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Bis(glycinato-κ^2*N*,*O*)dinitrosylmolybdenum(0) and bis(2-aminoethanethiolato-κ^2*N*,*S*)dinitrosylmolybdenum(0) acetonitrile monosolvate

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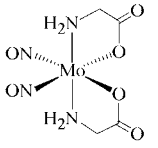
The title compounds, [Mo($C_2H_4NO_2$)$_2$(NO)$_2$], (I), and [Mo(C_2H_6NS)$_2$(NO)$_2$]·CH_3CN, (II), contain distorted octahedral complexes in which the monoanionic *N*,*S*- and *N*,*O*-bidentate ligands coordinate the molybdenum centres in different modes. The anionic O atoms of the glycinate ligands in (I) are coordinated *trans* to the nitrosyl ligands and the amine N atoms are located *trans* to each other, whereas in (II) the anionic S atoms are coordinated *trans* to each other and the amine N atoms are located *trans* to the nitrosyl ligands. Each compound has a single complete complex in the asymmetric unit on a general position. Six N—H···O contacts with N···O distances of less than 3.2 Å are observed in (I) between the amine groups and the nitrosyl and carboxylate O atoms. In the 1:1 solvate (II), the acetonitrile molecule forms short N—H···N contacts (N···N < 3.2 Å) between the solvent N atoms and one of the amine H atoms. In addition, three weak intermolecular N—H···S interactions (N···S > 3.3 Å) contribute to the stabilization of the structure of (II).

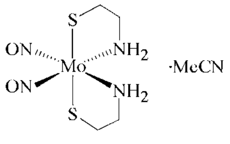
Comment

With the aim of preparing water-soluble dinitrosyl–molybdenum complexes to study their ability to release NO in aqueous solution, the title compounds, [Mo(H_2NCH_2COO)$_2$(NO)$_2$], (I), and [Mo($H_2NCH_2CH_2S$)$_2$(NO)$_2$]·CH_3CN, (II), resulting from the reactions of the [Mo(NO)$_2$]$^{2+}$ cation with bidentate monoanionic *N*,*X*-donor ligands (*X* = O and S), were prepared.

In (I) and (II), the Mo atoms adopt distorted octahedral coordinations, with nearly linear Mo—N—O angles and normal Mo—NO bond distances (Figs. 1 and 2). The amine N atoms of the glycinate ligand in (I) are bound to molybdenum in *trans* positions, showing a significantly closed N3—Mo1—N4 bond angle, whereas the anionic O atoms are located *cis* to each other and *trans* to the nitrosyl ligands, with nearly linear O—Mn—N angles (Table 1). The crystal structure of (II) reveals a different coordination mode in comparison with (I), since the monoanionic bidentate ligands coordinate to the metal centre with the anionic S atoms in *trans* positions to each other, with a significantly closed S1—Mo1—S2 angle and the amine N atoms located *trans* to the nitrosyl ligands with relatively undistorted N—Mn—N angles (Table 3). The known molybdenum–dinitrosyl complexes of 2-picolinate (Perpiñán *et al.*, 1987) and 2-pyrimidinethiolate (Yonemura *et al.*, 2001) show the same systematic trend, at least in the coordination manner of the *N*,*S*- and *N*,*O*-bidentate ligands.



(I)



(II)

In order to trace the electronic causes for this phenomenon at the molecular orbital level, simple density functional theory (DFT) calculations were carried out using the *TURBOMOLE* program package (Von Arnim & Ahlrichs, 1998; Treutler & Ahlrichs, 1995; Ahlrichs *et al.*, 1989). Two different coordination geometries have been optimized for each complex: (*a*) with the amine N atoms *trans* to the nitrosyl ligands and (*b*) with the anionic chalcogen atoms [O in (I) and S in (II)] *trans* to the nitrosyl ligands. The computed total energies confirm the solid-state structures of (I) and (II) as the global energetic minima. Indeed, the thermodynamically most favourable geometries show the amine N atoms [(I*b*), 8.7 kcal mol^{-1} below I(*a*)] and the anionic S atoms [(II*a*), 5.1 kcal mol^{-1} below (II*b*)] *trans* to each other. From basic considerations,

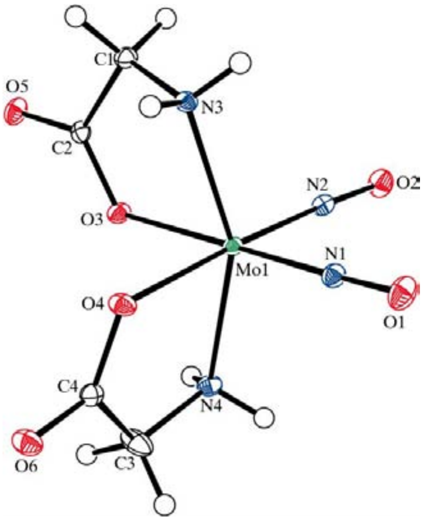


Figure 1
A view of the molecular structure of (I), showing the atomic labelling scheme and 30% probability displacement ellipsoids.

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the van der Waals radius of the S atom is significantly larger than those of the O and N atoms (1.815 Å *versus* 1.060 and 1.050 Å, respectively), and consequently *trans*-*S*,*S* geometry should be preferred to *cis*-*S*,*S* geometry. The computed highest occupied molecular orbitals (HOMOs) of (I) and (II) indicate that the electron population of the sulfur lone pairs is, as expected, larger than that in the oxygen lone pairs, leading to a strong antibonding interaction between the in-plane sulfur lone pairs in the energetically high-lying HOMO of the *trans*-*N*,*N* geometry of (II). In the case of the *trans*-*N*,*N* geometry of (I), the HOMO exhibits a π-type antibonding character between the oxygen lone pairs and a *d* orbital of the metal, but with a less destabilizing effect than in (II).

Six N—H···O contacts with N···O distances of less than 3.2 Å, between the amine groups and the nitrosyl and carboxylate O atoms, are observed in (I) (Fig. 3 and Table 2). Not surprisingly, the shortest and most linear of these interactions are with the noncoordinating carboxylate O atoms. Acetonitrile solvent molecules cocrystallize with compound (II), forming short N—H···N contacts (N···N < 3.2 Å) between the solvent N atoms and one of the amine H atoms (Fig. 4 and Table 4). In addition, three weak N—H···S intermolecular interactions (N···S > 3.3 Å) contribute to the stabilization of the structure of (II).

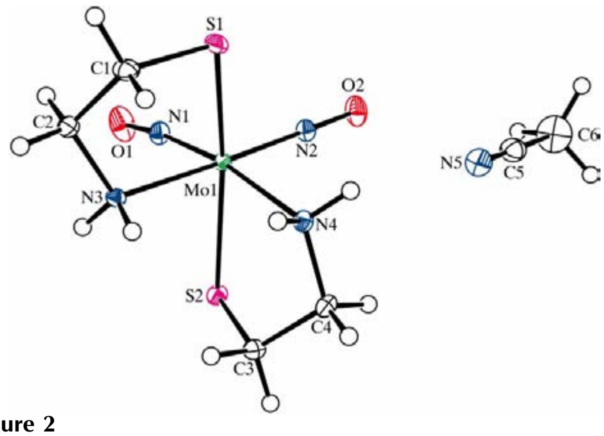

Figure 2
A view of the molecular structure of (II), showing the atomic labelling scheme and 30% probability displacement ellipsoids.

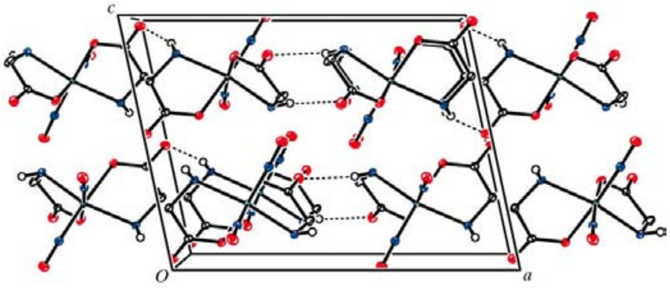

Figure 3
A projection of the structure of (I) normal to (010), showing the shortest hydrogen-bonding interactions, *viz*. H3*B*···O5 and H4*B*···O6 (dashed lines), in the crystal structure.

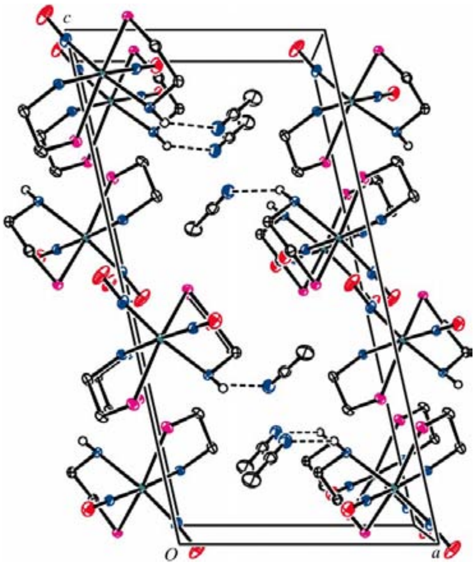

Figure 4
A projection of the structure of (II) normal to (010), showing the short intermolecular interactions between (II) and the acetonitrile solvent molecules (dashed lines).

Experimental

For the preparation of (I), a solution of H_2NCH_2COOLi (154 mg, 1.90 mmol) in methanol (5 ml) was added to a solution of the bromide polymer $[Mo(NO)_2Br_2]_n$ (300 mg, 0.95 mmol) in the same solvent (5 ml), and the reaction mixture was stirred for 2 h. During that time, a colour change from green to dark green was observed. The reaction solution was filtered over Celite to remove insoluble materials, and the solvent was removed under vacuum, leaving the product and LiBr. Adding some tetrahydrofuran and stirring the mixture for 10 min resulted in dissolution of LiBr. The green solid was filtered off over a frit, washed with cold tetrahydrofuran (243 K) and dried under vacuum. The obtained powder was redissolved in methanol and green crystals of (I) were formed on slow evaporation at room temperature in a low yield of about 20%. Analysis calculated for $C_4H_8MoN_4O_6$: C 15.80, H 2.65, N 18.42%; found: C 16.02, H 2.48, N 18.14%.

For the preparation of (II), a solution of $H_2NCH_2CH_2SLi$ (130 mg, 0.156 mmol) in acetonitrile (4 ml) was added to a green solution of the bromide polymer $[Mo(NO)_2Br_2]_n$ (247 mg, 0.78 mmol) in the same solvent (4 ml). During the course of addition, the colour of the solution changed from green to red–brown. After the addition was complete, the reaction mixture was stirred for 2 h and then filtered over Celite. Slow evaporation of acetonitrile at room temperature gave, after a few days, 90 mg of (II) as red–brown microcrystals. Analysis calculated for $C_4H_{12}MoN_4O_2S_2$: C 15.59, H 3.92, N 18.18%; found: C 15.87, H 3.92, N 17.99% (the elemental analysis was carried out after desolvation of the crystals).

DFT calculations were performed with the *TURBOMOLE* program package (Version 5.5; Von Arnim & Ahlrichs, 1998; Treutler & Ahlrichs, 1995; Ahlrichs *et al.*, 1989). The Vosko–Wilk–Nusair (Vosko *et al.*, 1980) local density approximation and the generalized gradient approximation (GGA) with corrections for exchange and correlation according to Becke (1988) and Perdew (1986*a*,*b*) (BP86) were used for all calculations. The *TURBOMOLE* approach to DFT GGA calculations is based on the use of Gaussian-type orbitals as basis functions. Geometries were optimized using accurate triple-ζ

valence basis sets augmented by one polarization function TZV(P) (Schäfer *et al.*, 1992, 1994) for all elements.

Compound (I)

Crystal data

$[Mo(C_2H_4NO_2)_2(NO)_2]$
$M_r = 304.08$
Monoclinic, $P2_1/c$
$a = 12.9088$ (15) Å
$b = 7.5727$ (6) Å
$c = 9.6922$ (11) Å
$\beta = 102.051$ (13)°
$V = 926.58$ (17) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 1.44$ mm^{-1}
$T = 183$ (2) K
0.43 × 0.41 × 0.39 mm

Data collection

Stoe IPDS diffractometer
Absorption correction: numerical (Coppens *et al.*, 1965)
$T_{\min} = 0.56$, $T_{\max} = 0.669$
17540 measured reflections
2745 independent reflections
2265 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.045$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.021$
$wR(F^2) = 0.051$
$S = 0.93$
2745 reflections
136 parameters
H-atom parameters constrained
$\Delta\rho_{\max} = 0.38$ e Å^{-3}
$\Delta\rho_{\min} = -0.68$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (I).

Mo1—N1	1.8264 (15)	N1—O1	1.1756 (19)
Mo1—N2	1.8318 (15)	N2—O2	1.1737 (19)
Mo1—O4	2.0945 (12)	O3—C2	1.289 (2)
Mo1—O3	2.0976 (12)	O4—C4	1.290 (2)
Mo1—N4	2.1843 (14)	O5—C2	1.230 (2)
Mo1—N3	2.1921 (14)	O6—C4	1.228 (2)
N1—Mo1—N2	87.59 (6)	O4—Mo1—N4	78.14 (5)
N2—Mo1—O4	177.12 (5)	O3—Mo1—N3	77.40 (5)
N1—Mo1—O3	175.03 (5)	N4—Mo1—N3	154.60 (6)
O4—Mo1—O3	84.03 (5)		

Table 2
Hydrogen-bond geometry (Å, °) for (I).

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3A···O3$^{\rm i}$	0.90	2.64	3.5357 (18)	177
N3—H3A···O5$^{\rm i}$	0.90	2.52	3.1347 (19)	126
N3—H3B···O5$^{\rm ii}$	0.90	2.08	2.9237 (19)	155
N3—H3B···O2$^{\rm iii}$	0.90	2.52	3.0408 (19)	117
N4—H4A···O4$^{\rm iv}$	0.90	2.41	3.1651 (19)	142
N4—H4A···O6$^{\rm iv}$	0.90	2.30	2.9920 (19)	133
N4—H4B···O6$^{\rm v}$	0.90	2.18	2.9377 (19)	142

Symmetry codes: (i) $x, -y-\frac{1}{2}, z-\frac{1}{2}$; (ii) $-x+2, y+\frac{1}{2}, -z+\frac{3}{2}$; (iii) $x, -y+\frac{1}{2}, z-\frac{1}{2}$; (iv) $x, -y-\frac{1}{2}, z+\frac{1}{2}$; (v) $-x+1, y+\frac{1}{2}, -z+\frac{3}{2}$.

Compound (II)

Crystal data

$[Mo(C_2H_6NS)_2(NO)_2]\cdot C_2H_3N$
$M_r = 349.29$
Monoclinic, $P2_1/c$
$a = 8.8660$ (7) Å
$b = 8.5980$ (7) Å
$c = 18.0218$ (16) Å
$\beta = 102.487$ (10)°
$V = 1341.30$ (19) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 1.28$ mm^{-1}
$T = 183$ (2) K
0.41 × 0.4 × 0.19 mm

Data collection

Stoe IPDS diffractometer
Absorption correction: numerical (Coppens *et al.*, 1965)
$T_{\min} = 0.621$, $T_{\max} = 0.793$
17511 measured reflections
3976 independent reflections
3459 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.087$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.145$
$S = 1.06$
3976 reflections
146 parameters
H-atom parameters constrained
$\Delta\rho_{\max} = 1.45$ e Å^{-3}
$\Delta\rho_{\min} = -1.35$ e Å^{-3}

Table 3
Selected geometric parameters (Å, °) for (II).

Mo1—N1	1.828 (2)	Mo1—S1	2.4870 (7)
Mo1—N2	1.837 (2)	S1—C1	1.825 (3)
Mo1—N3	2.243 (2)	S2—C3	1.823 (3)
Mo1—N4	2.255 (2)	N1—O1	1.175 (3)
Mo1—S2	2.4584 (7)	N2—O2	1.173 (3)
N1—Mo1—N2	90.91 (11)	N4—Mo1—S2	80.33 (6)
N2—Mo1—N3	176.49 (9)	N3—Mo1—S1	79.32 (6)
N1—Mo1—N4	170.91 (10)	S2—Mo1—S1	158.78 (3)
N3—Mo1—N4	87.20 (8)		

Table 4
Hydrogen-bond geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3A···S2$^{\rm i}$	0.92	2.55	3.372 (2)	150
N3—H3B···S1$^{\rm ii}$	0.92	2.60	3.459 (2)	155
N4—H4C···N5	0.92	2.32	3.146 (4)	150
N4—H4D···S1$^{\rm ii}$	0.92	2.53	3.419 (2)	162

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

All H-atom positions were calculated after each cycle of refinement with *SHELXL97* (Sheldrick, 1997) using a riding model in both structures, with C—H distances in the range 0.97–0.99 Å and N—H distances in the range 0.90–0.92 Å. $U_{\rm iso}$(H) values were set equal to $1.3U_{\rm eq}$ of the parent C or N atoms in (I), and $1.2U_{\rm eq}$(C,N) in (II) [$1.5U_{\rm eq}$(C) for the methyl H atoms].

For both compounds, data collection: *IPDS Software* (Stoe & Cie, 1999); cell refinement: *IPDS Software*; data reduction: *X-RED* (Stoe & Cie, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3117). Services for accessing these data are described at the back of the journal.

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