)	0.1105(3)	−0.1200(3)	5.3(3)
C65	−0.0724(5)	0.1607(3)	−0.0789(3)	5.0(3)
C66	−0.0052(5)	0.1715(3)	−0.0081(3)	4.1(3)
Cl1	0.5658(4)	0.9398(2)	0.0345(3)	29.2(5)
C8	0.5866(9)	1.0199(6)	0.0260(7)	5.8(7)
(g) $[Mo(Et_2NCS_2)(CO)(NO)\{P(OMe)_3\}_2]$ (**10**)				
Mo	0.2141(1)	0.15129(4)	0.21547(9)	3.06(5)
P1	0.2454(4)	0.1653(1)	0.0036(3)	3.4(2)
P2	0.1790(5)	0.1306(2)	0.4247(3)	4.5(2)
S1	0.2311(4)	0.0470(1)	0.1683(3)	4.6(2)
S2	0.4911(4)	0.1152(2)	0.2638(3)	5.3(2)
C1	0.422(2)	0.0520(6)	0.216(1)	5.8(8)
N1	0.516(2)	0.0073(5)	0.213(2)	10(1)
C2	0.458(2)	−0.0478(8)	0.175(3)	16(2)
C3	0.408(3)	−0.0834(9)	0.265(3)	22(3)
C4	0.682(2)	0.0101(9)	0.249(3)	15(2)
C5	0.777(3)	0.024(1)	0.160(3)	20(3)
N2	0.005(1)	0.1630(4)	0.1795(9)	4.7(6)
O2	−0.134(1)	0.1724(4)	0.1600(8)	6.3(6)
C6	0.242(1)	0.2274(5)	0.2473(9)	3.2(6)
O6	0.261(1)	0.2748(4)	0.2610(8)	6.4(6)
O7	0.190(1)	0.2264(3)	−0.0369(7)	4.8(5)
C7	0.199(2)	0.2460(6)	−0.158(1)	6.4(8)
O8	0.407(1)	0.1585(4)	−0.0432(7)	4.8(5)
C8	0.531(2)	0.1936(8)	0.003(2)	9(1)
O9	0.160(1)	0.1245(4)	−0.0964(7)	5.0(5)
C9	0.004(2)	0.1101(6)	−0.096(1)	5.9(8)
O10	0.305(1)	0.1492(4)	0.5320(7)	7.1(6)
C10	0.398(2)	0.1958(7)	0.533(1)	7.4(10)
O11	0.023(1)	0.1552(5)	0.4519(8)	7.3(6)
C11	−0.035(2)	0.1411(9)	0.567(2	12(1)
O12	0.166(1)	0.0672(4)	0.4683(8)	6.7(5)
C12 [b]	0.023(4)	0.040(1)	0.426(3)	8.1(9)
C12′ [b]	0.311(3)	0.031(1)	0.469(3)	6.5(8)

[a] B_{eq} (Å^2) is the mean of the principal axes of the thermal ellipsoid.

[b] Mean atoms with occupancy = 0.5.

Table 3
Selected bond lengths (Å) and angles (°)

(a) $[PPN][Mo(Et_2NCS_2)(CO)_2(NO)(NCS)]$ (**1**)			
Mo–S(1)	2.543(2)	C(1)–N(1)	1.156(8)
Mo–S(2)	2.539(2)	C(2)–N(2)	1.327(8)
Mo–N(1)	2.180(5)	N(2)–C(3)	1.467(8)
Mo–N(3)	1.782(5)	N(2)–C(5)	1.458(8)
Mo–C(7)	2.001(7)	C(3)–C(4)	1.50(1)
Mo–C(8)	1.991(7)	C(5)–C(6)	1.51(1)
S(1)–C(2)	1.721(6)	N(3)–O(1)	1.201(6)
S(2)–C(2)	1.713(6)	C(7)–O(2)	1.142(9)
S(3)–C(1)	1.618(6)	C(8)–O(3)	1.143(8)
S(1)–Mo–S(2)	69.27(5)	S(1)–Mo–C(8)	100.6(2)
N(1)–Mo–N(3)	173.0(2)	S(2)–Mo–C(7)	99.7(2)
C(7)–Mo–C(8)	90.3(3)	C(3)–N(2)–C(5)	116.3(5)
S(3)–C(1)–N(1)	179.1(5)	Mo–N(3)–O(1)	175.1(4)
Mo–N(1)–C(1)	172.8(5)	Mo–C(7)–O(2)	174.7(5)
S(1)–C(2)–S(2)	114.5(3)	Mo–C(8)–O(3)	178.3(5)
(b) $[PPN][Mo(Et_2NCS_2)(CO)_2(NO)(\eta^1\text{-}N_3)]$ (**3**)			
Mo–S(1)	2.524(2)	N(2)–N(3)	1.152(8)
Mo–S(2)	2.526(2)	N(4)–O(4)	1.193(6)
Mo–N(1)	2.195(5)	C(1)–O(1)	1.142(8)
Mo–N(4)	1.795(5)	C(2)–O(2)	1.143(8)
Mo–C(1)	2.002(7)	C(3)–N(5)	1.335(7)
Mo–C(2)	2.005(7)	N(5)–C(4)	1.475(8)
S(1)–C(3)	1.707(6)	N(5)–C(6)	1.460(8)
S(2)–C(3)	1.710(6)	C(4)–C(5)	1.50(1)
N(1)–N(2)	1.160(8)	C(6)–C(7)	1.50(1)
S(1)–Mo–S(2)	70.04(5)	N(1)–N(2)–N(3)	177.3(7)
S(1)–Mo–C(1)	98.8(2)	Mo–N(4)–O(4)	177.5(4)
S(2)–Mo–C(2)	96.1(2)	Mo–C(1)–O(1)	176.4(5)
N(1)–Mo–N(4)	173.4(2)	Mo–C(2)–O(2)	176.9(6)
C(1)–Mo–C(2)	94.5(3)	S(1)–C(3)–S(2)	116.0(3)
Mo–N(1)–N(2)	129.2(4)	C(4)–N(5)–C(6)	116.6(4)
(c) $[Et_4N][Mo(Et_2NCS_2)(CO)_2(NO)(Br)]$ (**4**)			
Mo–Br	2.659(1)	C(3)–C(4)	1.52(1)
Mo–S(1)	2.528(2)	C(5)–O(5)	1.146(9)
Mo–S(2)	2.550(2)	C(6)–O(6)	1.137(9)
Mo–C(5)	2.004(8)	N(7)–O(7)	1.181(7)
Mo–C(6)	2.004(8)	C–N(1)	1.328(8)
Mo–N(7)	1.786(5)	N(1)–C(1)	1.47(1)
S(1)–C	1.720(6)	N(1)–C(3)	1.49(1)
S(2)–C	1.708(6)	C(1)–C(2)	1.46(1)
C(1)–N(1)–C(3)	115.5(5)	Br–Mo–N(7)	172.4(1)
S(1)–Mo–S(2)	69.61(6)	N(1)–C(3)–C(4)	109.6(7)
S(1)–Mo–C(5)	98.9(2)	Mo–C(5)–O(5)	177.6(6)
Mo–C(6)–O(6)	176.3(7)	C(5)–Mo–C(6)	88.2(3)
Mo–N(7)–O(7)	175.8(4)	S(1)–C–S(2)	115.4(3)
S(2)–Mo–C(6)	102.7(2)		
(d) $[Mo(Et_2NCS_2)(CO)_2(NO)py]$ (**6**)			
Mo–S(1)	2.523(2)	C(2)–C(3)	1.34(2)
Mo–S(2)	2.518(2)	C(4)–C(5)	1.35(1)
Mo–N(2)	1.813(6)	N(2)–O(2)	1.196(8)
Mo–C(6)	1.993(6)	C(6)–O(6)	1.144(7)
Mo–C(7)	1.968(6)	C(7)–O(7)	1.146(7)
Mo–N(8)	2.280(5)	N(8)–C(9)	1.329(7)
S(1)–C(1)	1.709(6)	N(8)–C(13)	1.340(7)
S(2)–C(1)	1.703(6)	C(9)–C(10)	1.369(9)
C(1)–N(1)	1.315(7)	C(10)–C(11)	1.371(9)
N(1)–C(2)	1.57(1)	C(11)–C(12)	1.360(9)
N(1)–C(4)	1.535(9)	C(12)–C(13)	1.374(9)
S(1)–Mo–S(2)	70.25(5)	S(1)–Mo–C(6)	100.2(2)
S(2)–Mo–C(7)	98.7(2)	Mo–N(2)–O(2)	177.5(5)

(*continued*)

3. Results and discussion

Ten monomeric substitution products of $M'[Mo(Et_2NCS_2)(CO)_2(NO)X]$ ($M'^+ = PPN^+$ or Et_4N^+; $X^- = NCS^-$ (**1**), NO_3^- (**2**), N_3^- (**3**), Br^- (**4**) or Cl^- (**5**)) and $[Mo(Et_2NCS_2)(CO)(NO)L_2]$ (L_2 = py and CO (**6**); dppe (**7**); 2PPh$_3$ (**8**); 2PMe$_3$ (**9**); 2P(OMe)$_3$ (**10**)) were obtained readily from the reactions of $[Mo(Et_2NCS_2)(CO)_2(NO)]_2$, a dinuclear compound with two μ:η^1,η^2-diethyldithiocarbamato bridging ligands [3], with suitable nucleophiles at 28 °C. The facile preparation reflects the fragile nature of the sulfur bridges in the dimeric compound.

From the similarity in the IR spectral data of complexes **1**–**5** and the structures of **1**, **3** and **4** (Figs. 1–3), it is possible that all five compounds have a similar geometry with the nitrosyl group *trans* to NCS^- in **1**, NO_3^- in **2**, N_3^- in **3**, Br^- in **4**, and Cl^- in **5**. This indicates that the higher electrophilic nitrosyl, compared with CO, prefers to occupy a position *trans* to a stronger electron donor, compared with η^2-$Et_2NCS_2^-$ in the

Table 3 (*continued*)

N(2)–Mo–N(8)	175.5(2)	Mo–N(8)–C(13)	120.3(4)
C(6)–Mo–C(7)	90.6(2)	S(1)–C(1)–S(2)	116.4(3)
Mo–C(6)–O(6)	177.9(6)	Mo–C(7)–O(7)	177.2(6)
Mo–N(8)–C(9)	122.3(4)	C(2)–N(1)–C(4)	116.7(5)
(e) [Mo(Et_2NCS_2)(CO)(NO)(dppe)] (7)			
Mo–P(1)	2.444(1)	P(2)–C(41)	1.820(5)
Mo–P(2)	2.620(1)	S(1)–C(2)	1.709(5)
Mo–S(1)	2.549(1)	S(2)–C(2)	1.714(5)
Mo–S(2)	2.535(1)	O(1)–N(1)	1.185(5)
Mo–N(1)	1.876(4)	O(2)–C(1)	1.175(5)
Mo–C(1)	1.857(4)	N(2)–C(2)	1.350(6)
P(1)–C(7)	1.824(4)	N(2)–C(3)	1.466(7)
P(1)–C(11)	1.821(4)	N(2)–C(5)	1.472(7)
P(1)–C(21)	1.828(4)	C(3)–C(4)	1.458(9)
P(2)–C(8)	1.829(4)	C(5)–C(6)	1.50(1)
P(2)–C(31)	1.835(5)	C(7)–C(8)	1.521(7)
P(1)–Mo–P(2)	79.00(4)	P(1)–C(7)–C(8)	109.3(3)
P(1)–Mo–N(1)	90.2(1)	P(2)–C(8)–C(7)	108.4(3)
S(1)–Mo–S(2)	69.31(4)	S(1)–Mo–C(1)	171.3(1)
Mo–P(1)–C(7)	109.8(1)	Mo–P(2)–C(41)	121.8(2)
Mo–P(1)–C(11)	116.0(1)	Mo–N(1)–O(1)	175.8(3)
Mo–P(1)–C(21)	119.3(1)	C(3)–N(2)–C(5)	118.0(4)
Mo–P(2)–C(8)	103.6(1)	Mo–C(1)–O(2)	176.6(4)
Mo–P(2)–C(31)	117.8(2)	S(1)–C(2)–S(2)	115.2(3)
P(2)–Mo–S(2)	90.02(4)		
P(2)–Mo–P(1)–C(7)	−9.4(1)	Mo–P(1)–C(7)–C(8)	42.8(2)
P(1)–C(7)–C(8)–P(2)	−61.2(2)	P(1)–Mo–P(2)–C(8)	−18.0(1)
Mo–P(2)–C(8)–C(7)	49.3(2)		
(f) [Mo(Et_2NCS_2)(CO)(NO)(PPh_3)$_2$] (**8**)			
Mo–S(1)	2.565(2)	P(2)–C(41)	1.822(5)
Mo–S(2)	2.576(1)	P(2)–C(51)	1.837(5)
Mo–P(1)	2.515(1)	P(2)–C(61)	1.832(5)
Mo–P(2)	2.533(1)	O(1)–N(1)	1.199(5)
Mo–N(1)	1.830(4)	O(2)–C(2)	1.173(6)
Mo–C(2)	1.889(5)	N(2)–C(3)	1.311(7)
S(1)–C(3)	1.707(5)	N(2)–C(4)	1.594(9)
S(2)–C(3)	1.710(5)	N(2)–C(6)	1.59(1)
P(1)–C(11)	1.821(5)	C(4)–C(5)	1.36(1)
P(1)–C(21)	1.831(5)	C(6)–C(7)	1.21(1)
P(1)–C(31)	1.826(5)		
S(1)–Mo–S(2)	68.70(5)	Mo–P(2)–C(41)	113.9(2)
S(1)–Mo–C(2)	97.0(1)	Mo–P(2)–C(51)	118.4(2)
S(2)–Mo–N(1)	104.1(1)	Mo–P(2)–C(61)	114.4(2)
P(1)–Mo–P(2)	172.17(4)	C(4)–N(2)–C(6)	109.8(5)
N(1)–Mo–C(2)	90.9(2)	Mo–N(1)–O(1)	177.7(4)
Mo–P(1)–C(11)	113.0(2)	Mo–C(2)–O(2)	177.5(4)
Mo–P(1)–C(21)	117.4(2)	S(1)–C(3)–S(2)	116.2(3)
Mo–P(1)–C(31)	117.2(2)		
(g) [Mo(Et_2NCS_2)(CO)(NO){P(OMe)$_3$}$_2$] (**10**)			
Mo–P(1)	2.469(3)	C(1)–N(1)	1.36(2)
Mo–P(2)	2.475(4)	N(1)–C(2)	1.46(2)
Mo–S(1)	2.565(4)	N(1)–C(4)	1.45(2)
Mo–S(2)	2.559(4)	C(2)–C(3)	1.44(4)
Mo–N(2)	1.84(1)	C(4)–C(5)	1.42(4)
Mo–C(6)	1.87(1)	N(2)–O(2)	1.22(2)
P(1)–O(7)	1.592(8)	C(6)–O(6)	1.16(1)
P(1)–O(8)	1.580(9)	O(7)–C(7)	1.46(1)
P(1)–O(9)	1.602(9)	O(8)–C(8)	1.42(2)
P(2)–O(10)	1.59(1)	O(9)–C(9)	1.40(2)
P(2)–O(11)	1.56(1)	O(10)–C(10)	1.38(2)
P(2)–O(12)	1.61(1)	O(11)–C(11)	1.46(2)
S(1)–C(1)	1.68(1)	O(12)–C(12)	1.42(4)
S(2)–C(1)	1.69(2)	O(12)–C(12′)	1.54(3)
P(1)–Mo–P(2)	176.2(1)	S(1)–C(1)–S(2)	117.6(8)
S(1)–Mo–N(2)	100.7(3)	C(2)–N(1)–C(4)	114.9(14)
S(2)–Mo–C(6)	101.2(4)	Mo–N(2)–O(2)	177.1(9)
N(2)–Mo–C(6)	89.6(5)	Mo–C(6)–O(6)	176.5(10)
Mo–P(1)–O(7)	109.6(3)	Mo–P(2)–O(10)	120.8(4)
Mo–P(1)–O(8)	122.0(3)	Mo–P(2)–O(11)	109.7(4)
Mo–P(1)–O(9)	120.0(3)	Mo–P(2)–O(12)	120.4(4)
S(1)–Mo–S(2)	68.6(1)		

(*continued*)

Table 3 (*continued*)

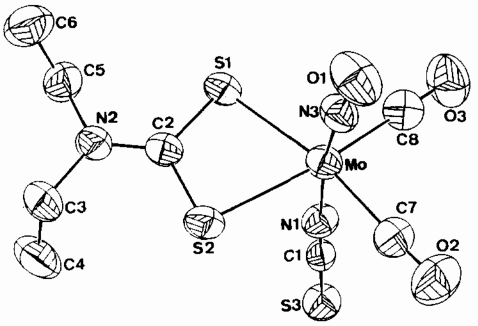


Fig. 1. ORTEP plot of [Mo(Et_2NCS_2)(CO)$_2$(NO)(NCS)]$^-$ (**1**$^-$).

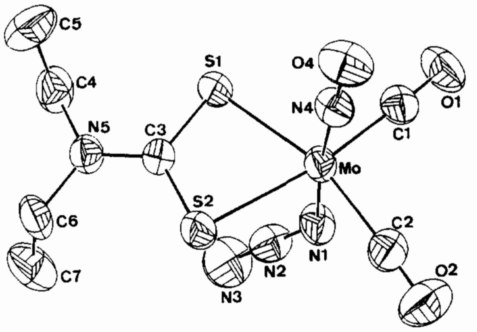


Fig. 2. ORTEP plot of [Mo(Et_2NCS_2)(CO)$_2$(NO)(η^1-N_3)]$^-$ (**3**$^-$).

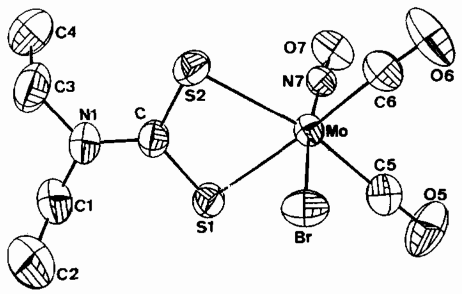


Fig. 3. ORTEP plot of [Mo(Et_2NCS_2)(CO)$_2$(NO)(Br)]$^-$ (**4**$^-$).

compounds. Apparently this unique nitrosyl position can help to dissipate any accumulated charge density after coordination of a strong electron donor through a metal-to-nitrosyl backbonding.

The structure of **6** was also found to have py *trans* to NO (Fig. 4). However, there are two nitrosyl frequencies observed both in solution and in the solid state, indicating that **6** may have two isomers. Only

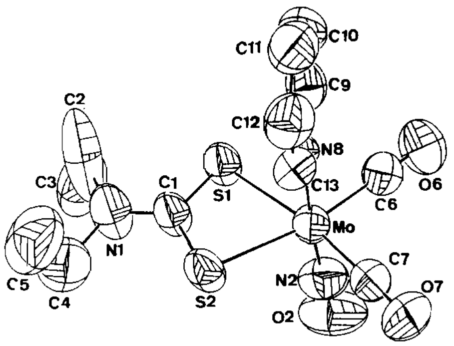


Fig. 4. ORTEP plot of $[Mo(Et_2NCS_2)(CO)_2(NO)py]$ (**6**).

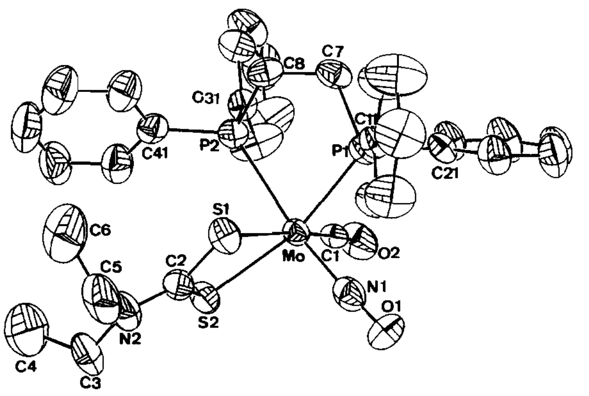


Fig. 5. ORTEP plot of $[Mo(Et_2NCS_2)(CO)(NO)(dppe)]$ (**7**). Carbon atoms of C(7), C(11) and C(21) are connected to P(1) and those of C(8), C(31) and C(41) are connected to P(2).

two rather than four carbonyl stretching bands observed for **6** may be due to the accidental overlap of the close bands or the poor resolution of the IR machine used. This may also explain why only one CN stretching band for the diethyldithiocarbamato ligands in the two isomers was observed. The isomer shown in Fig. 4 may represent the one more easily crystallized from the solution, while the other is believed to have a different disposition of py, possibly py *trans* to CO.

Although only one ^{31}P singlet is observed for **8**, **9** and **10** at 43.05, −6.62 and 159.30 ppm, respectively, there are four singlets observed at 67.76, 64.22, 41.10 and 23.07 ppm for **7**. From the spectral data of **7**–**10** and the structures of **7**, **8** and **10** (Figs. 5–7), we believe that the structure of **9** is similar to that of **8** or **10**, with the two bulky phosphine ligands *trans* to each other, apparently to minimize the steric hindrance between the ligands, and that like **6**, two isomeric structures are also present for **7**. However, the two probable isomeric structures may involve either different orientations of phenyl groups with respect to the five-membered ring formed by dppe and Mo, or may have different dispositions of the nitrosyl and carbonyl groups. By comparing the torsional angles in a range between −61.2 and 49.3° (Table 3), the five-membered ring has close to a skew-boat geometry [7]. Based on the ^{31}P NMR chemical shifts and theory of Letcher and Van Wazer [8], structures with different arrangements of NO and CO appear more probable. According to this theory, the singlet at 67.76 (or 64.22) and the one at 41.10 ppm are assigned to one isomer, with this signal for the phosphorus atom *trans* to NO, and the singlet at 64.22 (or 67.76) and the one at 23.07 ppm are assigned to the other isomer, with this signal for the phosphorus atom also *trans* to NO. The two possible arrangements for **6** and **7**, we believe, may reflect the weaker σ-donicity of py and phosphine ligands than the uninegative anionic ligand such as NCS^- in **1**, NO_3^- in **2**, N_3^- in **3**, Br^- in **4**, and Cl^- in **5**. It is worth remembering that the different preferred geometries of $[Mo(L\text{-}L)(CO)_2(\eta^3\text{-allyl})X]$ (L-L = 2,2′-bipyridine (bpy) and dppe; X^- = halide anion) were previously attributed to the σ-donicity difference between the two ligands [9].

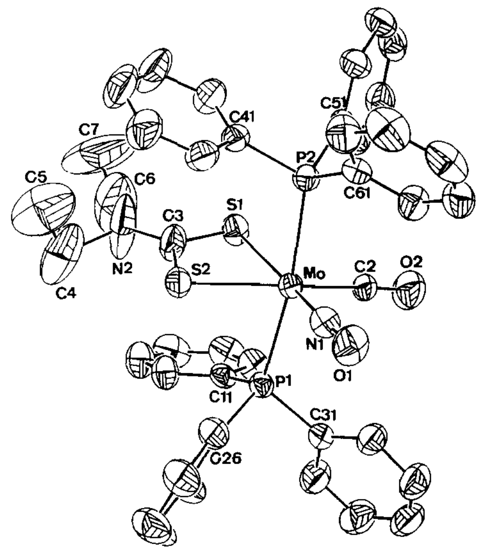


Fig. 6. ORTEP plot of $[Mo(Et_2NCS_2)(CO)(NO)(PPh_3)_2]$ (**8**). Carbon atoms of C(11), C(21) and C(31) are connected to P(1) and those of C(41), C(51) and C(61) are connected to P(2); C(21) is below C(26).

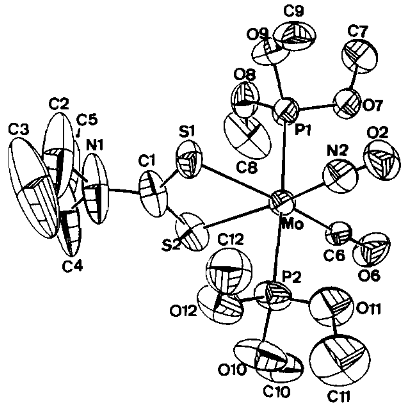


Fig. 7. ORTEP plot of $[Mo(Et_2NCS_2)(CO)(NO)\{P(OMe)_3\}_2]$ (**10**).

The metal atom in each of the seven X-ray structures is six-coordinate. The angles, formed by two ligands and the metal atom are in the range 68.6–104.1° (Table

Table 4
Relevant parameters of molybdenum(0) compounds containing dithiocarbamato ligands

Compound	MO–S (Å)	C–S (Å)	C–N (Å)	S···S (Å)	∠SCS (°)	Ref.
[PPN][Mo($C_4H_8NCS_2$)$(CO)_4$] [a]	2.600(1) 2.631(1)	1.704(4) 1.716(4)	1.319(5)	2.908(2)	116.4(2)	[12]
[PPN][Mo($C_5H_{10}NCS_2$)$(CO)_4$] [b]	2.598(5) 2.597(5)	1.72(2) 1.69(2)	1.34(2)	2.892(6)	116.1(10)	[12]
[PPN][Mo(Et_2NCS_2)$(CO)_4$] [c]	2.596(1)	1.704(3)	1.343(7)	2.90(1)	116.4(3)	[11]
[PPN][Mo(Et_2NCS_2)$(CO)_2$(NO)(NCS)]	2.543(2) 2.549(2)	1.721(6) 1.713(6)	1.327(8)	2.889(2)	114.5(3)	this work
[PPN][Mo(Et_2NCS_2)$(CO)_2$(NO)(η^1-N_3)]	2.524(2) 2.526(2)	1.707(6) 1.710(6)	1.335(7)	2.898(2)	116.0(3)	this work
[Et_4N][Mo(Et_2NCS_2)$(CO)_2$(NO)(Br)]	2.528(2) 2.550(2)	1.720(6) 1.708(6)	1.328(8)	2.898(3)	115.4(3)	this work
[Mo(Et_2NCS_2)$(CO)_2$(NO)(py)]	2.523(2) 2.518(2)	1.709(6) 1.703(6)	1.315(7)	2.900(2)	116.4(3)	this work
[Mo(Et_2NCS_2)(CO)(NO)(dppe)]	2.549(1) 2.535(1)	1.709(5) 1.714(5)	1.350(6)	2.891(2)	115.2(3)	this work
[Mo(Et_2NCS_2)(CO)(NO)$(PPh_3)_2$]	2.565(2) 2.576(1)	1.707(5) 1.710(5)	1.311(7)	2.901(2)	116.2(3)	this work
[Mo(Et_2NCS_2)(CO)(NO)(P{OMe}$_3$)$_2$]	2.565(4) 2.559(4)	1.68(1) 1.69(2)	1.36(2)	2.888(5)	117.6(8)	this work

[a] $C_4H_8NCS_2^-$ = pyrrolidine-1-carbodithioato.

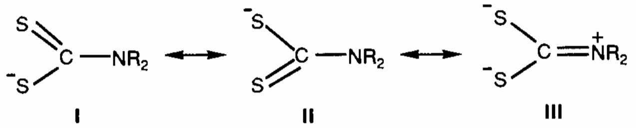
[b] $C_5H_{10}NCS_2^-$ = piperidine-1-carbodithioato.

[c] The structure contains a crystallographically imposed two-fold axis, through the Mo atom and the C–N bond.

3), indicating a quasi-octahedral environment. The observed bond angles, ∠M–N–O, which lie within the range 175.1–177.7°, show that the nitrosyl group can be considered linear 'NO^+' in these Mo^0 compounds [10].

The S···S 'bite' distances of the diethyldithiocarbamato ligands between 2.888 and 2.901 Å (Table 4) are typical for bidentate geometry [13]. This is also compatible with the expectation of the ligand as a four-electron donor, based on a simple electron counting rule (e.g., 18-electron rule). This conclusion is further supported by the two nearly identical C–S bond lengths in each ligand. However, the angles, ∠S–C–S, which lie in the range 114.5–117.6°, contain the value of 115.7° observed for the monodentate diethyldithiocarbamato ligand in [Pt(η^1-Et_2NCS_2)({PhP($CH_2CH_2PPh_2$)$_2$}]BPh_4 [13] so that this angle cannot be used as a criterion for judging a mono- or bidentate coordination mode for the ligand.

Although the S···S values of **1**, **3**, **4**, **6**, **7**, **8** and **10** are similar to that of 2.908(2) Å in [PPN][Mo($C_4H_8NCS_2$)$(CO)_4$] (**11**), 2.892(6) Å in [PPN][Mo($C_5H_{10}NCS_2$)$(CO)_4$] (**12**) ($C_4H_8NCS_2^-$ = pyrroline-1-carbodithioato; $C_5H_{10}NCS_2^-$ = piperidine-1-carbodithioato) [12], and 2.90(1) Å in [PPN][Mo(Et_2NCS_2)$(CO)_4$] (**13**) [11], comparison of the Mo–S distances in **1**–**13** (Table 4) reveals two types with the longer values (2.597–2.631 Å) for the tetracarbonyl complexes, **11**–**13**, and the shorter values (2.518–2.576 Å) for [Mo(Et_2NCS_2)(NO)(CO)L_2]$^{m-}$. Apparently, if relative contribution of the canonical forms **I**, **II** and **III** is used to represent the σ-donicity of a dialkyldithiocarbamato ligand, as depicted below, the presence of a stronger π-acid, NO, in the structures can permit a greater contribution of **III** of the diethyldithiocarbamato



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ligand. However, as reflected in the similar C–N distances (Table 4), one should also be cautious in that some modest difference, as large as 0.03 Å [11,14], in the singly bonded distances may not indicate chemical effects but may be caused by the crystal packing effects.

4. Supplementary material

Tables of complete bond lengths and angles, anisotropic displacement parameters, hydrogen coordinates, observed and calculated structure factors can be obtained from the authors upon request.

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