

Data collection

Siemens R3m diffractometer
 ω scans
 Absorption correction:
 ψ scan (North *et al.*,
 1968)
 $T_{\min} = 0.52$, $T_{\max} = 0.64$
 2722 measured reflections
 2628 independent reflections
 2236 reflections with
 $I > 2\sigma(I)$

$R_{\text{int}} = 0.021$
 $\theta_{\max} = 27.54^\circ$
 $h = 0 \rightarrow 18$
 $k = 0 \rightarrow 14$
 $l = -18 \rightarrow 17$
 2 standard reflections
 every 120 reflections
 intensity decay: 1.0%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.035$
 $wR(F^2) = 0.091$
 $S = 1.07$
 2625 reflections
 152 parameters
 H atoms riding
 $w = 1/[\sigma^2(F_o^2) + (0.0416P)^2 + 2.9507P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.33 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.42 \text{ e } \text{Å}^{-3}$
 Extinction correction: none
 Scattering factors from
*International Tables for
 Crystallography* (Vol. C)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)

$$U_{\text{eq}} = (1/3)\sum_i\sum_j U^{ij}a'_i a'_j a'_k$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Ni1	0	0.22794 (3)	1/4	0.02252 (12)
N1	0	0.4198 (2)	1/4	0.0277 (5)
N2	0	1.0395 (2)	1/4	0.0292 (6)
C1	0.0709 (2)	0.4813 (2)	0.2948 (2)	0.0292 (5)
C2	0.0735 (2)	0.6016 (2)	0.2968 (2)	0.0298 (5)
C3	0	0.6650 (2)	1/4	0.0256 (6)
C4	0	0.7944 (2)	1/4	0.0267 (6)
C5	-0.0828 (2)	0.8575 (2)	0.2369 (2)	0.0313 (5)
C6	-0.0794 (2)	0.9782 (2)	0.2358 (2)	0.0321 (5)
N3	0.13429 (14)	0.2369 (2)	0.19467 (14)	0.0319 (4)
N4	-0.06264 (14)	0.2286 (2)	0.10513 (13)	0.0317 (4)
C7	0.1539 (2)	0.1753 (2)	0.1048 (2)	0.0422 (6)
C8	0.0814 (2)	0.2036 (3)	0.0214 (2)	0.0487 (7)
C9	-0.0168 (2)	0.1595 (2)	0.0323 (2)	0.0432 (6)
Cl1	0.30158 (4)	-0.05766 (5)	-0.06716 (4)	0.0389 (2)
O1	0.2729 (2)	-0.1459 (2)	-0.1360 (2)	0.0670 (6)
O2	0.40058 (15)	-0.0623 (2)	-0.0436 (2)	0.0651 (6)
O3	0.2552 (2)	-0.0769 (3)	0.0175 (2)	0.0799 (8)
O4	0.2762 (2)	0.0530 (2)	-0.1075 (2)	0.0861 (9)

Table 2. Selected geometric parameters (Å , $^\circ$)

Ni1—N4	2.131 (2)	Ni1—N2 ⁱ	2.165 (3)
Ni1—N3	2.145 (2)	Ni1—N1	2.205 (3)
N4—Ni1—N3	88.39 (8)	C1—N1—Ni1	121.76 (13)
N4 ⁱⁱ —Ni1—N3	91.59 (8)	C6—N2—Ni1 ⁱⁱⁱ	121.78 (13)
N4—Ni1—N1	89.79 (5)	C7—N3—Ni1	121.8 (2)
N3—Ni1—N1	87.24 (5)	C9—N4—Ni1	118.0 (2)

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

Data collection: *SHELXTL-Plus* (Sheldrick, 1990). Cell refinement: *SHELXTL-Plus*. Data reduction: *SHELXTL-Plus*. Program(s) used to solve structure: *SHELXTL-Plus*. Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEP-3* (Farrugia, 1997). Software used to prepare material for publication: *SHELXL93*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1408). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). **C55**, 182–186

Tricarbonyl[1,1,1-tris(dimethylphosphinomethyl)ethane]chromium(0), -molybdenum(0) and -tungsten(0) complexes

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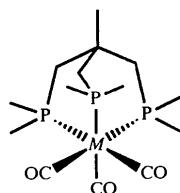
Abstract

The structures of chromium(0)–, molybdenum(0)– and tungsten(0)–tricarbonyl complexes containing the tripodal tridentate phosphine ligand 1,1,1-tris(dimethyl-

phosphinomethyl)ethane (tdmme) (systematic name: {2-[(dimethylphosphino)methyl]-2-methyl-1,3-propanediyl}bis(dimethylphosphine)), were determined by X-ray diffraction studies. The $M-C$ ($M = Cr, Mo$ and W) bond lengths in the complexes, $[M(C_{11}H_{27}P_3)(CO)_3]$, are noticeably shorter than those in the corresponding hexacarbonyl complexes owing to the *trans* influence of tdmme being weaker than that of CO. The Mo—P bond lengths in the tdmme complex are slightly shorter than those in the analogous 1,1,1-tris(diphenylphosphino)methyl)ethane and 1,5,9-tris(isopropyl)-1,5,9-triphosphacyclododecane complexes, indicating the smaller steric requirement of tdmme.

Comment

Although a large number of group 6 metal carbonyls containing phosphine ligands have been characterized by X-ray diffraction, a limited number of systematic studies are reported for direct comparison of the structures with the triad metal carbonyls containing the same phosphines. For example, only one series of $[M(CO)_3(P)_3]$ -type ($M = Cr, Mo$ and W) complexes has been reported for dinuclear hexacarbonyl complexes with hexadentate phosphine, $[\{M(CO)_3\}_2\{\mu-(Et_2PCH_2CH_2)_2PCH_2P(CH_2CH_2PEt_2)_2\}]$ (Saum *et al.*, 1988). We report here the X-ray structure analyses of the chromium(0), (I), molybdenum(0), (II), and tungsten(0), (III), tricarbonyls containing $MeC(CH_2PMe_2)_3$ (tdmme), and make a comparison of their $M-C$ and $M-P$ bond lengths with those of the related hexacarbonyl and tricarbonyl complexes.



- (I) $M = Cr$
 (II) $M = Mo$
 (III) $M = W$

The chromium complex, (I), crystallizes in the monoclinic space group $P2_1/c$ with $Z = 8$; two crystallographically independent molecules (complex molecules 1 and 2) are present in the asymmetric unit. The structures of the two molecules are essentially similar to each other, but the twist angles of the three arms of tripodal phosphine are slightly different. The molybdenum, (II), and the tungsten, (III), complexes are isomorphous and crystallize in the monoclinic space group $P2_1/n$ with $Z = 4$. The molecular structures of these three metal carbonyls are comparable to each other, as shown in Figs. 1, 2 and 3.

The average $M-C$ bond lengths in complexes (I), (II) and (III) are 1.828, 1.976 and 1.975 Å, respectively. These bond lengths are comparable to those in the above-mentioned dinuclear complexes, $[\{M(CO)_3\}_2\{\mu-(Et_2PCH_2CH_2)_2PCH_2P(CH_2CH_2PEt_2)_2\}]$, but are noticeably shorter than those in the corresponding hexacarbonyl complexes: 1.910 Å in $[Cr(CO)_6]$ (Whitaker & Jeffery, 1967), 2.059 Å in $[Mo(CO)_6]$ (Mak, 1984) and 2.027 Å in $[W(CO)_6]$ (Heinemann *et al.*, 1992). These differences in $M-C$ bond lengths result from the weaker *trans* influence of tdmme compared with CO. Interestingly, the extent of $M-C$ bond shortening in the triad metal series is not in a periodical order: 0.082 for Cr, 0.083 for Mo and 0.052 Å for W. A similar non-periodical order of *trans* influence among the d^6 triad metal ions is observed for *fac*- $[M'(NH_2CH_2CH_2PMe_2)_3]^{3+}$ ($M' = Co^{III}, Rh^{III}$ and Ir^{III}) complexes (Suzuki *et al.*, 1994). Since the Mo—C and W—C bond lengths in complexes (II) and (III) are almost equal to each other, this non-periodical order of the *trans* influence of CO is mainly caused by $[W(CO)_6]$ having weaker π back donation than $[Mo(CO)_6]$.

Comparison of Mo—P bond lengths in complex (II) (average 2.483(1) Å) with those in the related

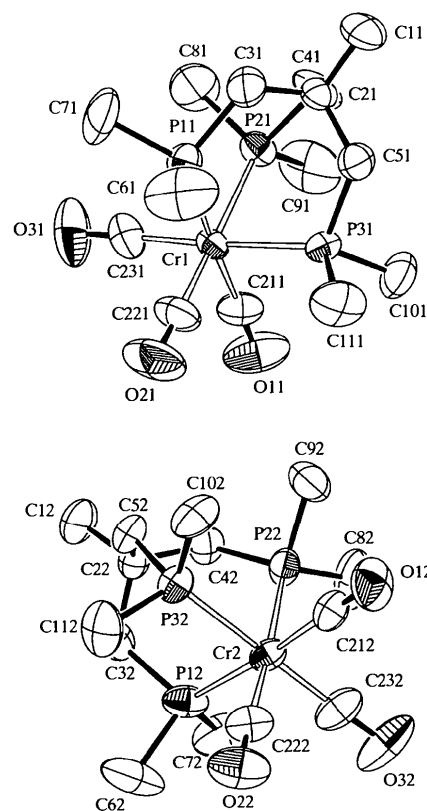


Fig. 1. The molecular structures of the two crystallographically independent chromium complex molecules, (I), showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

fac-[Mo(CO)₃(P)₃]-type complexes reveals the steric effect of phosphines on the elongation of Mo—P bonds. The corresponding molybdenum tricarbonyls of MeC(CH₂PPh₂)₃, which is the diphenylphosphino analogue of tdmme (Walter *et al.*, 1993), and of 1,5,9-tris(isopropyl)-1,5,9-triphosphacyclododecane (Coles *et al.*, 1995) give slightly longer Mo—P bonds (2.516 and 2.527 Å, respectively), while that of 1,5,9-triphosphacyclododecane (Diel *et al.*, 1989) shows slightly shorter Mo—P bonds (2.476 Å). These differences in bond lengths are rather small, but clearly illustrate the steric requirement of the tridentate phosphines: *cyclo*-(PHCH₂CH₂CH₂)₃ < MeC(CH₂PMe₂)₃ < MeC(CH₂PPh₂)₃ < *cyclo*-(PⁱPrCH₂CH₂CH₂)₃.

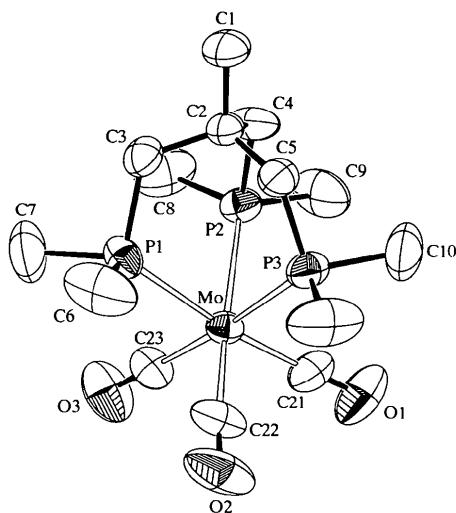


Fig. 2. The molecular structure of the molybdenum complex, (II), showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

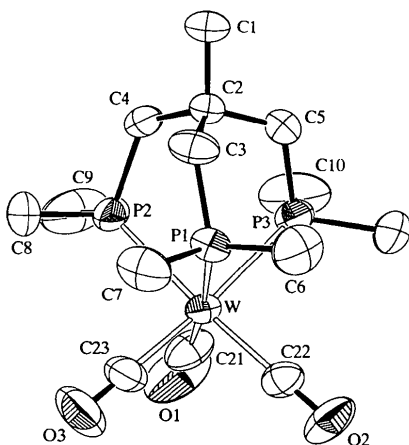


Fig. 3. The molecular structure of the tungsten complex, (III), showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

Experimental

The title complexes were prepared by reaction of [M(CO)₆] (*M* = Cr, Mo, W) and tdmme (molar ratio 1:1) in mesitylene at 413 K for 24 h, and recrystallized from a mixture of CH₂Cl₂ and MeOH.

Compound (I)

Crystal data

[Cr(C₁₁H₂₇P₃)(CO)₃]

M_r = 388.28

Monoclinic

*P*2₁/*c*

a = 15.684 (3) Å

b = 16.170 (3) Å

c = 17.222 (3) Å

β = 116.75 (1)°

V = 3900 (1) Å³

Z = 8

D_x = 1.322 Mg m⁻³

D_m not measured

Mo *K*α radiation

λ = 0.7107 Å

Cell parameters from 25

reflections

θ = 10.19–14.02°

μ = 0.838 mm⁻¹

T = 296.2 K

Prism

0.30 × 0.20 × 0.20 mm

Colorless

Data collection

Rigaku AFC-7R diffractometer

ω-2θ scans

Absorption correction:

ψ scan (North *et al.*, 1968)

T_{min} = 0.780, *T_{max}* = 0.846

11 758 measured reflections

11 384 independent

reflections

6367 reflections with

I > 2σ(*I*)

R_{int} = 0.026

θ_{max} = 30°

h = 0 → 22

k = 0 → 22

l = -24 → 21

3 standard reflections

every 150 reflections

intensity decay: 0.12%

Refinement

Refinement on *F*²

R = 0.057

wR = 0.060

S = 1.53

6367 reflections

379 parameters

H atoms not refined

w = 1/[σ²(*F_o*)

+ 0.00010|*F_o*|²]

(Δ/σ)_{max} = 0.001

Δρ_{max} = 0.46 e Å⁻³

Δρ_{min} = -0.41 e Å⁻³

Extinction correction: none

Scattering factors from

International Tables for Crystallography (Vol. C)

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

Cr1—P11	2.333 (1)	Cr2—C212	1.839 (5)
Cr1—P21	2.328 (1)	Cr2—C222	1.833 (4)
Cr1—P31	2.345 (1)	Cr2—C232	1.825 (5)
Cr1—C211	1.821 (4)	O11—C211	1.166 (5)
Cr1—C221	1.818 (5)	O12—C212	1.156 (5)
Cr1—C231	1.829 (5)	O21—C221	1.165 (5)
Cr2—P12	2.336 (1)	O22—C222	1.162 (5)
Cr2—P22	2.335 (1)	O31—C231	1.157 (5)
Cr2—P32	2.335 (1)	O32—C232	1.168 (5)
P11—Cr1—P21	86.23 (4)	P22—Cr2—P32	85.18 (4)
P11—Cr1—P31	84.51 (4)	P22—Cr2—C222	176.6 (2)
P11—Cr1—C211	176.2 (2)	P32—Cr2—C232	177.1 (1)
P21—Cr1—P31	85.24 (4)	C212—Cr2—C222	91.7 (2)
P21—Cr1—C221	175.8 (2)	C212—Cr2—C232	90.2 (2)
P31—Cr1—C231	176.3 (2)	C222—Cr2—C232	89.3 (2)
C211—Cr1—C221	89.9 (2)	Cr1—C211—O11	177.8 (4)
C211—Cr1—C231	90.4 (2)	Cr2—C212—O12	178.4 (4)
C221—Cr1—C231	90.0 (2)	Cr1—C221—O21	178.4 (5)

P12—Cr2—P22	84.95 (4)	Cr2—C222—O22	178.5 (4)
P12—Cr2—P32	85.45 (5)	Cr1—C231—O31	178.3 (5)
P12—Cr2—C212	175.3 (1)	Cr2—C232—O32	177.7 (4)
Cr1—P11—C31—C21	-16.9 (4)	P11—C31—C21—C11	-171.0 (3)
Cr1—P21—C41—C21	-15.3 (5)	P21—C41—C21—C11	-170.9 (4)
Cr1—P31—C51—C21	-13.6 (4)	P31—C51—C21—C11	-171.1 (3)
Cr2—P12—C32—C22	23.3 (4)	P12—C32—C22—C12	166.5 (3)
Cr2—P22—C42—C22	25.2 (4)	P22—C42—C22—C12	164.6 (3)
Cr2—P32—C52—C22	23.1 (4)	P32—C52—C22—C12	167.0 (3)

Compound (II)*Crystal data*[Mo(C₁₁H₂₇P₃)(CO)₃] $M_r = 432.23$

Monoclinic

 $P2_1/n$ $a = 8.601 (2) \text{ \AA}$ $b = 16.324 (4) \text{ \AA}$ $c = 14.422 (2) \text{ \AA}$ $\beta = 96.59 (2)^\circ$ $V = 2011.4 (7) \text{ \AA}^3$ $Z = 4$ $D_x = 1.427 \text{ Mg m}^{-3}$ D_m not measured*Data collection*

Rigaku AFC-5R diffractometer

 ω -2 θ scans

Absorption correction:

 ψ scan (North *et al.*, 1968) $T_{\min} = 0.662$, $T_{\max} = 0.712$

6204 measured reflections

5854 independent reflections

*Refinement*Refinement on F $R = 0.041$ $wR = 0.050$ $S = 1.75$

4492 reflections

190 parameters

H atoms not refined

 $w = 1/[\sigma^2(F_o) + 0.00010|F_o|^2]$ Table 2. Selected geometric parameters (\AA , $^\circ$) for (II)

Mo—P1	2.494 (1)	Mo—C23	1.973 (4)
Mo—P2	2.4747 (9)	O1—C21	1.144 (5)
Mo—P3	2.480 (1)	O2—C22	1.149 (5)
Mo—C21	1.981 (4)	O3—C23	1.160 (4)
Mo—C22	1.973 (4)		
P1—Mo—P2	82.82 (3)	C21—Mo—C22	90.1 (2)
P1—Mo—P3	83.02 (3)	C21—Mo—C23	91.6 (2)
P1—Mo—C21	173.2 (1)	C22—Mo—C23	91.4 (2)
P2—Mo—P3	83.60 (3)	Mo—C21—O1	178.5 (4)
P2—Mo—C22	173.1 (1)	Mo—C22—O2	176.0 (5)
P3—Mo—C23	175.1 (1)	Mo—C23—O3	179.0 (3)
Mo—P1—C3—C2	-19.3 (3)	P1—C3—C2—C1	-168.8 (3)
Mo—P2—C4—C2	-22.4 (4)	P2—C4—C2—C1	-166.6 (3)
Mo—P3—C5—C2	-22.2 (4)	P3—C5—C2—C1	-165.7 (3)

Compound (III)*Crystal data*[W(C₁₁H₂₇P₃)(CO)₃] $M_r = 520.14$

Monoclinic

 $P2_1/n$ $a = 8.566 (1) \text{ \AA}$ $b = 16.281 (2) \text{ \AA}$ $c = 14.410 (2) \text{ \AA}$ $\beta = 96.77 (1)^\circ$ $V = 1995.5 (4) \text{ \AA}^3$ $Z = 4$ $D_x = 1.731 \text{ Mg m}^{-3}$ D_m not measured*Data collection*

Rigaku AFC-5R diffractometer

 ω -2 θ scans

Absorption correction:

by integration (Coppens *et al.*, 1965) $T_{\min} = 0.155$, $T_{\max} = 0.326$

6158 measured reflections

5808 independent reflections

*Refinement*Refinement on F $R = 0.027$ $wR = 0.035$ $S = 1.38$

4703 reflections

190 parameters

H atoms not refined

 $w = 1/[\sigma^2(F_o) + 0.000225|F_o|^2]$ Mo $K\alpha$ radiation $\lambda = 0.7107 \text{ \AA}$

Cell parameters from 25

reflections

 $\theta = 14.9$ – 15.0° $\mu = 6.041 \text{ mm}^{-1}$ $T = 296.2 \text{ K}$

Prismatic

 $0.48 \times 0.36 \times 0.22 \text{ mm}$

Colorless

4703 reflections with

 $I > 2\sigma(I)$ $R_{\text{int}} = 0.032$ $\theta_{\text{max}} = 30^\circ$ $h = 0 \rightarrow 12$ $k = -22 \rightarrow 0$ $l = -20 \rightarrow 20$

3 standard reflections

every 150 reflections

intensity decay: -0.24%

Table 3. Selected geometric parameters (\AA , $^\circ$) for (III)

W—P1	2.475 (1)	W—C23	1.969 (5)
W—P2	2.477 (1)	O1—C21	1.153 (6)
W—P3	2.490 (1)	O2—C22	1.151 (5)
W—C21	1.977 (5)	O3—C23	1.153 (6)
W—C22	1.979 (4)		
P1—W—P2	83.53 (4)	C21—W—C22	92.0 (2)
P1—W—P3	82.88 (4)	C21—W—C23	90.0 (2)
P1—W—C21	172.6 (1)	C22—W—C23	91.5 (2)
P2—W—P3	83.01 (4)	W—C21—O1	176.9 (5)
P2—W—C22	175.4 (1)	W—C22—O2	178.5 (4)
P3—W—C23	173.1 (2)	W—C23—O3	178.2 (5)
W—P1—C3—C2	-23.6 (4)	P1—C3—C2—C1	-166.6 (3)
W—P2—C4—C2	-24.0 (4)	P2—C4—C2—C1	-164.3 (3)
W—P3—C5—C2	-20.5 (4)	P3—C5—C2—C1	-167.7 (3)

For all compounds, data collection: *Rigaku/AFC Diffractometer Control Software* (Rigaku Co. Ltd, 1985); cell refinement: *Rigaku/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1995); program(s) used to solve structures: *SHELXS86* (Sheldrick, 1985); program(s) used to refine structures: *TEXSAN*; molecular graphics: *ORTEP* (Johnson, 1970) in *TEXSAN*; software used to prepare material for publication: *TEXSAN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OA1069). Services for accessing these data are described at the back of the journal.

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Aquabis(2,2'-bipyridine-*N,N'*)(perchlorato-*O*)manganese(II) perchlorate

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Abstract

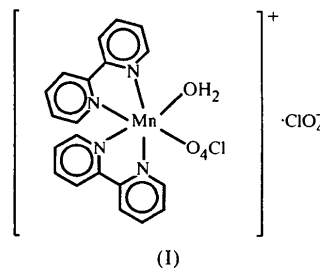
The crystal structure of the title compound, [Mn(ClO₄)(C₁₀H₈N₂)₂(H₂O)]ClO₄, contains monomeric [Mn(bipy)₂(ClO₄)(H₂O)]⁺ cations (bipy is 2,2'-bipyridine) in which

the Mn^{II} ion is surrounded by a pair of chelating bipy ligands [Mn—N 2.222 (5)–2.228 (5) Å], an aqua ligand [Mn—O 2.142 (4) Å] and a perchlorate ligand [Mn—O 2.289 (5) Å] in a distorted octahedral arrangement. Adjacent cations are linked into dimers by pairs of O···O hydrogen bonds [O···O 2.795 (7) Å].

Comment

Manganese complexes have attracted considerable interest recently because of the frequent occurrence of such metal centres in biological systems (Wieghardt, 1989). The complexation behaviour of 2,2'-bipyridine (bipy) or bipy-related ligands with Mn ions gives rise to a wide variety of coordination complexes, depending on the nature of the bipy ligand, the oxidation state of the Mn ion and the nature of the other coordinating ligands. Mn^{II} complexes with bipy-type ligands are well known: there are over 100 structures of this type in the Cambridge Structural Database (Allen & Kennard, 1993).

The crystal structure of the title compound, (I), consists of discrete [Mn(bipy)₂(ClO₄)(H₂O)]⁺ cations and perchlorate anions. As illustrated in Fig. 1, the Mn^{II} ion in each cation is in a distorted octahedral environment, coordinated by a pair of *cis*-related chelating bipy ligands, one aqua ligand and one O atom of the ClO₄[−] ligand.



The bipyridine groups exhibit their usual acute N···N bite distance [N1···N2 2.670 (7) and N3···N4 2.652 (7) Å] and N—Mn—N angles [N1—Mn1—N2 73.75 (18) and N3—Mn1—N4 73.16 (17)°]. The values are very close to those found in [Mn(bipy)₂Cl₂] (Lumme & Lindell, 1988), [Mn(bipy)₂(NCS)₂] (Veidis *et al.*, 1981) and [MnCl(bipy)₂(H₂O)] (Chen *et al.*, 1995), in which pairs of bipy ligands are also *cis* related, but are markedly different from those of some other [M(bipy)₂L₂]ⁿ⁺ species, in which the two bipy ligands are *trans* related.

Both bipy molecules are nearly planar; the largest deviation from either mean plane is 0.131 (7) Å. The mean planes of the two bipy molecules are inclined at 97.77 (11)° with respect to one another. The aromatic bond distances of both bipy molecules are normal, within the range 1.324 (8)–1.353 (6) Å for aromatic N—C bonds and 1.343 (9)–1.389 (7) Å for aromatic