

N11—Mo—N21	89.0 (2)	N21—Mo—Cl ⁱ	89.97 (14)
N21 ⁱ —Mo—N21	92.6 (3)	Cl—Mo—Cl ⁱ	179.75 (9)
N11—Mo—Cl	89.86 (14)	Br1 ⁱⁱ —Br—Br1	178.24 (6)

Symmetry codes: (i) $-x, y, \frac{1}{2} - z$; (ii) $1 - x, y, \frac{1}{2} - z$.

The space group *Pbcn* (No. 60) was chosen from the systematic absences. All H atoms were found in the difference electron-density map, but were included in the refinement at calculated positions with 1.4 times the isotropic displacement parameters of the attached heavy atoms. Calculations were performed on a PC 486. Additionally, *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989) and *PLUTON* (Spek, 1991) were used for data processing and final interpretation of structural geometry.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *NRCVAX*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1971) and *PLUTON*. Software used to prepare material for publication: *SHELXL93*.

We are indebted to the Ministry of Science and Research of the Republic of Slovenia and the University of Ljubljana for financial support.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: JZ1125). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). **C52**, 2157–2159

Tris(*N,N*-diethyldithiocarbamato-*S,S'*)-(thionitrosyl-*N*)molybdenum(III), [Mo(η^2 -S₂CNEt₂)₃(NS)]

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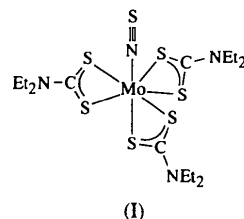
(Received 24 April 1996; accepted 30 May 1996)

Abstract

The structure of the title compound consists of a neutral [Mo(C₅H₁₀NS₂)₃(NS)] unit, with the ligands arranged in a distorted pentagonal bipyramidal configuration. The thionitrosyl ligand occupies an axial site, with an N—S bond length of 1.568 (4) Å. At 2.6083 (14) Å, the axial Mo—S bond is considerably elongated with respect to those in the pentagonal plane [average 2.509 (16) Å].

Comment

Nitrosyl complexes of transition metals have been the subject of considerable interest for many years, while in comparison, compounds containing the heavier thionitrosyl ligand are relatively rare (Roesky & Pandey, 1983; Hübener, Abram & Strähle, 1994). One of the earliest reports of thionitrosyl complexes concerned the preparation of the molybdenum(III) complexes [Mo(η^2 -S₂CNR₂)₃(NS)] [*R* = Me, Et or (CH₂)₂], formed upon thermolysis of the dioxo complexes [MoO₂(η^2 -S₂CNR₂)₂] with trimethylsilyl azide (Bishop, Chatt & Dilworth, 1979). The dimethyldithiocarbamate complex (*R* = Me) was the first thionitrosyl complex to be characterized by X-ray crystallography (Hursthouse & Motevalli, 1979) and revealed some interesting features of the ligand, namely an essentially linear Mo—N—S vector and a short sulfur–nitrogen interaction. During the course of our studies on the thermal rearrangement of the dithiocarbamate ligand at high-valent molybdenum centres (Coffey, Forster & Hogarth, 1996), we serendipitously prepared the title complex, (I), and report here its crystal structure.



A view of the molecular structure of (I) with the atomic numbering scheme is presented in Fig. 1. The title compound is made up of neutral [Mo(η^2 -S₂CNEt₂)₃(NS)] units in which the metal centre has a distorted pentagonal bipyramidal environment, with the metal atom displaced by 0.237 Å from the plane of the five equatorial S atoms. The thionitrosyl ligand occupies an axial site, is essentially linear at nitrogen [Mo(1)—N(4)—S(7) 174.8(2)°] and is characterized by a short N—S distance of 1.568(4) Å, while the Mo—N distance of 1.765(4) Å can be compared with that of 1.74(1) Å found in the dimethyldithiocarbamate analogue (Hursthouse & Motevalli, 1979). The second axial position is occupied by an S atom, S(1), and the N(4)—Mo(1)—S(1) angle of 164.62(11)° represents the largest deviation from an ideal pentagonal bipyramid and results from the bite-angle constraints of the dithiocarbamate ligand occupying both axial and equatorial sites. The molybdenum–sulfur vector *trans* to the thionitrosyl ligand [Mo(1)—S(1) 2.6083(14) Å] is significantly elongated with respect to those occupying equatorial sites, which vary between 2.4817(14) and 2.5320(13) Å [average 2.509(16) Å]. This *trans* influence of multiply-bonded ligands has previously been noted for molybdenum(III)–dithiocarbamate complexes. Thus, while in compound (I) the effect manifests itself with an average difference in bond lengths (Δ) between axial and equatorial sites of 0.098 Å, related complexes [Mo(η^2 -S₂CNMe₂)₃(NS)] (Hursthouse & Motevalli, 1979) and [Mo(η^2 -S₂CNEt₂)₃(NO)] (Brennan & Bernal, 1973) are characterized by Δ values of 0.087 and 0.060 Å, respectively, while the effect is even more pronounced in the molybdenum(VI)–nitrido complex [Mo(η^2 -S₂CNEt₂)₃(N)] (Hursthouse & Motevalli, 1979), where Δ is 0.329 Å.

Experimental

The title complex was serendipitously prepared as a low-yield by-product from the reaction of [MoCl₂(η^2 -MeOCH₂CH₂OMe)(C₆H₄N-*p*-CH₃)₂] (Coffey & Hogarth, 1996) with two equivalents of NH₄S₂CNEt₂ in diethyl ether under a blanket of N₂ at room temperature. After stirring for 12 h, a small amount of yellow solid precipitated from the reaction mixture. This was washed with diethyl ether and slow diffusion of methanol into a dichloromethane solution in air afforded orange crystals of (I).

Crystal data

[Mo(C₅H₁₀NS₂)₃(NS)]

M_r = 586.79

Monoclinic

*P*2₁/*c*

a = 9.686(3) Å

b = 17.512(4) Å

c = 15.470(5) Å

β = 96.35(2)°

V = 2608.0(12) Å³

Z = 4

D_x = 1.494 Mg m⁻³

D_m not measured

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 30

reflections

θ = 10–20°

μ = 1.073 mm⁻¹

T = 293(2) K

Block

0.50 × 0.40 × 0.30 mm

Orange

Data collection

Nicolet R3m/V diffractometer

ω –2 θ scans

Absorption correction:

empirical based on ψ scans (North, Phillips & Mathews, 1968)

T_{min} = 0.711, *T_{max}* = 0.974

4869 measured reflections

4588 independent reflections

3395 observed reflections

[*I* > 2 σ (*I*)]

R_{int} = 0.0199

θ_{max} = 25.07°

h = 0 → 11

k = 0 → 20

l = –18 → 18

3 standard reflections

monitored every 97

reflections

intensity decay: none

Refinement

Refinement on *F*²

R(*F*) = 0.0410

wR(*F*²) = 0.1033

S = 0.979

4574 reflections

253 parameters

H atoms fixed

w = 1/[$\sigma^2(F_o^2) + (0.0318P)^2 + 5.4597P$]
where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} = 0.002

$\Delta\rho_{max}$ = 0.35 e Å⁻³

$\Delta\rho_{min}$ = –0.41 e Å⁻³

Extinction correction: none

Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
Mo(1)	0.80339(4)	0.08735(2)	0.78350(2)	0.04920(13)
S(1)	0.69624(13)	–0.01498(7)	0.67330(8)	0.0581(3)
S(2)	0.82794(13)	0.12681(7)	0.63188(8)	0.0576(3)
S(3)	1.03111(12)	0.02744(7)	0.75338(8)	0.0598(3)
S(4)	0.88101(13)	–0.01402(7)	0.89206(7)	0.0612(3)
S(5)	0.62514(14)	0.07494(9)	0.88920(9)	0.0710(4)
S(6)	0.58578(13)	0.16167(8)	0.73554(8)	0.0670(3)
S(7)	0.96146(14)	0.24365(7)	0.86763(9)	0.0665(3)

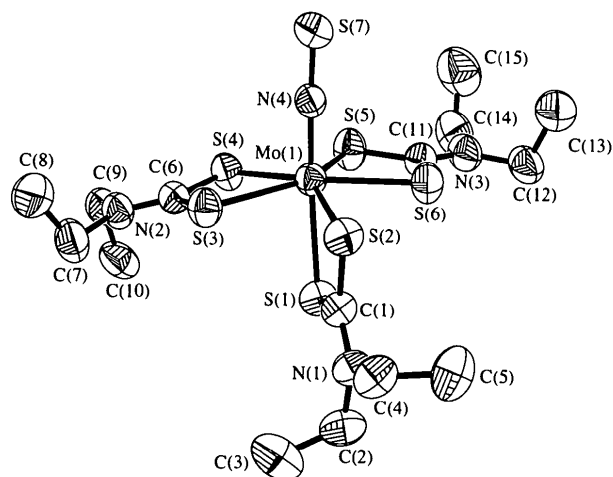


Fig. 1. The molecular structure of (I) showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity. One C atom is disordered over two sites, C(8) and C(8A), with occupancies of 0.65 and 0.35, respectively, and only the first of these is shown.

N(1)	0.7292 (4)	0.0278 (2)	0.5100 (2)	0.0554 (9)
N(2)	1.1049 (4)	-0.0924 (2)	0.8574 (2)	0.0637 (10)
N(3)	0.3874 (4)	0.1504 (3)	0.8441 (3)	0.0730 (12)
N(4)	0.8881 (4)	0.1682 (2)	0.8324 (2)	0.0501 (9)
C(1)	0.7468 (4)	0.0430 (3)	0.5943 (3)	0.0514 (10)
C(2)	0.6710 (6)	-0.0451 (3)	0.4768 (3)	0.0725 (14)
C(3)	0.7823 (8)	-0.1024 (4)	0.4668 (4)	0.104 (2)
C(4)	0.7700 (5)	0.0827 (3)	0.4456 (3)	0.0639 (13)
C(5)	0.6548 (6)	0.1367 (3)	0.4163 (4)	0.083 (2)
C(6)	1.0205 (5)	-0.0347 (3)	0.8377 (3)	0.0553 (11)
C(7)	1.2142 (6)	-0.1127 (4)	0.8029 (4)	0.080 (2)
C(8)†	1.3437 (16)	-0.0741 (8)	0.8287 (11)	0.100 (4)
C(8A)‡	1.356 (4)	-0.1165 (16)	0.851 (2)	0.114 (11)
C(9)	1.0784 (6)	-0.1468 (3)	0.9256 (3)	0.0712 (14)
C(10)	0.9760 (7)	-0.2076 (3)	0.8916 (4)	0.089 (2)
C(11)	0.5140 (5)	0.1319 (3)	0.8256 (3)	0.0644 (13)
C(12)	0.2970 (6)	0.1991 (3)	0.7830 (4)	0.082 (2)
C(13)	0.3225 (7)	0.2819 (4)	0.7992 (5)	0.101 (2)
C(14)	0.3356 (6)	0.1246 (4)	0.9248 (4)	0.097 (2)
C(15)	0.3617 (9)	0.1800 (5)	0.9965 (5)	0.127 (3)

† Occupancy of 0.65. ‡ Occupancy of 0.35.

Table 2. Selected geometric parameters (Å, °)

Mo(1)—N(4)	1.765 (4)	Mo(1)—S(6)	2.5182 (14)
Mo(1)—S(2)	2.4817 (14)	Mo(1)—S(3)	2.5320 (13)
Mo(1)—S(4)	2.5016 (13)	Mo(1)—S(1)	2.6083 (14)
Mo(1)—S(5)	2.5152 (15)	S(7)—N(4)	1.568 (4)
S(5)—Mo(1)—S(6)	67.90 (5)	S(2)—Mo(1)—S(1)	69.29 (4)
S(4)—Mo(1)—S(3)	68.05 (4)	S(7)—N(4)—Mo(1)	174.8 (2)
N(4)—Mo(1)—S(1)	164.62 (11)		

One of the C atoms was disordered over two sites, C(8) and C(8A). Their occupancies and those of the attached H atoms were refined to 0.65 and 0.35, respectively.

Data collection: Nicolet R3 software. Cell refinement: Nicolet R3 software. Data reduction: XDISK (Siemens, 1991). Program(s) used to solve structure: SHELXTL-Plus (Sheldrick, 1986). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: SHELXTL-Plus. Software used to prepare material for publication: SHELXL93.

The authors thank the EPSRC for supporting this work in the form of studentships to TAC and GDF.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BM1082). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). **C52**, 2159–2161

(4-Chlorobenzenethiolato-S)(η^5 -cyclopentadienyl)(triphenylphosphine-P)nickel(II)

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(Received 24 August 1995; accepted 7 May 1996)

Abstract

The Ni atom in [Ni(C₆H₄ClS)(C₅H₅)(C₁₈H₁₅P)] has a distorted trigonal geometry, with bond angles Cp—Ni—S 132.3 (1), Cp—Ni—P 135.3 (5) and P—Ni—S 92.4 (1)°, where Cp represents the centroid of the C₅H₅ ring. The bond distances Cp—Ni, Ni—S and Ni—P are 1.763 (1), 2.190 (1) and 2.144 (1) Å, respectively, which are close to distances found in similar compounds. A structural model with disordered cyclopentadienyl ligands was used.

Comment

The use of [(η^5 -C₅H₅)Ru(PPh₃)₂Cl] as a starting material for entry into (cyclopentadienyl)ruthenium chemistry is very well documented (Bruce, Cifuentes, Snow & Tiekink, 1989; Davies, McNally & Smallbridge, 1990). The effectiveness of this complex as a starting material is aided by the substitutionally labile PPh₃ groups and also by the ability of the complex to react metathetically with replacement of the halide atom. We have been using the isoelectronic complex [(η^5 -C₅H₅)Ni(PPh₃)X] (X = Cl, Br, I) for a similar purpose. Our results so far indicate that the metathetical replacement of the halide in our starting compound leads to complexes of the type [(η^5 -C₅H₅)Ni(PPh₃)(ER)] (E = S, Se; R = alkyl, aryl) (Darkwa, Bothata & Koczon, 1993; Darkwa, 1994) and is similar to the analogous ruthenium reactions. In an attempt to study the effect of halide-substituted organosulfur ligands on the Ni—P bond in these compounds, we isolated [(η^5 -C₅H₅)Ni(PPh₃)(SC₆H₄Cl-4)], (1), whose structure is reported here.