

Intramolecular π – π stacking and bromine interactions in (2,2′-bipyridine- κ^2N,N')-dibromo-*cis*-bis[1,1-diphenylhydrazido(2–)]-molybdenum(VI)

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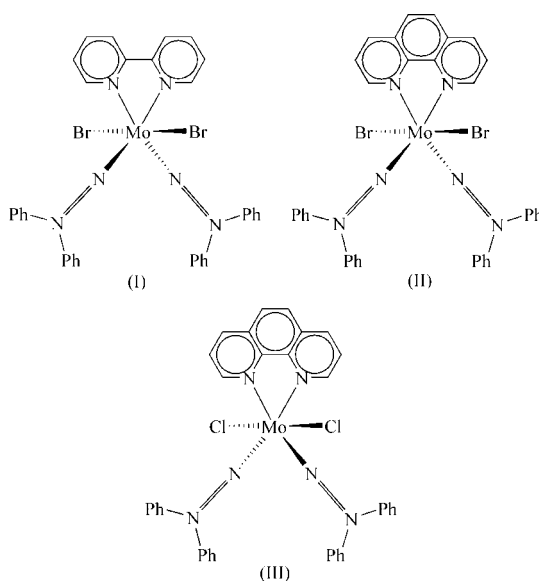
Key indicators

Single-crystal X-ray study
 $T = 298$ K
Mean $\sigma(\text{C}-\text{C}) = 0.008$ Å
 R factor = 0.042
 wR factor = 0.100
Data-to-parameter ratio = 16.6

Molecules of the title compound, $[\text{Mo}(\text{C}_{12}\text{H}_{10}\text{N}_2)_2\text{Br}_2(\text{C}_{10}\text{H}_8\text{N}_2)]$, are linked *via* several weak $\text{C}-\text{H}\cdots\text{Br}$ interactions. The crystal structure shows similar unit cell parameters and packing scheme to two analogous previously reported structures. All three structures exhibit an intramolecular aromatic π – π interaction.

Comment

We have previously studied molybdenum complexes containing both organohydrazido(1–), NHNPhR , and organohydrazido(2–), NNPhR , in the same inner coordination sphere of the Mo centre, of the formula $[\text{Mo}(\text{NHNPh}_2)(\text{NNPh}_2)(\text{acac})X_2]$ (where acac is acetylacetonate, R is Me or Ph and X is Cl, Br or I) (Bustos *et al.*, 1994a). We have also studied the chemical reactivity they exhibit towards tertiary phosphines, such as $\text{PPh}_{3-x}\text{Me}_x$ ($x = 0, 1, 2$) and bis-diphenylphosphinoethane (dppe; Bustos *et al.*, 1994b), and organonitrogen ligands, such as 2,2′-bipyridine (bpy), *o*-phenanthroline (*o*-phen; Manzur *et al.*, 1997; Bustos *et al.*, 2002), tris-pyrazolylborate (Tp) and 3,5-dimethylpyrazolylborate (Tp*; Manzur *et al.*, 1998). These have proved to be suitable starting materials for obtaining several complexes containing the *cis*- $[\text{MoO}(\text{NNPhR})]$ or *cis*- $[\text{Mo}(\text{NNPhR})_2]$ systems (Bustos *et al.*, 1994b; Manzur *et al.*, 1997, 1998). We report here the crystal structure of the title compound, (I), whose analytical and spectroscopic characterization have been reported in a previous article (Bustos *et al.*, 2002).



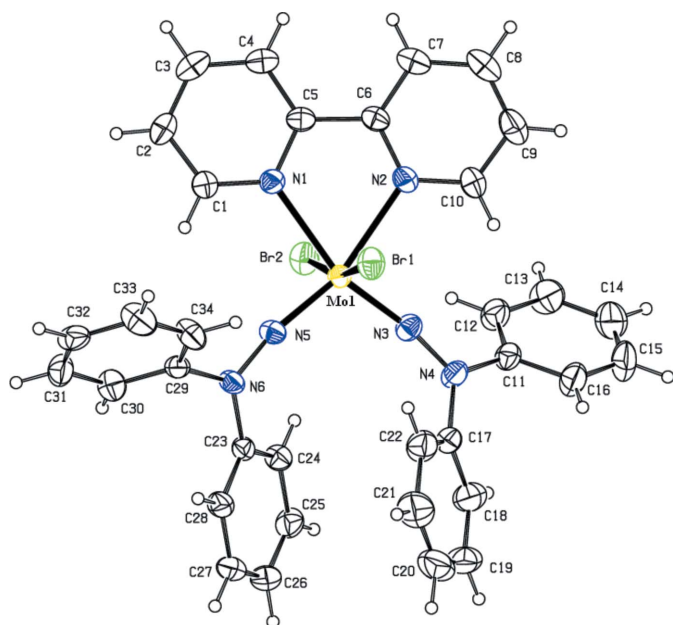


Figure 1

The molecular structure of the title compound, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 40% probability level.

The molecular structure of (I) is shown in Fig. 1. The three compounds (I), (II) (Bustos *et al.*, 2002) and (III) (Manzur *et al.*, 1997) are equivalent in topology, *i.e.* each one crystallizes in space group $P\bar{1}$, and they have similar unit cell parameters, packing schemes and interactions.

In compound (I), the dihedral angle between the mean planes formed by the two pyridine rings is $12.2(2)^\circ$, while that between the mean planes of the C29–C34 and C23–C28 rings is $67.2(2)^\circ$ and that between the mean planes of the C11–C16 and C17–C22 rings is $67.2(2)^\circ$. An intramolecular π – π interaction is also observed between the slipped phenyl rings C17–C22 and C23–C28, with a centroid-to-centroid distance of $3.751(3) \text{ \AA}$. The wide N3–Mo1–N5 angle [$106.63(15)^\circ$] can most probably be ascribed to repulsions between the two diphenylhydrazido(2–) ligands.

The geometry of the three complexes about the Mo atom is distorted octahedral (Table 1), with the Br (Cl) ligands occupying mutually *trans* positions and inclined toward the five-membered Mo1/N2/C6/C5/N1 ring [$\text{Br1–Mo1–Br2 } 166.50(2)^\circ$].

There are no conventional intermolecular hydrogen bonds in (I) and the supramolecular structure is constructed mainly by weak C–H...Br interactions [C–H...Cl for (III)] (Desiraju & Steiner, 1999; Jones & Lozano, 2004). For the sake of clarity, the supramolecular structure of (I) is described as a combination of three chains forming a three-dimensional structure: firstly, a chain along [001] formed by the C15–H15...Br1ⁱ and C2–H2...Br2ⁱⁱ contacts (Fig. 2); secondly, a chain along [110] formed by the C33–H33...Br2ⁱⁱⁱ contact (Fig. 3); and thirdly, a chain along [100] formed by the C19–H19...Br1^{iv} contact (Fig. 4) (symmetry codes as in Table 2). An identical packing scheme is observed in compounds (II) and (III).

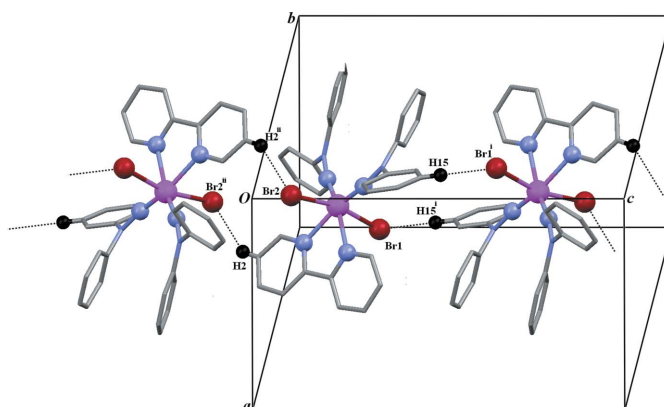


Figure 2

Part of the crystal structure of (I), showing the formation of a chain along the [001] direction. H atoms not involved in interactions (dotted lines) have been omitted. [Symmetry codes: (i) $-x, -y, 1-z$; (ii) $-x, -y, -z$.]

Experimental

Both complexes, *i.e.* both the precursor $[\text{Mo}(\text{NHNPh}_2)(\text{NNPh}_2)(\text{acac})\text{Br}_2]$ and $[\text{Mo}(\text{NNPh}_2\text{Br}_2)(\text{bpy})]$, (I), were obtained as described in the respective literature (Bustos *et al.*, 1994a, 2002). Single crystals suitable for X-ray analysis were obtained by diffusion of diethyl ether into a solution containing (I) (25 mg) in chloroform (8 ml). After 2 d, the crystalline product was filtered off, washed with diethyl ether and dried under vacuum.

Crystal data

$[\text{Mo}(\text{C}_{12}\text{H}_{10}\text{N}_2)_2\text{Br}_2(\text{C}_{10}\text{H}_8\text{N}_2)]$
 $M_r = 776.36$
 Triclinic, $P\bar{1}$
 $a = 9.7449(11) \text{ \AA}$
 $b = 10.6706(12) \text{ \AA}$
 $c = 17.883(2) \text{ \AA}$
 $\alpha = 96.731(2)^\circ$
 $\beta = 98.989(2)^\circ$
 $\gamma = 117.028(2)^\circ$

$V = 1598.2(3) \text{ \AA}^3$
 $Z = 2$
 $D_x = 1.613 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 $\mu = 2.94 \text{ mm}^{-1}$
 $T = 298 \text{ K}$
 Polyhedron, red
 $0.38 \times 0.28 \times 0.12 \text{ mm}$

Data collection

Bruker SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan [SADABS (Sheldrick, 1996) in SAINT (Bruker, 2000)]
 $T_{\min} = 0.383$, $T_{\max} = 0.702$

12970 measured reflections
 6449 independent reflections
 4921 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.026$
 $\theta_{\max} = 26.4^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.042$
 $wR(F^2) = 0.100$
 $S = 0.99$
 6449 reflections
 388 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0517P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.63 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.31 \text{ e \AA}^{-3}$

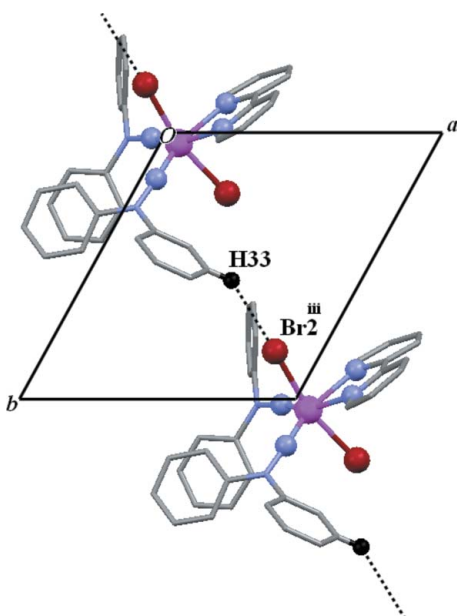


Figure 3
Part of the crystal structure of (I), showing the formation (dotted lines) of a chain along the [110] direction. [Symmetry code: (iii) $1 + x, 1 + y, z$.]

Table 1
Selected geometric parameters (\AA , $^\circ$).

Mo1—Br1	2.5950 (7)	Mo1—N3	1.760 (3)
Mo1—Br2	2.5906 (6)	Mo1—N5	1.767 (3)
Mo1—N1	2.300 (3)	N3—N4	1.323 (5)
Mo1—N2	2.307 (4)	N5—N6	1.312 (4)
Br1—Mo1—Br2	166.50 (2)	Br2—Mo1—N3	91.99 (10)
Br1—Mo1—N1	87.98 (8)	Br2—Mo1—N5	96.97 (10)
Br1—Mo1—N2	79.40 (8)	N1—Mo1—N2	69.91 (12)
Br1—Mo1—N3	97.03 (10)	N3—Mo1—N5	106.63 (15)
Br1—Mo1—N5	90.07 (10)	Mo1—N3—N4	170.9 (3)
Br2—Mo1—N1	80.18 (8)	N3—N4—C11	118.6 (3)
Br2—Mo1—N2	90.37 (8)	Mo1—N5—N6	169.6 (3)

Table 2
Hydrogen-bond geometry (\AA , $^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C15—H15 \cdots Br1 ⁱ	0.93	2.88	3.799 (6)	171
C2—H2 \cdots Br2 ⁱⁱ	0.93	2.95	3.770 (5)	147
C33—H33 \cdots Br2 ⁱⁱⁱ	0.93	3.06	3.765 (5)	134
C19—H19 \cdots Br1 ^{iv}	0.93	3.03	3.646 (8)	126

Symmetry codes: (i) $-x, -y, -z + 1$; (ii) $-x, -y, -z$; (iii) $x + 1, y + 1, z$; (iv) $x - 1, y, z$.

H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with $C-H = 0.93 \text{ \AA}$ and $U_{\text{iso}}(H) = 1.2 U_{\text{eq}}(C)$.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL/PC* (Sheldrick, 1994); software used to prepare material for publication: *PLATON* (Spek, 2003) and *Mercury* (Macrae *et al.*, 2006).

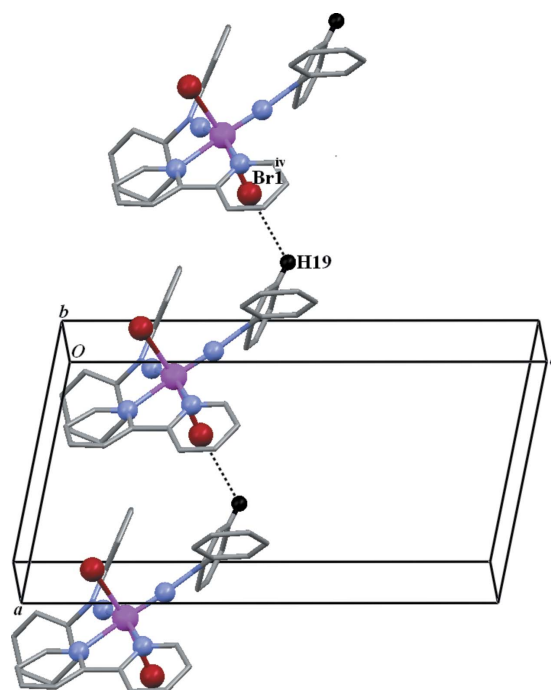


Figure 4
Part of the crystal structure of (I), showing the formation (dotted lines) of a chain along the [100] direction. [Symmetry code: (iv) $-1 + x, y, z$.]

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