# The Structures of Two Mononuclear Six-Coordinate Oxomolybdenum(V) Complexes Stabilized by the Hydrotris(3,5-dimethyl-1-pyrazolylborate) Ligand

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**Abstract.** (I) [Hydrotris(3,5-dimethyl-1-pyrazolyl)-borato]bis(isothiocyanato)oxomolybdenum(V) 1,2-dichloroethane solvate, [Mo($C_{15}H_{22}BN_6$)O(SCN)$_2$], $M_r = 624.3$, monoclinic, $P2_1/m$, $a = 8.640$ (5), $b = 19.635$ (9), $c = 8.761$ (3) Å, $\beta = 112.58$ (3)°, $V = 1372.3$ Å$^3$, $Z = 2$, $D_x = 1.51$ g cm$^{-3}$, $\lambda$(Mo $K\alpha$) = 0.71073 Å, $\mu = 8.36$ cm$^{-1}$, $F(000) = 634$, $T = 293$ K, $R = 0.060$ for 1636 reflections. (II) Diazido-[hydrotris(3,5-dimethyl-1-pyrazolyl)borato]oxomolybdenum(V), [Mo($C_{15}H_{22}BN_6$)O(N$_3$)$_2$], $M_r = 493.2$, orthorhombic, $P2_12_12_1$, $a = 8.958$ (4), $b = 10.273$ (2), $c = 22.928$ (6) Å, $V = 2110$ Å$^3$, $Z = 4$, $D_x = 1.55$ g cm$^{-3}$, $\lambda$(Mo $K\alpha$) = 0.71073 Å, $\mu = 6.25$ cm$^{-1}$, $F(000) = 1004$, $T = 293$ K, $R = 0.057$ for 1382 reflections. In each complex the molybdenum atom is six-coordinate, ligated by a terminal oxygen atom, a tridentate pyrazolylborate group and two pseudohalide groups. The molecular structures of the complexes are nearly identical, differing only in the geometry of the pseudohalide ligands. In (I), the molybdenum atom and the NCS ligand are nearly collinear (Mo—N—C = 171°), whereas in (II) the average Mo—N—N angle is 133°.

**Introduction.** As part of a continuing investigation of the chemistry of mononuclear molybdenum(V) compounds stabilized by the hydrotris(3,5-dimethyl-1-pyrazolyl)borate ligand (*L*) (Cleland, Barnhart, Yamanouchi, Collison, Mabbs, Ortega & Enemark, 1986), we report the crystal structures of the *L*MoO*X*$_2$ complexes with *X* = NCS$^-$ (I) and *X* = N$_3^-$ (II). The structures of these complexes are of additional interest because their electron paramagnetic resonance (EPR) spectra in frozen solution can be simulated assuming *m* site symmetry at the molybdenum(V) atom (Collison, Mabbs, Enemark & Cleland, 1986).

**Experimental.** The compounds were prepared as described elsewhere (Cleland *et al.*, 1986).

*Crystal data* (I). Red needles, dimensions 0.45 × 0.20 × 0.10 mm, Syntex $P2_1$ diffractometer, cell constants from 20 reflections with $6 < 2\theta < 20°$. Data collection using $\theta$–$2\theta$ scans initiated to $2\theta_{max} = 45°$, but after decomposition was observed data collection was limited to $2\theta_{max} = 35°$. Three standard reflections collected every 97 reflections decayed 38%; linear decay correction made. No absorption corrections ($\mu = 8.36$ cm$^{-1}$). Space group either $P2_1$ or $P2_1/m$. Structure solved in latter space group. 1936 of the 2518 unique reflections with $F_o^2 > 3\sigma(F_o^2)$ and $2\theta < 35°$ used in the refinement. $R_{int} = 3.9\%$. Mo position found from Patterson map, other atoms from succeeding difference maps. H atoms included at calculated positions. Final refinement on $F$ (1636 reflections, 169 parameters) resulted in $R = 0.060$, $wR = 0.066$, $S = 1.99$.† Weights for each reflection were assigned as $w = 4F_o^2/[\sigma^2(I) + (pF_o^2)^2]$ with $p$ set to 0.03. $(\Delta/\sigma)_{max} = 0.63$ (a solvent C thermal parameter). $(\Delta\rho)_{max} = 0.90$ e Å$^{-3}$ near Cl. Atomic scattering factors from Cromer & Waber (1974) and anomalous-dispersion factors from Cromer (1974). Programs *SDP* (Frenz, 1978) run on a PDP 11/34a.

*Crystal data* (II). Brown needles, dimensions 0.42 × 0.17 × 0.13 mm. Data collected by $\theta$–$2\theta$ scan method. Cell constants from 15 reflections in the range $20 < 2\theta < 22°$. No absorption corrections ($\mu = 6.25$ cm$^{-1}$). $2\theta_{max} = 50°$. Three check reflections every 100 reflections; no decay. Space group $P2_12_12_1$. 2152 reflections measured, 1382 with $F_o^2 > 3\sigma(F_o^2)$ were used in the refinement. Final refinement on $F$ (161 parameters) resulted in $R = 0.057$, $wR = 0.060$, $S = 1.50$. $(\Delta/\sigma)_{max} = 0.035$. Refinement of the enantiomer gave $wR = 0.0611$. The difference is significant at the 99.5% confidence level (Hamilton, 1974). $(\Delta\rho)_{max} = 1.16$ e Å$^{-3}$ near Mo. Other experimental parameters same as (I).

**Discussion.** Each complex contains a six-coordinate Mo atom in a pseudo-octahedral geometry. Both

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† Lists of structure factors, anisotropic thermal parameters, calculated H-atom positions, and all bond distances and angles not involving hydrogen have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43318 (28 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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complexes are restricted to facial stereochemistry by the pyrazolylborate ligand. Figs. 1 [(I), $X = NCS^-$] and 2 [(II), $X = N_3^-$] show the atom labelling. Tables 1 and 2 list the final positional and equivalent isotropic thermal parameters for (I) and (II), respectively. Table 3 gives selected bond distances and angles for both compounds. (I) is required to possess $m$ symmetry by the space group; (II) approximates $m$ symmetry although no symmetry is imposed by the space group. The two molecular structures are nearly identical, differing primarily in the geometry of the triatomic pseudohalide ligands. In (I) the Mo—N(1)—C(1) angle

is 171·0 (5)°, whereas in (II) the Mo—N(1)—N(2) and Mo—N(4)—N(5) angles are 129 and 136°, respectively. The structure of the pyrazolylborate ligand is normal in both complexes (Lincoln, Soong, Koch, Sato &

### Table 1. Atomic coordinates and equivalent isotropic thermal parameters for LMoO(NCS)$_2$ (I)

Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $8\pi^2(U_{11} + U_{22} + U_{33})/3$.

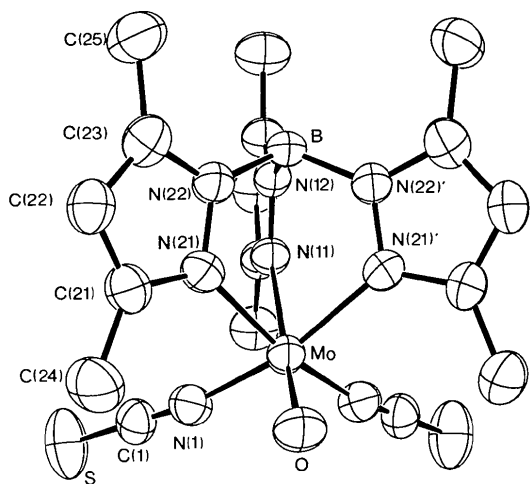|  | $x$ | $y$ | $z$ | $B_{eq}(\text{Å}^2)$ |
|---|---|---|---|---|
| Mo | 0·0709 (1) | 0·250 | 0·0719 (1) | 3·27 (2) |
| S | 0·3908 (3) | 0·4283 (1) | −0·0288 (4) | 8·03 (8) |
| O | −0·1052 (9) | 0·250 | −0·0981 (8) | 4·9 (2) |
| N(1) | 0·1982 (7) | 0·3238 (3) | 0·0079 (6) | 4·1 (2) |
| N(11) | 0·3015 (9) | 0·250 | 0·3173 (9) | 3·4 (2) |
| N(12) | 0·2773 (9) | 0·250 | 0·4628 (9) | 3·4 (2) |
| N(21) | −0·0143 (7) | 0·3229 (3) | 0·2004 (6) | 3·8 (1) |
| N(22) | 0·0061 (7) | 0·3134 (3) | 0·3620 (6) | 3·6 (1) |
| C(1) | 0·2785 (9) | 0·3682 (4) | −0·0071 (9) | 4·3 (2) |
| C(11) | 0·467 (1) | 0·250 | 0·357 (1) | 3·9 (3) |
| C(12) | 0·541 (1) | 0·250 | 0·526 (1) | 4·9 (3) |
| C(13) | 0·424 (1) | 0·250 | 0·591 (1) | 3·8 (3) |
| C(14) | 0·546 (1) | 0·250 | 0·235 (1) | 5·2 (3) |
| C(15) | 0·442 (1) | 0·250 | 0·763 (1) | 5·5 (3) |
| C(21) | −0·0970 (9) | 0·3822 (4) | 0·1494 (8) | 4·4 (2) |
| C(22) | −0·127 (1) | 0·4098 (4) | 0·2789 (9) | 5·0 (2) |
| C(23) | −0·0610 (9) | 0·3670 (4) | 0·4102 (8) | 4·4 (2) |
| C(24) | −0·146 (1) | 0·4084 (5) | −0·022 (1) | 6·1 (2) |
| C(25) | −0·055 (1) | 0·3739 (5) | 0·5829 (9) | 5·7 (2) |
| B | 0·098 (1) | 0·250 | 0·454 (1) | 3·5 (3) |
| Cl | 0·2885 (6) | 0·4457 (3) | −0·5728 (8) | 19·6 (2) |
| C(S) | 0·460 (1) | 0·032 (2) | 0·484 (3) | 30 (1) |



Fig. 1. View of (I) showing the atom labelling scheme. Hydrogen atoms omitted for clarity. Primed atoms are related to unprimed atoms by a mirror plane. The numbering of the atoms in the pyrazole ring containing N(11) parallels that shown for the ring containing N(21).

### Table 2. Atomic coordinates and equivalent isotropic thermal parameters for LMoO(N$_3$)$_2$ (II)

Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $8\pi^2(U_{11} + U_{22} + U_{33})/3$.

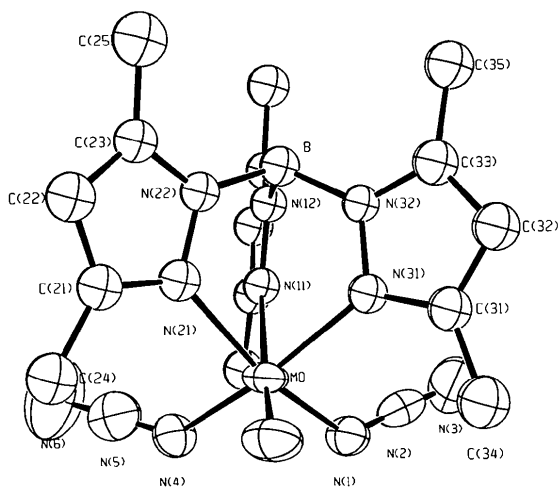|  | $x$ | $y$ | $z$ | $B_{eq}(\text{Å}^2)$ |
|---|---|---|---|---|
| Mo | 0·1347 (1) | 0·0471 (1) | 0·11651 (5) | 3·32 (2) |
| O | 0·0576 (9) | 0·1918 (9) | 0·1031 (4) | 5·0 (2) |
| N(1) | 0·055 (1) | 0·011 (1) | 0·1978 (4) | 4·0 (3) |
| N(2) | 0·121 (1) | −0·0133 (9) | 0·2407 (4) | 4·0 (2) |
| N(3) | 0·181 (2) | −0·036 (1) | 0·2840 (5) | 6·7 (4) |
| N(4) | −0·017 (1) | −0·068 (1) | 0·0825 (5) | 3·9 (2) |
| N(5) | −0·018 (1) | −0·149 (1) | 0·0479 (5) | 5·5 (3) |
| N(6) | −0·023 (2) | −0·233 (2) | 0·0130 (7) | 10·8 (6) |
| N(11) | 0·276 (1) | −0·138 (1) | 0·1321 (4) | 3·0 (2)* |
| N(12) | 0·4284 (9) | −0·1378 (9) | 0·1215 (4) | 3·0 (2)* |
| N(21) | 0·267 (1) | 0·047 (1) | 0·0389 (4) | 3·2 (2)* |
| N(22) | 0·419 (1) | 0·0264 (9) | 0·0409 (4) | 2·9 (2)* |
| N(31) | 0·323 (1) | 0·1375 (9) | 0·1559 (4) | 2·9 (2)* |
| N(32) | 0·468 (1) | 0·0978 (9) | 0·1429 (4) | 2·6 (2)* |
| C(11) | 0·245 (1) | −0·263 (1) | 0·1503 (5) | 3·4 (3)* |
| C(12) | 0·377 (2) | −0·333 (1) | 0·1501 (5) | 4·1 (3)* |
| C(13) | 0·488 (1) | −0·251 (1) | 0·1320 (5) | 3·2 (2)* |
| C(14) | 0·092 (1) | −0·302 (1) | 0·1662 (6) | 4·1 (3)* |
| C(15) | 0·652 (2) | −0·283 (1) | 0·1238 (6) | 4·4 (3)* |
| C(21) | 0·229 (1) | 0·070 (1) | −0·0163 (5) | 3·6 (3)* |
| C(22) | 0·360 (2) | 0·073 (1) | −0·0495 (5) | 4·1 (3)* |
| C(23) | 0·474 (1) | 0·045 (1) | −0·0135 (5) | 3·3 (2)* |
| C(24) | 0·072 (2) | 0·101 (1) | −0·0363 (6) | 4·3 (3)* |
| C(25) | 0·638 (2) | 0·038 (1) | −0·0264 (6) | 5·3 (3)* |
| C(31) | 0·336 (1) | 0·238 (1) | 0·1934 (5) | 3·4 (3)* |
| C(32) | 0·486 (1) | 0·265 (1) | 0·2039 (5) | 3·9 (3)* |
| C(33) | 0·566 (1) | 0·171 (1) | 0·1725 (6) | 3·8 (3)* |
| C(34) | 0·205 (2) | 0·308 (1) | 0·2162 (6) | 4·7 (3)* |
| C(35) | 0·732 (1) | 0·154 (1) | 0·1683 (6) | 4·4 (3)* |
| B | 0·497 (2) | −0·009 (1) | 0·0987 (6) | 3·1 (3)* |



Fig. 2. View of (II) showing the atom labelling scheme. Hydrogen atoms omitted for clarity. The numbering of the atoms in the pyrazole ring containing N(11) parallels that shown for the rings containing N(21) and N(31).

Table 3. *Selected bond distances* (Å) *and angles* (°)

*L*MoO(NCS)₂ (I)

| | | | |
|---|---|---|---|
| Mo—O | 1·671 (5) | O—Mo—N(1) | 99·1 (2) |
| Mo—N(1) | 2·024 (5) | O—Mo—N(11) | 175·8 (3) |
| Mo—N(11) | 2·303 (6) | O—Mo—N(21) | 95·2 (2) |
| Mo—N(21) | 2·119 (4) | N(1)—Mo—N(1)' | 91·4 (3) |
| | | N(1)—Mo—N(11) | 83·7 (2) |
| | | N(1)—Mo—N(21) | 90·0 (2) |
| | | N(1)—Mo—N(21) | 165·2 (2) |
| | | N(11)—Mo—N(21) | 81·8 (2) |
| | | N(21)—Mo—N(21) | 84·9 (2) |
| | | Mo—N(1)—C(1) | 171·0 (5) |

*L*MoO(N₃)₂ (II)

| | | | |
|---|---|---|---|
| Mo—O | 1·668 (8) | N(31)—Mo—O | 91·0 (4) |
| Mo—N(4) | 1·966 (10) | N(31)—Mo—N(11) | 81·9 (3) |
| Mo—N(1) | 2·030 (9) | N(31)—Mo—N(1) | 88·2 (3) |
| Mo—N(11) | 2·315 (9) | N(31)—Mo—N(4) | 168·7 (4) |
| Mo—N(21) | 2·137 (8) | N(31)—Mo—N(21) | 85·1 (3) |
| Mo—N(31) | 2·130 (8) | O—Mo—N(11) | 171·3 (3) |
| N(5)—N(6) | 1·18 (2) | O—Mo—N(1) | 100·9 (4) |
| N(1)—N(2) | 1·171 (12) | O—Mo—N(4) | 100·2 (4) |
| N(2)—N(3) | 1·155 (13) | O—Mo—N(21) | 94·3 (4) |
| N(4)—N(5) | 1·146 (13) | N(11)—Mo—N(1) | 84·1 (3) |
| | | N(11)—Mo—N(4) | 86·8 (4) |
| | | N(11)—Mo—N(21) | 80·0 (3) |
| | | N(1)—Mo—N(4) | 90·7 (4) |
| | | N(1)—Mo—N(21) | 163·5 (4) |
| | | N(4)—Mo—N(21) | 93·0 (4) |
| | | Mo—N(1)—N(2) | 129·3 (8) |
| | | Mo—N(4)—N(5) | 136· (1) |

Enemark, 1985). As expected, the Mo—N(11) distances *trans* to the oxo ligands [2·303 Å (I) and 2·315 Å (II)] are longer than the Mo—N(21) and Mo—N(31) distances *trans* to the N atoms of the NCS⁻ or N₃⁻ ligands [2·119 Å in (I), 2·137 and 2·130 Å in (II)]. The

high thermal parameters of the solvate atoms in (I) may reflect loss of solvent during crystal decay. No evidence of disorder is present in the difference maps.

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# Structure of Tetraaqua-bis[μ-(glycylglycinato)-*NOO'*]-dicopper(II) Bis(diphenyl phosphate) Dihydrate

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**Abstract.** [Cu₂(C₄H₇N₂O₃)₂(H₂O)₄].2[P(C₆H₅O)₂O₂].-2H₂O, $M_r$ = 995·8, orthorhombic, *Pca*2₁, *a* = 16·994 (4), *b* = 5·953 (2), *c* = 41·537 (8) Å, *V* = 4202·1 Å³, *Z* = 4, $D_m$ = 1·57 (1), $D_x$ = 1·57 Mg m⁻³, $\bar{\lambda}$(Cu *K*α) = 1·5418 Å, μ = 2·72 mm⁻¹, *F*(000) = 2056, *T* = 294 K, final *R* = 0·032 for 4132 non-zero reflections. The structure consists of discrete dimeric [Cu₂(C₄H₇N₂O₃)₂(H₂O)₄]²⁺ units, uncoordinated diphenyl phosphate monoanions and water of crystallization.

Within the dimeric complex unit each dipeptide molecule acts as a tridentate ligand through N(amino), O(peptide) and O(carboxyl) atoms. The square-pyramidal environment of each Cu is achieved by two coordinated water molecules, in each case one being in the axial position. There is also evidence of 'semi-coordination' of the second O(carboxylate) atom from an adjacent peptide molecule, at the second axial position of each Cu atom, Cu···O, 2·874 (3) and 2·727 (4) Å. The crystal structure is strongly stabilized by a three-dimensional network of N—H···O and O—H···O hydrogen bonds.

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