

**Structure of  $\mu$ -(Dimethylhydrazido)-bis( $\eta$ -cyclopentadienylidonitrosylmolybdenum),  
[ $\mu$ -NN(CH<sub>3</sub>)<sub>2</sub>{( $\eta$ -C<sub>5</sub>H<sub>5</sub>)Mo(NO)I}]<sub>2</sub>**

BY PAUL R. MALLINSON, GEORGE A. SIM AND DAVID I. WOODHOUSE

*Chemistry Department, University of Glasgow, Glasgow G12 8QQ, Scotland*

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**Abstract.** C<sub>12</sub>H<sub>16</sub>I<sub>2</sub>Mo<sub>2</sub>N<sub>4</sub>O<sub>2</sub>,  $M_r = 694.0$ , monoclinic,  $P2_1/c$ ,  $a = 14.673$  (2),  $b = 7.732$  (1),  $c = 16.867$  (2) Å,  $\beta = 102.30$  (2)°,  $U = 1870$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 2.47$  Mg m<sup>-3</sup>,  $F(000) = 1288$ ,  $\mu(\text{Mo } K\alpha) = 4.66$  mm<sup>-1</sup>. The structure was refined to  $R = 0.053$  with 3850 diffractometer data. The bridging dimethylhydrazido ligand, Me<sub>2</sub>N(4)N(3), is unsymmetrically bound to the ( $\eta$ -C<sub>5</sub>H<sub>5</sub>)Mo(NO)I moieties, with N(3) at 1.907 (5) Å from Mo(1) and 2.070 (6) Å from Mo(2) whereas N(4) is at 3.066 (6) Å from Mo(1) and 2.139 (6) Å from Mo(2).

**Introduction.** The dimeric complexes [( $\eta$ -C<sub>5</sub>H<sub>5</sub>)Mo(NO)X<sub>2</sub>]<sub>2</sub> react with hydrazines R<sup>1</sup>R<sup>2</sup>NNH<sub>2</sub> to produce complexes of composition [( $\eta$ -C<sub>5</sub>H<sub>5</sub>)Mo(NO)X]<sub>2</sub>-(N<sub>2</sub>R<sup>1</sup>R<sup>2</sup>) (Kita, McCleverty, Mann, Seddon, Sim & Woodhouse, 1974). We undertook an X-ray diffraction study of the complex with R<sup>1</sup> = R<sup>2</sup> = CH<sub>3</sub> and X = I in order to define the molecular structure. Mo  $K\alpha$  radiation was employed and intensities for reflections in the range  $\theta < 27^\circ$  were measured by the  $\omega$ -2 $\theta$  step-scan procedure on a Hilger & Watts four-circle diffractometer. 3850 intensity measurements satisfied the criterion  $I > 3\sigma(I)$ .

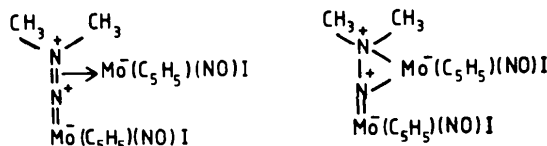
The coordinates of the Mo and I atoms were deduced from a Patterson synthesis and the C, N and O atoms were located in electron-density distributions. After initial least-squares adjustment of the atomic parameters the H atoms of the C<sub>5</sub>H<sub>5</sub> rings were included at ideal positions and the weighting scheme adopted was  $w = (22.8 - 0.8390|F| + 0.0095|F|^2)^{-1}$ . Refinement converged at  $R = 0.053$ ,  $R_w = 0.062$ . Scattering factors and dispersion corrections were taken from *International Tables for X-ray Crystallography* (1962). Calculations were performed with XRAY 70 (Stewart, Kundell & Baldwin, 1970) and a locally developed full-matrix least-squares routine.\*

\* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34881 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates ( $\times 10^5$  for Mo and I,  $\times 10^4$  for C, N and O)

	<i>x</i>	<i>y</i>	<i>z</i>
C(1)	8807 (7)	1766 (12)	3132 (6)
C(2)	9644 (6)	2625 (13)	3474 (6)
C(3)	9874 (6)	3695 (14)	2883 (7)
C(4)	9150 (7)	3586 (15)	2190 (5)
C(5)	8487 (7)	2403 (15)	2345 (6)
C(6)	5132 (7)	1825 (24)	3746 (6)
C(7)	5698 (9)	484 (16)	3617 (9)
C(8)	6238 (8)	1116 (21)	3091 (7)
C(9)	5989 (9)	2800 (21)	2902 (5)
C(10)	5319 (9)	3269 (15)	3308 (7)
C(11)	8274 (6)	5012 (12)	5364 (4)
C(12)	6950 (7)	6604 (12)	4520 (6)
N(1)	9147 (4)	6464 (9)	3883 (4)
N(2)	7616 (4)	1167 (8)	4784 (4)
N(3)	7668 (4)	4247 (8)	3942 (3)
N(4)	7468 (4)	4927 (8)	4655 (3)
O(1)	9657 (5)	7505 (10)	4254 (5)
O(2)	8196 (5)	113 (9)	5059 (5)
Mo(1)	85263 (4)	47786 (8)	32733 (3)
Mo(2)	67224 (4)	25812 (8)	42943 (3)
I(1)	75241 (4)	69906 (9)	21518 (4)
I(2)	60263 (4)	29741 (9)	56848 (3)

**Discussion.** Atomic coordinates, bond lengths and angles, and torsion angles are listed in Tables 1–3 and the molecular structure is illustrated in Fig. 1. The ( $\eta$ -C<sub>5</sub>H<sub>5</sub>)Mo(NO)I moieties are attached in two distinct ways to the bridging hydrazido ligand, with Mo(1) bonded to N(3) and Mo(2) bonded to both N(3) and N(4), and the complex can be formulated as (A) or (B).



(A)

(B)

The geometry of the NNMo(1) unit appears to be profoundly affected by the interaction with Mo(2).

Thus, the N(4)–N(3)–Mo(1) angle is  $136^\circ$  and the Mo(1)–N(3) distance is  $1.907 \text{ \AA}$ , whereas in  $[\{\text{S}_2\text{CN}(\text{CH}_2)_5\}_3\text{MoNN}(\text{EtPh})^+\text{BPh}_4^-]$  the N–N–Mo angle is  $170^\circ$  and the Mo–N distance is  $1.72 \text{ \AA}$  (March, Mason & Thomas, 1975). Moreover the N–N–W angle is  $171^\circ$  in  $[(\text{diphos})_2\text{ClWNNH}_2]^+\text{BPh}_4^-$  (Heath, Mason & Thomas, 1974) and  $174^\circ$  in  $[(\text{diphos})_2\text{BrWNNHMe}]^+\text{Br}^-$  (March, Mason & Thomas, 1975) and the W–N distances are  $1.73$  and  $1.77 \text{ \AA}$ . It can be argued, however, that the Mo(1)–N(3) link must have some double-bond character since it is only  $0.01 \text{ \AA}$  longer than the Cr–NPh<sub>2</sub> distance of  $1.894 \text{ \AA}$  in  $(\eta\text{-C}_5\text{H}_5)\text{Cr}(\text{NO})(\text{NPh}_2)\text{I}$  (Sim, Woodhouse & Knox, 1979); for comparison, the Mo–NO and Cr–NO distances in these complexes differ by  $0.11 \text{ \AA}$ .

The organometallic moieties  $(\eta\text{-C}_5\text{H}_5)\text{Mo}(\text{NO})\text{I}$  adopt different orientations with respect to the  $(\text{CH}_3)_2\text{NN}$  ligand. The Mo(1)–NO bond is approximately in the plane of Mo(1), N(3) and N(4) and the

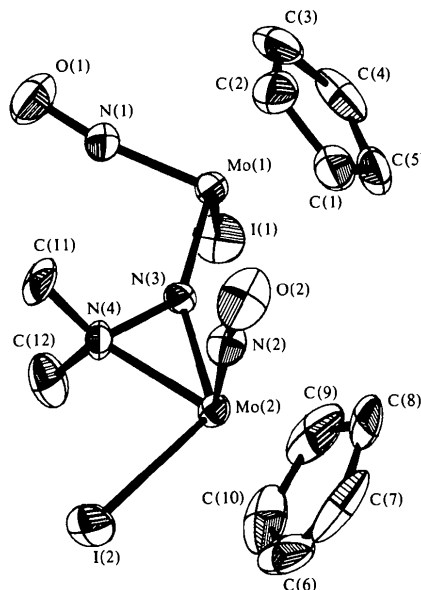


Fig. 1. The molecular structure. The thermal ellipsoids are drawn at the 50% probability level.

Table 2. Bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ )

Mo(1)–I(1)	2.735 (1)	Mo(2)–I(2)	2.767 (1)
Mo(1)–C(1)	2.386 (9)	Mo(2)–C(6)	2.393 (11)
Mo(1)–C(2)	2.311 (9)	Mo(2)–C(7)	2.337 (13)
Mo(1)–C(3)	2.366 (10)	Mo(2)–C(8)	2.300 (13)
Mo(1)–C(4)	2.395 (10)	Mo(2)–C(9)	2.371 (9)
Mo(1)–C(5)	2.407 (11)	Mo(2)–C(10)	2.415 (12)
Mo(1)–N(1)	1.784 (7)	Mo(2)–N(2)	1.771 (6)
Mo(1)–N(3)	1.907 (5)	Mo(2)–N(3)	2.070 (6)
N(4)–C(11)	1.493 (10)	Mo(2)–N(4)	2.139 (6)
N(4)–C(12)	1.496 (11)	N(3)–N(4)	1.399 (8)
N(1)–O(1)	1.184 (10)	N(2)–O(2)	1.198 (10)
C(1)–C(2)	1.408 (13)	C(6)–C(7)	1.374 (20)
C(2)–C(3)	1.390 (14)	C(7)–C(8)	1.397 (18)
C(3)–C(4)	1.404 (14)	C(8)–C(9)	1.372 (22)
C(4)–C(5)	1.400 (15)	C(9)–C(10)	1.362 (17)
C(5)–C(1)	1.400 (14)	C(10)–C(6)	1.398 (20)
N(1)–Mo(1)–I(1)	94.3 (2)	N(2)–Mo(2)–I(2)	92.4 (2)
N(3)–Mo(1)–I(1)	102.6 (2)	N(3)–Mo(2)–I(2)	124.4 (2)
N(1)–Mo(1)–N(3)	97.9 (3)	N(2)–Mo(2)–N(3)	92.5 (3)
C(11)–N(4)–Mo(2)	122.4 (5)	N(2)–Mo(2)–N(4)	96.2 (3)
C(12)–N(4)–Mo(2)	118.6 (5)	N(3)–Mo(2)–N(4)	38.8 (2)
C(11)–N(4)–C(12)	112.0 (6)	N(4)–Mo(2)–I(2)	85.7 (2)
N(3)–N(4)–Mo(2)	67.9 (3)	N(4)–N(3)–Mo(2)	73.3 (3)
N(3)–N(4)–C(11)	115.4 (6)	N(4)–N(3)–Mo(1)	135.5 (5)
N(3)–N(4)–C(12)	112.8 (6)	Mo(2)–N(3)–Mo(1)	150.6 (3)
Mo(1)–N(1)–O(1)	171.5 (6)	Mo(2)–N(2)–O(2)	174.2 (6)
C(2)–C(1)–C(5)	108.0 (8)	C(10)–C(6)–C(7)	109.0 (10)
C(1)–C(2)–C(3)	108.1 (8)	C(6)–C(7)–C(8)	106.3 (12)
C(2)–C(3)–C(4)	107.8 (9)	C(7)–C(8)–C(9)	108.7 (11)
C(3)–C(4)–C(5)	108.4 (9)	C(8)–C(9)–C(10)	108.7 (11)
C(4)–C(5)–C(1)	107.5 (8)	C(9)–C(10)–C(6)	107.3 (12)

Mo–I bond is approximately perpendicular to this plane (Table 3). The situation is reversed for the substituents on Mo(2), with Mo(2)–NO approximately perpendicular to the plane of Mo(2), N(3) and N(4) and Mo(2)–I close to this plane. These orientations maximize the  $\pi$ -bonding of the Mo atoms and can be compared with results for metal–carbene and metal–ethylene complexes. The orientation found for Mo(1) is analogous to that in  $(\eta\text{-C}_5\text{H}_5)(\text{NO})\text{LMo}(\text{C}=\text{CR}_2)$  complexes where the conformation of lowest energy is that in which the NO group is close to the plane of the carbene, *i.e.* the N–Mo–C–R torsion angles are *ca*  $0$  and  $180^\circ$  (Schilling, Hoffmann & Faller, 1979). The orientation around Mo(2) is analogous to that in  $(\eta\text{-C}_5\text{H}_5)(\text{NO})\text{LMo}(\text{R}_2\text{C}=\text{CR}_2)$  complexes, where the preferred conformation has the Mo–NO bond perpendicular to the MoC<sub>2</sub> plane of the complexed ethylene (Schilling, Hoffmann & Faller, 1979).

The Mo–C(cyclopentadienyl) distances range from  $2.300$  to  $2.415 \text{ \AA}$ , mean  $2.368 \text{ \AA}$ , and the longest distance for each ring is situated approximately *trans* to the nitrosyl ligand. A similar effect has been noted in other complexes and probably has its origin in strong metal–nitrosyl  $\pi$ -bonding. The C–C lengths are  $1.372$ – $1.408 \text{ \AA}$ , mean  $1.391 \text{ \AA}$ .

Table 3. Torsional angles ( $^\circ$ ) about N–N and Mo–N(3)

C(11)–N(4)–N(3)–Mo(1)	–56.2 (8)	N(1)–Mo(1)–N(3)–Mo(2)	–161.4 (6)	N(2)–Mo(2)–N(3)–N(4)	–96.8 (4)
C(11)–N(4)–N(3)–Mo(2)	116.5 (5)	N(2)–Mo(2)–N(3)–Mo(1)	72.8 (7)	I(1)–Mo(1)–N(3)–N(4)	–92.0 (6)
C(12)–N(4)–N(3)–Mo(1)	74.3 (8)	I(1)–Mo(1)–N(3)–Mo(2)	102.4 (6)	I(2)–Mo(2)–N(3)–N(4)	–2.1 (4)
C(12)–N(4)–N(3)–Mo(2)	–113.0 (6)	I(2)–Mo(2)–N(3)–Mo(1)	167.4 (5)	N(4)–Mo(2)–N(3)–Mo(1)	169.6 (9)
Mo(2)–N(4)–N(3)–Mo(1)	–172.7 (6)	N(1)–Mo(1)–N(3)–N(4)	4.3 (7)		

Table 4. Comparison of Mo—C distances (Å) with values calculated from the equation

$$l^2 = p^2 + r^2 - 2pr \cos 87^\circ \cos (20 + 72j)^\circ$$

<i>j</i>	<i>l</i> <sub>obs</sub>	<i>l</i> <sub>calc</sub>
0	2.311, 2.300	2.317
1	2.386, 2.371	2.370
2	2.407, 2.415	2.419
3	2.395, 2.393	2.398
4	2.366, 2.337	2.335

The different Mo—C distances for each C<sub>5</sub>H<sub>5</sub> ring can be treated as a tilt of the ring plane so that the line joining the Mo atom to the C<sub>5</sub>H<sub>5</sub> centroid is not perpendicular to the ring. If a metal atom is situated above a planar polygon circumscribed by a circle, the distance *l* from the metal *M* to any point *S* on the circle is given by:

$$l^2 = p^2 + r^2 - 2pr \cos \theta \cos \omega. \quad (1)$$

Here, *p* is the distance from *M* to the ring centre *O*, *r* is the radius of the circle,  $\theta$  is the angle between *OM* and the plane of the circle, and  $\omega$  is the angle *SOR*, *R* being the point on the circumference closest to the metal. If the polygon is regular *r* is simply related to the length of the polygon side and the angles  $\omega$  appropriate to the *n* vertices will be given by  $\omega = \Delta + j2\pi/n$ , *j* = 0...(*n* - 1), where  $\Delta$  will be 0° if the vertex *j* = 0 coincides with *R*. For an isolated ( $\eta$ -C<sub>5</sub>H<sub>5</sub>)Mo(NO) unit with mirror symmetry and longest Mo—C distance *trans* to NO  $\Delta$  is 36° but when the metal atom is attached to other atoms in an unsymmetrical pattern  $\Delta$  is expected to depart from this value. In the present case,  $\Delta$  is *ca* 20° and  $\theta$  *ca* 87°. For ring C(1...5) *p* is

2.053 and *r* is 1.191 Å, while for ring C(6...10) *p* is 2.051 and *r* is 1.174 Å; the mean values are *p* = 2.052 and *r* = 1.183 Å and with these values (1) reproduces the experimental Mo—C distances with a r.m.s. deviation of 0.013 Å (Table 4). The parameters *p*, *r*,  $\theta$  and  $\Delta$  may be of utility for the comparison of metal-cyclopentadienyl systems. Finally, we observe that a notable spread of Mo—C distances in a ( $\eta$ -C<sub>5</sub>H<sub>5</sub>)Mo system is associated with even a small tilt of the ring, values of  $l_{\max} - l_{\min}$  for various values of  $\theta$  being

$\theta$	90	89	88	87	86	85°
$l_{\max} - l_{\min}$	0.00	0.03	0.07	0.10	0.13	0.16 Å.

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## (1,5-Diazacyclooctane)dinitratocopper(II)

BY PETER MURRAY-RUST, JUDITH MURRAY-RUST AND ROBERT CLAY

*Department of Chemistry, University of Stirling, Stirling FK9 4LA, Scotland*

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**Abstract.** C<sub>6</sub>H<sub>14</sub>CuN<sub>4</sub>O<sub>6</sub>, [Cu(C<sub>6</sub>H<sub>14</sub>N<sub>2</sub>)(NO<sub>3</sub>)<sub>2</sub>], *M<sub>r</sub>* = 301.75, monoclinic, *P*2<sub>1</sub>/*c*, *a* = 8.56 (2), *b* = 10.39 (5), *c* = 13.38 (5) Å,  $\beta$  = 78.52 (3)°, from diffractometer measurements (Mo *K* $\alpha$  radiation). *V* = 1167.8 Å<sup>3</sup>, *Z* = 4, *D<sub>m</sub>* = 1.73, *D<sub>c</sub>* = 1.72 Mg m<sup>-3</sup>, *F*(000) = 592,  $\mu$  = 1.752 mm<sup>-1</sup>. The ligand adopts a boat-chair conformation.

**Introduction.** Systematic absences (from precession photographs) *h*0*l*, *l* odd and 0*k*0, *k* odd indicated space

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group *P*2<sub>1</sub>/*c*. Data were collected for *h*0–10*l* with  $\theta_{\max}$  = 27.5° on a Stoe STADI-2 two-circle diffractometer (graphite-monochromated Mo *K* $\alpha$  radiation). This gave 2136 data of which 1711 unique reflexions with *I* > 3 $\sigma$ (*I*) were used in subsequent calculations. Lorentz and polarization corrections (but none for extinction or absorption) were applied, and the data scaled by a Wilson plot. The structure was solved by direct methods with *SHELX* 76 (Sheldrick, 1976), which was used for all calculations. Complex neutral scattering © 1980 International Union of Crystallography