Journal of Organometallic Chemistry, 461 (1993) 117–125

JOM 23739

Synthesis, characterization and crystal structures of $[Mo(CO)_4]_2$TPTA and $[W(CO)_4]_2$TPTA (TPTA = 1,4,8,11-tetrakis-(methyldiphenylphosphino)-1,4,8,11-tetraazacyclotetradecane)

Dubravka Matković-Čalogović

Laboratory of General and Inorganic Chemistry, Faculty of Science, University of Zagreb, Zvonimirova 8, 41000 Zagreb (Croatia)

Henrika Meider and Pavica Planinić

Department of Physical Chemistry, Rudjer Bošković Institute, Bijenička 54, 41000 Zagreb (Croatia)

(Received March 25, 1993)

Abstract

1,4,8,11-Tetrakis(methyldiphenylphosphino)-1,4,8,11-tetraazacyclotetradecane (TPTA) reacts with molybdenum(0) and tungsten(0) hexacarbonyls to give yellow crystalline diamagnetic complexes of the formula $[M(CO)_4]_2$TPTA. Each metal atom in these binuclear species is coordinated by two phosphorus atoms from the pendant methyldiphenylphosphino groups and by four carbonyls in a *cis* octahedral arrangement.

1. Introduction

Ligands capable of simultaneous binding to several metal ions are of interest because of their potential use in coordinating two different metal ions or identical metal ions in different oxidation states. In this way heterometallic complexes and mixed-valence complexes can be prepared, of particular significance in biologically important systems and in catalysis. Derivatives of polyamine macrocyclic ligands bearing functionalized side chains belong to the mentioned class of ligands wherein the pendant groups may provide additional ligating sites.

Such a derivative of 1,4,8,11-tetraazacyclotetradecane (cyclam, TA) with two pairs of $-CH_2P(C_6H_5)_2$ groups on N_1, N_4 and N_8, N_{11} atoms on the opposite sides of the TA ring, namely 1,4,8,11-tetrakis(methyldiphenylphosphino)-1,4,8,11-tetraazacyclotetradecane (TPTA), is a very interesting, potentially octadentate ligand. It was prepared for the first time nine years ago [1] by a relatively smooth procedure but no information is available concerning its ability for complex formation. A good reason for this is surely the high sensitivity of the ligand towards many solvents and media.

In spite of the continuously increasing number of reports on polyamine macrocyclic ligands, data concerning their metal carbonyl complexes are very limited. A molybdenum tricarbonyl complex with 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane [2] and a chromium complex of the same type with TA were reported only recently [3]. Cyclic triamines such as 1,4,7-triazacyclononane or 1,5,9-triazacyclododecane also give the *fac*-$M(CO)_3$ complexes (M = Cr, Mo, W) [4].

Our interest in metal carbonyl chemistry [5,6] and in studying the ability for complex formation of polydentate ligands led us to investigate the reaction between molybdenum and tungsten hexacarbonyls and the above-mentioned 1,4,8,11-tetrakis(methyldiphenylphosphino)-1,4,8,11-tetraazacyclotetradecane [7]. We now report the synthesis, spectral and structural characterization of two binuclear complexes with TPTA, the first containing this interesting ligand.

2. Results and discussion

2.1. Preparation and properties

By allowing TPTA to react with $Mo(CO)_6$ and $W(CO)_6$ under gentle reflux in dry deoxygenated alcohols and with a ligand to metal ratio of 1:2, we were

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Correspondence to: Dr. P. Planinić.

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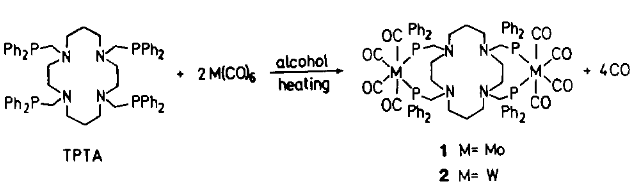


Scheme 1.

able to isolate yellow crystalline solids of the composition $[Mo(CO)_4]_2$TPTA (1) and $[W(CO)_4]_2$TPTA (2) formed according to the equation shown in Scheme 1.

The molybdenum complex was formed in good yield in refluxing ethanol. Reaction of tungsten carbonyl, however, required a higher temperature, and in order to avoid the problem of sublimation the reaction was carried out in n-butanol in a sealed tube. In general, the purest crystalline solids were obtained by carrying out the reaction in a sealed tube under argon.

The solubility of the tungsten complex in n-butanol is about ten times that of the molybdenum analogue; for this reason different concentrations of the reaction components had to be used in the preparation of the two compounds. Crystals suitable for X-ray diffraction studies were obtained from more dilute solutions.

Compounds **1** and **2** are moderately air-stable but can be kept under dry argon for months. The solubility of both complexes is poor except in CH_2Cl_2, and they slowly decompose in most solvents except aliphatic alcohols. Conductivity measurements show the complexes to be non-electrolytes, and magnetic susceptibility measurements show them to be diamagnetic.

2.2. IR spectra

Selected infrared spectral data for the ligand and complexes are given in Table 1. The presence of four absorption bands in the ν(CO) region indicates a C_{2v} symmetry around the metal atoms and *cis* disubstituted tetracarbonyl complexes. The spectra showed an identical pattern for the two complexes with the ν(CO) bands shifted slightly to higher values in the molybdenum complex, suggesting that there is a lower electron density on molybdenum than on tungsten. The frequencies of the CO stretching vibrations (~ 2015–1880 cm^{-1}) are in agreement with those found for the corresponding complexes containing phosphorus rather than nitrogen donor ligands.

The spectra of the complexes show a noticeable change from that for the free ligand in the region associated with the C–H vibrations of $:N(CH_2\text{–})_3$ groups. In place of a very characteristic pattern consisting of three sharp bands at 2800, 2770 and 2735 cm^{-1}, the spectra of both complexes exhibit just one absorption band, at 2792 cm^{-1}. This is explained by an increase of the P–C bond order upon complexation through phosphorus, which also causes a change in the $N(CH_2\text{–})_3$ moiety.

2.3. X-ray structures of complexes 1 and 2

The structures of complexes **1** and **2** were determined by single crystal X-ray diffraction studies. The ORTEP [8] drawing of the complex **1** is shown in Fig. 1 and PLUTON [9] drawing of **2** is shown in Fig. 2. Selected bond distances and angles for both complexes are listed in Tables 2 and 3. Because of the poor quality of the data for **2** only the overall geometries are considered, and the distances and angles are not discussed.

Compounds **1** and **2** have similar molecular structures, which involve two metal atoms (molybdenum in

TABLE 1. Selected IR spectral data (cm^{-1}) [a] for the TPTA ligand and for complexes 1 and 2

TPTA	1	2	Assignments
3070w	3050w	3055w	ν(C–H) aromatic
2950m	3000–2850vw	3000–2850vw	ν(C–H) aliphatic
2800m, sp	2792m	2792m	vibr. assoc. with $:N(CH_2\text{–})_3$
2770m, sp			
2735m, sp			
1960w	2012s, sp	2010s, sp	overtone and combination bands; ν(CO) [b]
1880w	1912vs	1908vs	
1810w	1900vs	1890vs	
1760w	1879vs	1877vs	
1435vs	1435s	1435s	P–C(phenyl) vibr.
747, 740s	748, 740s	750, 740s	C–H out of plane bending and ring bending
695vs	694vs	694vs	(of monosubst. benzene)
	618m	609m	δ(M–CO)
	587s	583s	
	488, 417m	490, 420m	ν(M–C)
	389m	391m	

[a] KBr pellets. [b] ν(CO) for CH_2Cl_2 solutions: 2024m, sp; 1917vs; 1882s (1); 2018m, sp; 1903vs; 1876s (2).

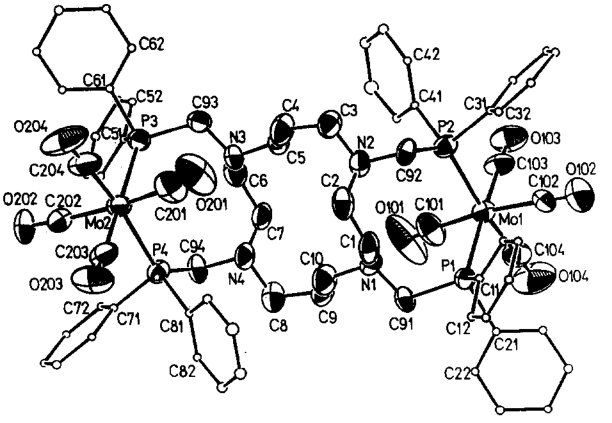


Fig. 1. ORTEP drawing of complex **1** with the atom-numbering scheme. Hydrogen atoms are omitted for clarity.

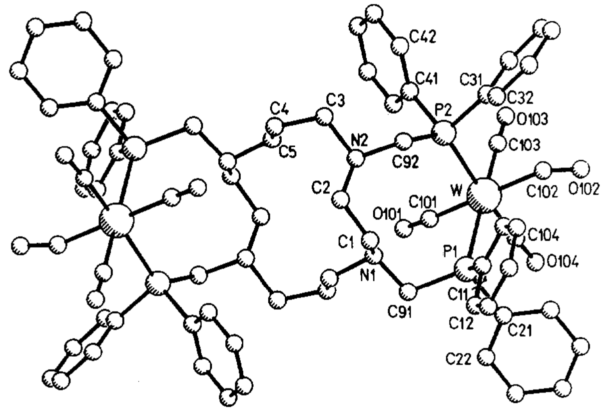


Fig. 2. PLUTON drawing of complex **2** with the atom-numbering scheme. Hydrogen atoms are omitted for clarity.

1 and tungsten in **2**) each coordinated by four carbonyl groups and two phosphorus atoms from the methyldiphenylphosphino groups of the TPTA ligand to form a distorted octahedron. The macrocycle is bound to the metal in the *cis* manner. Molecule of complex **2** has a crystallographically-imposed centre of symmetry whereas the molecule of complex **1** has no element of symmetry, as confirmed by the MISSYM program [10].

The difference in the structures of the free TPTA ligand and the Mo and W complexes can be seen in Fig. 3. The metal complexes differ very little from each other, but the methyldiphenylphosphino groups have quite different configurations in the free TPTA molecule from those in the complexes. The Mo–P (and W–P) bond in the metal complexes is achieved by closer approach of the phosphorus atoms and rotation of the phenyl groups away from the metal atom. The distances Mo–P are in the range 2.540(4) to 2.588(4) Å, as in *cis*-$Mo(CO)_4(PPh_3)_2$ and *cis*-$Mo(CO)_4(PCH_3Ph_2)_2$ [11]. In the nine-membered chelate rings in **1** the P–Mo–P angles of 99.3(1)° and 99.5(1)° represent the greatest deviation from the octahedral geometry in this complex. These values are similar to those in the

TABLE 2. Selected bond lengths (Å) with e.s.d.'s in parentheses for **1** and **2**

Mo1–P1	2.540(4)	Mo2–P3	2.543(4)	W–P1	2.59(1)
Mo1–P2	2.588(4)	Mo2–P4	2.579(4)	W–P2	2.56(1)
Mo1–C101	1.99(2)	Mo2–C201	2.02(2)	W–C101	2.00(4)
Mo1–C102	2.02(2)	Mo2–C202	2.02(2)	W–C102	2.01(4)
Mo1–C103	1.93(1)	Mo2–C203	1.99(2)	W–C103	1.98(4)
Mo1–C104	1.98(2)	Mo2–C204	1.95(2)	W–C104	1.92(4)
O101–C101	1.15(3)	O201–C201	1.13(3)	C101–O101	1.17(5)
O102–C102	1.13(2)	O202–C202	1.15(2)	C102–O102	1.17(5)
O103–C103	1.17(2)	O203–C203	1.16(2)	O103–C103	1.12(5)
O104–C104	1.14(3)	O204–C204	1.19(3)	O104–C104	1.22(6)
P1–C91	1.86(2)	P3–C93	1.84(2)	P1–C91	1.81(4)
P1–C11	1.86(1)	P3–C51	1.84(1)	P1–C11	1.91(2)
P1–C21	1.84(1)	P3–C61	1.84(1)	P1–C21	1.77(2)
P2–C92	1.86(2)	P4–C94	1.87(2)	P2–C92	1.87(4)
P2–C31	1.84(1)	P4–C71	1.83(1)	P2–C31	1.82(2)
P2–C41	1.83(1)	P4–C81	1.85(1)	P2–C41	1.81(2)
N1–C1	1.48(2)	N3–C5	1.48(2)	N1–C1	1.45(5)
N1–C10	1.49(2)	N3–C6	1.46(3)	N1–C5 [i]	1.52(5)
N1–C91	1.45(2)	N3–C93	1.47(2)	N1–C91	1.46(5)
C1–C2	1.51(2)	C6–C7	1.52(2)	C1–C2	1.48(4)
C2–N2	1.47(2)	C7–N4	1.48(2)	C2–N2	1.47(4)
N2–C3	1.48(2)	N4–C8	1.49(2)	N2–C3	1.54(5)
N2–C92	1.46(2)	N4–C94	1.47(2)	N2–C92	1.51(5)
C3–C4	1.50(2)	C8–C9	1.53(2)	C3–C4	1.52(5)
C4–C5	1.47(3)	C9–C10	1.55(3)	C4–C5	1.54(6)

[i] Symmetry code: (i) $-x$, $-y$, $1-z$.

ten-membered $Mo_2P_4C_4$ ring in $[Mo_2(CO)_8(\mu$-*trans*-$Ph_2PCH{=}CHPPh_2)_2]$ [12]. With a decrease in the chelate ring size the P–Mo–P angles become smaller. The chelate bite angle is 91.65(4)° in the seven-membered chelate ring in [1,4-bis(diphenylphosphino)-butane]tetracarbonylmolybdenum(0) and 89.74(4)° in the six-membered ring in [1,3-bis(diphenylphosphino) propane]tetracarbonyl-molybdenum(0) [13]. In the *meso* and *rac* isomers of [1,2-diphenyl-1,2-bis(diphenylphosphino)ethane]tetracarbonylmolybdenum(0) [14] five-membered rings are formed with P–Mo–P angles of 80.5(2) and 79.8(1)°. When the ring has more than ten members there is not necessarily a further increase in the value of the bite angle. In the fourteen-membered ring in *cis*-$Mo(CO)_4[Ph_2P(CH_2CH_2O)_3$-$CH_2CH_2PPh_2]$ an angle of 93.78(2)° was obtained [15]. Another deviation from octahedral geometry is caused by bending of the carbonyl groups that are *trans* to each other away from the ligand, with C–Mo–C angles of 169.7(8) and 168.4(8)°. A similar distortion was found in other complexes [14]. All the *cis* C–Mo–C angles are acute (in the range 82.2(9) to 89.5(7)°), which is a

TABLE 3. Selected bond angles (°) with e.s.d.'s in parentheses for **1** and **2**

P1–Mo1–P2	99.3(1)	P3–Mo2–P4	99.5(1)	P1–W–P2	101.1(4)
C101–Mo1–P1	88.3(5)	C201–Mo2–P3	89.0(5)	C101–W–P1	82(1)
C101–Mo1–P2	97.8(7)	C201–Mo2–P4	99.9(7)	C101–W–P2	98(1)
C101–Mo1–C102	169.7(8)	C201–Mo2–C202	168.4(8)	C101–W–C102	172(2)
C101–Mo1–C103	89.5(7)	C201–Mo2–C203	85.5(7)	C101–W–C103	95(2)
C101–Mo1–C104	83.5(8)	C201–Mo2–C204	82.2(9)	C101–W–C104	83(2)
C102–Mo1–P1	92.5(5)	C202–Mo2–P3	95.1(5)	C102–W–P1	104(1)
C102–Mo1–P2	92.2(5)	C202–Mo2–P4	90.2(5)	C102–W–P2	87(1)
C102–Mo1–C103	88.9(7)	C202–Mo2–C203	89.5(7)	C102–W–C103	80(2)
C102–Mo1–C104	86.3(7)	C202–Mo2–C204	87.1(8)	C102–W–C104	92(2)
C103–Mo1–P1	174.9(4)	C203–Mo2–P3	173.1(5)	C103–W–P1	174(1)
C103–Mo1–P2	85.5(4)	C203–Mo2–P4	85.5(5)	C103–W–P2	84(1)
C103–Mo1–C104	85.9(6)	C203–Mo2–C204	86.1(7)	C103–W–C104	90(2)
C104–Mo1–P1	89.3(5)	C204–Mo2–P3	89.0(5)	C104–W–P1	84(1)
C104–Mo1–P2	171.3(5)	C204–Mo2–P4	171.2(5)	C104–W–P2	175(1)
Mo1–C101–O101	166.4(17)	Mo2–C201–O201	172.2(20)	W–C101–O101	164(3)
Mo1–C102–O102	174.6(15)	Mo2–C202–O202	175.9(16)	W–C102–O102	161(4)
Mo1–C103–O103	175.9(13)	Mo2–C203–O203	173.6(16)	W–C103–O103	175(4)
Mo1–C104–O104	175.3(16)	Mo2–C204–O204	175.4(15)	W–C104–O104	174(3)
Mo1–P1–C11	121.9(3)	Mo2–P3–C51	122.3(4)	W–P1–C11	116(1)
Mo1–P1–C21	113.1(4)	Mo2–P3–C61	112.5(4)	W–P1–C21	112(1)
Mo1–P1–C91	115.0(5)	Mo2–P3–C93	115.5(5)	W–P1–C91	117(1)
C11–P1–C21	96.2(5)	C51–P3–C61	97.3(5)	C11–P1–C21	96(1)
C91–P1–C21	100.6(6)	C93–P3–C51	105.5(6)	C91–P1–C21	107(2)
C91–P1–C11	106.7(6)	C93–P3–C61	100.3(6)	C91–P1–C11	107(1)
Mo1–P2–C31	108.6(3)	Mo2–P4–C71	107.9(3)	W–P2–C31	110(1)
Mo1–P2–C41	115.2(4)	Mo2–P4–C81	115.4(4)	W–P2–C41	116(1)
Mo1–P2–C92	127.4(5)	Mo2–P4–C94	129.2(6)	W–P2–C92	128(1)
C31–P2–C41	101.4(5)	C71–P4–C81	100.5(5)	C31–P2–C41	102(1)
C92–P2–C31	99.6(6)	C94–P4–C71	99.1(6)	C92–P2–C31	99(1)
C92–P2–C41	100.9(6)	C94–P4–C81	100.4(6)	C92–P2–C41	98(1)
C10–N1–C91	112.2(12)	C5–N3–C93	111.1(11)	C5 [i]–N1–C91	103(3)
C1–N1–C91	110.8(11)	C6–N3–C93	109.4(12)	C1–N1–C91	114(3)
C1–N1–C10	108.0(12)	C5–N3–C6	112.1(12)	C1–N1–C5[i]	111(3)
N1–C1–C2	114.9(13)	N3–C6–C7	113.8(14)	N1–C1–C2	116(3)
C1–C2–N2	116.0(13)	C6–C7–N4	114.5(13)	C1–C2–N2	113(3)
C2–N2–C92	111.4(11)	C7–N4–C94	113.7(12)	C2–N2–C92	113(3)
C2–N2–C3	109.7(12)	C7–N4–C8	111.6(12)	C2–N2–C3	113(3)
C3–N2–C92	109.1(12)	C8–N4–C94	107.6(12)	C3–N2–C92	105(3)
N2–C3–C4	114.0(13)	N4–C8–C9	114.2(14)	N2–C3–C4	112(3)
C3–C4–C5	115.7(13)	C8–C9–C10	109.7(13)	C3–C4–C5	112(3)
C4–C5–N3	116.4(13)	C9–C10–N1	110.5(12)	C4–C5–N1[i]	116(3)
P1–C91–N1	114.3(10)	P3–C93–N3	115.9(10)	P1–C91–N1	112(3)
P2–C92–N2	113.2(10)	P4–C94–N4	114.3(11)	P2–C92–N2	114(2)

[i] Symmetry code: (i) $-x$, $-y$, $1-z$.

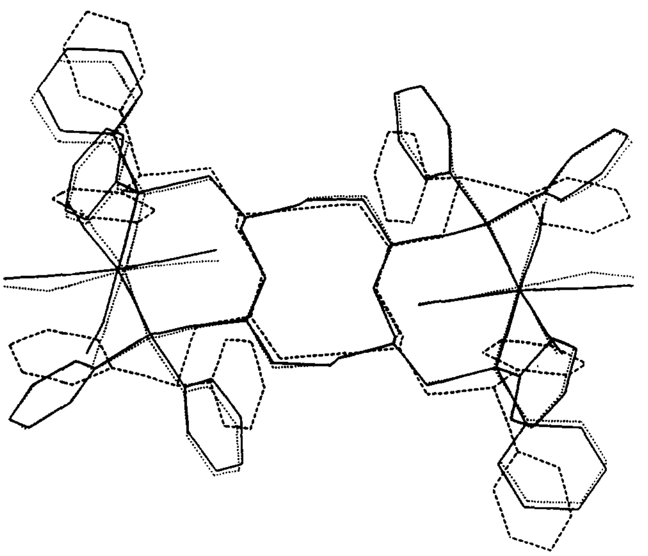
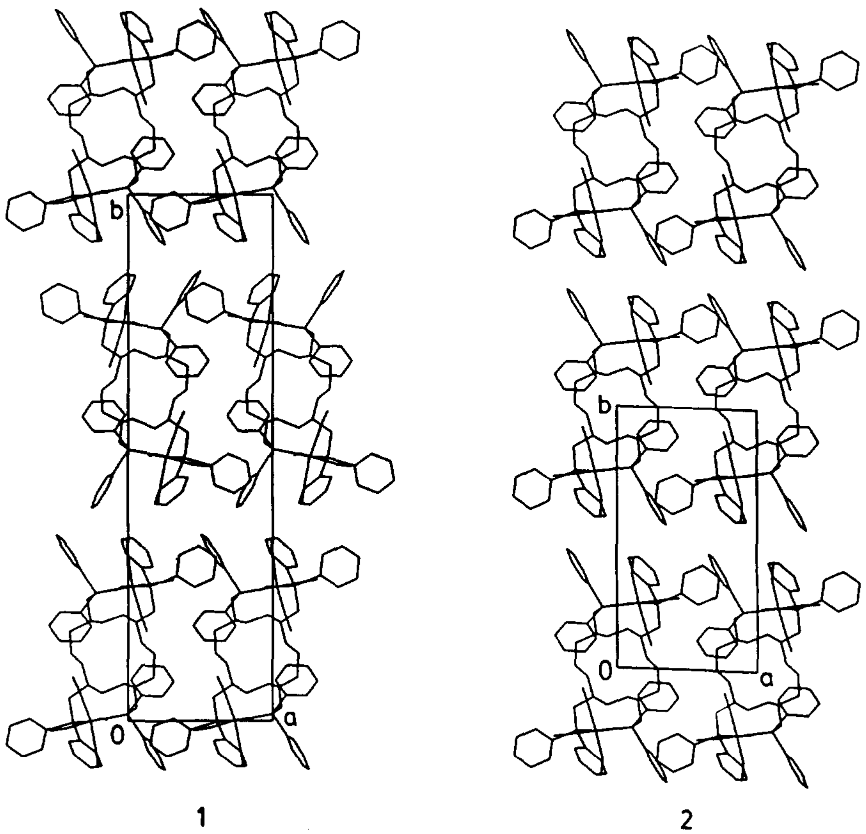


Fig. 3. Overlapping plot obtained by superimposing molecules of TPTA (dashed lines), complex 1 (full lines) and complex 2 (dotted lines). Four nitrogen atoms were used as fitting atoms.

consequence of the large values of the P–Mo–P angles and the deviation of the *trans* C–Mo–C linkage from collinearity.

The carbonyl groups *trans* to phosphorus atoms have shorter Mo–C and longer C–O bond lengths (mean values 1.96(1) and 1.17(1) Å, respectively) than those that are mutually *trans* (mean values 2.01(1) and 1.14(1) Å, respectively). Shortening of the Mo–C bonds *trans* to phosphorus is observed in many structures, and is consistent with the weaker π acidity of the ligand in comparison with that of the carbonyl group, which results in a greater degree of π-back bonding. Although there is a difference between the mean values of the two sets of C–O bonds it is not significant in this complex. All the Mo–C–O angles deviate from linearity, with values ranging from 166(2) to 176(2)°.

No bond lengths and angles within the TPTA ligand in complex 1 differ significantly from the corresponding ones in the free TPTA. The conformation of the macrocyclic ring is very similar, with differences in torsion angles of at most 13°. The greatest difference is in the values of torsion angles involving methyldiphenylphosphino groups. The size of the cavity inside the macrocyclic ring and the positions of nitrogen atoms in the present conformation are not favourable for incorporation of another metal atom. The hypothetical atom inside the ring would be 2.14 Å from C5 and C10 and 2.63 Å from the four nitrogen atoms.



1 2

Fig. 4. Packing diagram of complexes 1 and 2. The structures are projected down the *c*-axis.

The difference between the crystal packings of the two complexes can be seen in Fig. 4. The unit cell of **1** is approximately twice the size of that of **2**. There are only van der Waals contacts between the molecules in both complexes.

3. Experimental details

3.1. Materials

The ligand, 1,4,8,11-tetrakis(methyldiphenylphosphino)-1,4,8,11-tetraazacyclotetradecane (TPTA) was prepared by the established procedure [1]. Metal hexacarbonyls obtained from commercial sources were resublimed prior to use. Solvents were purified and dried by standard methods and freshly distilled under argon before use.

3.2. Physical measurements

The IR spectra on dichloromethane solutions and KBr pellets were recorded in the region 4000–200 cm^{-1} on a Perkin-Elmer Model 580B spectrophotometer. Conductivity measurements were carried out at room temperature on 10^{-3} M nitrobenzene solutions, with a Tacussel conductivity bridge, type Cd 7. Magnetic susceptibility measurements were performed at 22°C by the Gouy method with $CuSO_4 \cdot 5H_2O$ for calibration. The complexes were diamagnetic.

3.3. Preparation of complexes 1 and 2

The binuclear complexes $[M(CO)_4]_2$TPTA (M = Mo, W) were obtained in two ways, (a) by heating molybdenum or tungsten hexacarbonyls with TPTA in a molar ratio of approximately 2:1 under reflux in the appropriate solvent (ethanol or n-butanol) and (b) by carrying out the reaction in n-butanol in a sealed tube. $[Mo(CO)_4]_2$TPTA was prepared in good yield by both procedures, whereas $[W(CO)_4]_2$TPTA was isolated in a pure form only when a sealed tube was used.

3.3.1. [Mo(CO)$_4$]$_2$TPTA (1)

Procedure a). Ethanol (30 cm^3) was added to a mixture of 0.264 g (1 mmol) of $Mo(CO)_6$ and 0.447 g (0.45 mmol) of TPTA. The mixture was stirred at room temperature for 0.5 h and then refluxed for 5 h, under a stream of dry argon. The pale-yellow crystalline product that separated was filtered off from the warm solution (40°C), washed with a small quantity of dry ethanol, and dried *in vacuo*. The yield was 0.336 g

TABLE 4. Crystal data, data collection parameters and refinement details for 1 and 2

	1	**2**
Empirical formula	$Mo_2C_{70}H_{68}N_4O_8P_4$	$W_2C_{70}H_{68}N_4O_8P_4$
Formula weight	1409.1	1584.9
Crystal system	monoclinic	triclinic
Space group	$P2_1$	$P\bar{1}$
a (Å)	10.044(2)	10.112(5)
b (Å)	34.861(6)	17.780(9)
c (Å)	10.043(3)	9.892(5)
α (°)		97.10(2)
β (°)	109.66(2)	109.38(2)
γ (°)		90.07(2)
V (Å^3)	3312(1)	1663(1)
Z	2	1
D_{calc} (g cm^{-3})	1.413	1.582
F(000)	1448	788
Crystal size (mm from centroid)	(100), (−100) 0.064; (−101), (10−1) 0.096; (001), (00−1) 0.103; (010), (0−10) 0.034	approx. (100) 0.11; (−100) 0.09; (0−10) 0.31; (10−1) 0.13; (001) 0.14
μ (cm^{-1})	45.5	36.8
Min., max. transmission coefficients	0.541, 0.757	1.393, 2.096
Range of collected data (°)	$3 < \theta < 63$	$2 < \theta < 27$
Scan type	$\omega - 2\theta$	$\omega - 2\theta$
No. of unique reflections	3327	2840
$n(I > n\sigma(I))$	2.0	4.0
No. of parameters refined	466	135
$R = \Sigma \lVert F_o \rvert - \lvert F_c \rVert / \Sigma \lvert F_o \rvert$	0.048	0.106
$R_w = [\Sigma w(F_o - F_c)^2 / \Sigma w(F_o)^2]^{1/2}$	0.069	0.134
Weighting scheme	$w = 0.9263/(\sigma^2(F) + 0.00313F^2)$	1.0
Largest final shift/esd	0.007	0.005

TABLE 5. Positional parameters and equivalent isotropic thermal parameters (from Mo1 to C94) and isotropic thermal parameters (from C11 to C86) ($Å^2$), with e.s.d.'s in parentheses for **1**

TABLE 5 (*continued*)

	x	y	z	U_{eq} [a] or U_{iso}
Mo1	0.0290(1)	0.2555(1)	0.3549(1)	0.0451(4) [a]
Mo2	−0.2624(1)	0	0.8137(1)	0.0472(4) [a]
P1	0.1534(3)	0.2580(1)	0.6207(4)	0.044(1) [a]
P2	−0.2270(4)	0.2435(1)	0.3497(4)	0.045(1) [a]
P3	−0.3856(3)	−0.0018(1)	0.5474(4)	0.046(1) [a]
P4	−0.0070(4)	0.0130(1)	0.8220(4)	0.046(1) [a]
O101	0.1345(23)	0.1720(4)	0.3428(15)	0.150(10) [a]
O102	−0.0115(17)	0.3452(4)	0.3263(16)	0.111(8) [a]
O103	−0.0888(11)	0.2508(4)	0.0277(12)	0.086(6) [a]
O104	0.3166(14)	0.2691(6)	0.3065(17)	0.129(9) [a]
O201	−0.3812(18)	0.0833(4)	0.8200(17)	0.125(8) [a]
O202	−0.2067(16)	−0.0895(3)	0.8446(16)	0.095(6) [a]
O203	−0.1446(13)	0.0045(5)	1.1451(12)	0.098(6) [a]
O204	−0.5494(14)	−0.0176(5)	0.8619(16)	0.123(9) [a]
C101	0.0886(22)	0.2010(6)	0.3595(17)	0.077(9) [a]
C102	0.0001(16)	0.3130(5)	0.3418(17)	0.062(7) [a]
C103	−0.0495(13)	0.2528(6)	0.1510(15)	0.058(6) [a]
C104	0.2122(17)	0.2656(5)	0.3274(16)	0.063(7) [a]
C201	−0.3309(23)	0.0545(6)	0.8148(17)	0.079(9) [a]
C202	−0.2217(17)	−0.0569(6)	0.8333(17)	0.064(7) [a]
C203	−0.1856(14)	0.0051(5)	1.0230(18)	0.061(6) [a]
C204	−0.4428(18)	−0.0117(6)	0.8381(17)	0.081(8) [a]
N1	0.0563(13)	0.1871(3)	0.6790(13)	0.053(5) [a]
N2	−0.2662(13)	0.1908(3)	0.5432(13)	0.054(6) [a]
N3	−0.2797(13)	0.0687(3)	0.4905(13)	0.053(5) [a]
N4	0.0391(13)	0.0649(3)	0.6274(14)	0.054(5) [a]
C1	−0.0418(18)	0.2029(4)	0.7475(17)	0.057(6) [a]
C2	−0.1890(17)	0.1864(4)	0.6948(17)	0.059(7) [a]
C3	−0.4062(15)	0.1720(4)	0.5067(20)	0.062(7) [a]
C4	−0.3992(18)	0.1293(4)	0.5230(21)	0.073(7) [a]
C5	−0.3160(16)	0.1092(4)	0.4495(15)	0.053(6) [a]
C6	−0.1854(18)	0.0525(5)	0.4218(19)	0.065(7) [a]
C7	−0.0369(15)	0.0695(4)	0.4736(19)	0.061(7) [a]
C8	0.1808(17)	0.0835(4)	0.6714(19)	0.063(7) [a]
C9	0.1765(17)	0.1269(4)	0.6453(20)	0.064(7) [a]
C10	0.0892(18)	0.1467(4)	0.7274(20)	0.067(7) [a]
C91	0.1824(16)	0.2105(4)	0.7109(18)	0.057(6) [a]
C92	−0.2864(16)	0.2313(4)	0.5028(15)	0.048(5) [a]
C93	−0.4077(15)	0.0449(4)	0.4576(17)	0.056(6) [a]
C94	0.0598(18)	0.0247(4)	0.6740(17)	0.054(6) [a]
C11	0.0967(9)	0.2915(2)	0.7355(9)	0.045(3)
C12	0.1713(9)	0.2937(2)	0.8801(9)	0.054(4)
C13	0.1340(9)	0.3210(2)	0.9628(9)	0.072(5)
C14	0.0220(9)	0.3461(2)	0.9008(8)	0.073(5)
C15	−0.0527(9)	0.3439(2)	0.7561(9)	0.070(5)
C16	−0.0153(9)	0.3165(2)	0.6734(9)	0.047(3)
C21	0.3362(8)	0.2755(3)	0.6707(11)	0.060(4)
C22	0.4550(8)	0.2538(3)	0.7440(11)	0.061(4)
C23	0.5892(8)	0.2704(3)	0.7845(11)	0.081(5)
C24	0.6046(8)	0.3086(3)	0.7516(11)	0.074(5)
C25	0.4858(8)	0.3303(3)	0.6783(11)	0.084(5)
C26	0.3517(8)	0.3138(3)	0.6378(11)	0.062(4)
C31	−0.3313(9)	0.2875(2)	0.2871(9)	0.048(4)
C32	−0.3715(9)	0.3111(2)	0.3792(9)	0.049(3)
C33	−0.4548(9)	0.3434(2)	0.3275(9)	0.074(5)
C34	−0.4980(9)	0.3521(2)	0.1836(9)	0.073(5)
C35	−0.4578(9)	0.3285(2)	0.0915(9)	0.068(4)
C36	−0.3744(9)	0.2962(2)	0.1433(9)	0.064(4)
C41	−0.3273(10)	0.2085(3)	0.2185(11)	0.052(4)
C42	−0.4747(10)	0.2101(3)	0.1656(11)	0.072(5)
C43	−0.5506(10)	0.1827(3)	0.0686(11)	0.085(6)
C44	−0.4793(10)	0.1537(3)	0.0245(11)	0.104(7)
C45	−0.3320(10)	0.1521(3)	0.0774(11)	0.126(8)
C46	−0.2560(10)	0.1795(3)	0.1745(11)	0.081(5)
C51	−0.3328(10)	−0.0353(3)	0.4323(9)	0.049(4)
C52	−0.4098(10)	−0.0371(3)	0.2881(9)	0.068(4)
C53	−0.3738(10)	−0.0639(3)	0.2027(9)	0.078(5)
C54	−0.2607(10)	−0.0889(3)	0.2616(9)	0.079(5)
C55	−0.1837(10)	−0.0870(3)	0.4058(9)	0.070(5)
C56	−0.2197(10)	−0.0603(3)	0.4911(9)	0.056(4)
C61	−0.5713(8)	−0.0170(3)	0.4979(11)	0.052(4)
C62	−0.6865(8)	0.0049(3)	0.4179(11)	0.062(4)
C63	−0.8231(8)	−0.0099(3)	0.3812(11)	0.068(5)
C64	−0.8445(8)	−0.0468(3)	0.4244(11)	0.081(5)
C65	−0.7293(8)	−0.0687(3)	0.5044(11)	0.068(5)
C66	−0.5927(8)	−0.0539(3)	0.5411(11)	0.059(4)
C71	0.0971(9)	−0.0301(2)	0.8891(9)	0.043(3)
C72	0.1337(9)	−0.0561(2)	0.8017(9)	0.051(4)
C73	0.2106(9)	−0.0890(2)	0.8593(9)	0.064(4)
C74	0.2508(9)	−0.0959(2)	1.0043(9)	0.068(4)
C75	0.2142(9)	−0.0699(2)	1.0917(9)	0.079(5)
C76	0.1373(9)	−0.0370(2)	1.0341(9)	0.059(4)
C81	0.0921(11)	0.0485(3)	0.9553(11)	0.060(4)
C82	0.2395(11)	0.0479(3)	1.0093(11)	0.072(5)
C83	0.3124(11)	0.0760(3)	1.1052(11)	0.089(6)
C84	0.2379(11)	0.1046(3)	1.1470(11)	0.102(7)
C85	0.0905(11)	0.1052(3)	1.0929(11)	0.106(7)
C86	0.0176(11)	0.0771(3)	0.9971(11)	0.076(5)

[a] $U_{eq} = (1/3)\Sigma_i \Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$.

(53%). Anal. Found: C, 59.43; H, 4.73; N, 4.05; Mo, 13.43. $C_{70}H_{68}Mo_2N_4O_8P_4$ requires: C, 59.66; H, 4.86; N, 3.98; Mo, 13.62%.

Procedure b). A mixture of 0.079 g (0.30 mmol) of $Mo(CO)_6$, 0.149 g (0.15 mmol) of TPTA, and 10 cm^3 of n-butanol was sealed under argon in a 25 cm Carius tube, which was then heated in a Carius furnace at 90°C for 3 days. The light-yellow crystals of $[Mo(CO)_4]_2$TPTA were formed in the yield of 56% (0.118 g). They were filtered off and treated further as described above.

3.3.2. $[W(CO)_4]_2TPTA$ (2)

A mixture of 0.106 g (0.30 mmol) of $W(CO)_6$, 0.149 g (0.15 mmol) of TPTA, and 4 cm^3 of n-butanol was placed in a 25 cm tube, which was thoroughly degassed with argon, sealed, and heated at 120°C for four days. After cooling of the mixture the pale-yellow crystalline product was filtered off, washed with a few cm^3 of dry n-butanol and dried *in vacuo*. The yield was 35%

(0.083 g). Anal. Found: C, 53.17; H, 4.44; N, 3.68; W, 22.95. $C_{70}H_{68}N_4O_8P_4W_2$ requires: C, 53.04; H, 4.32; N, 3.54; W, 23.20%.

3.4. Crystal structure determination

Crystals of both compounds suitable for X-ray diffraction analysis were obtained directly by gradual heating of the reaction components in a sealed tube as above, but using more dilute solutions. Compound **2** crystallizes in the form of very thin prisms, mostly forming layered and dendritic crystals of poor quality. The crystal for X-ray analysis was cut from this aggregate. Single crystals of **1** were small but well formed.

X-ray diffraction data were collected at room temperature on a Philips PW1100 diffractometer (upgraded by STOE) using graphite-monochromatized Cu K_α radiation (λ = 1.54242 Å) for **1** and Mo K_α radiation (λ = 0.71073 Å) for **2**. An orthorhombic unit cell was first obtained for **1** but analysis of the equivalent reflections indicated the monoclinic system. Unit cell dimensions were obtained by least-squares refinement of 22 reflections ($11 < \theta < 24°$) and 20 reflections ($10 < \theta < 16°$) for **1** and **2**, respectively. The unit cell parameters and details of data collection and refinement are given in Table 4. Standard reflections monitored every 80 min indicated no significant change in intensities for **1** and a continuous decay amounting to 13% for **2**. The intensities were corrected for decay (in the case of **2**), Lorentz, polarization and absorption effects. Program ACXR was used for a Gaussian absorption correction in **1** [16] and an empirical absorption correction with DIFABS [17] was made for **2**.

Mo and W atoms were located by the Patterson method. Subsequent full-matrix least-squares refinement and difference Fourier maps revealed all non-hydrogen atoms. The hydrogen atoms were included in calculated positions (C–H 1.08 Å) with grouped isotropic thermal parameters. Although all C atoms of the phenyl groups were found, the rings were treated as regular hexagons (C–C 1.395 Å) and refined as rigid groups in order to reduce the number of parameters in the refinement in **1** and because of low data quality in **2**. In **1** all non-H atoms except the C atoms from the phenyl groups were refined anisotropically whereas in **2** only the W and P atoms were refined anisotropically. Atomic scattering factors and anomalous dispersion coefficients were taken from International Tables for X-ray Crystallography [18]. No extinction correction was made, only the low angle reflections 100, 020 and 001 were omitted from calculations in the last cycles in **2**. Refinement with inverted signs of *if*″ in **1** gave poorer agreement factors, which confirmed the correct assignment of absolute configuration. An attempt was made to refine **2** in the $P1$ space group, but a satisfactory refinement could not be achieved. Computing was carried out on an IBM PC/AT-compatible computer using SHELX76 [19].

TABLE 6. Positional parameters and equivalent isotropic thermal parameters (W, P1 and P2) and isotropic thermal parameters (from O101 to C46) (Å^2), with e.s.d.'s in parentheses for **2**

	x	y	z	U_{eq} [a] or U_{iso}
W	0.1514(2)	0.2530(1)	0.3258(2)	0.0377(6) [a]
P1	0.2852(12)	0.2529(7)	0.5987(11)	0.060(6) [a]
P2	−0.1026(10)	0.2316(6)	0.3154(9)	0.044(3) [a]
O101	0.241(4)	0.085(2)	0.286(4)	0.118(12)
O102	0.119(4)	0.428(2)	0.321(4)	0.071(8)
O103	0.027(3)	0.244(2)	−0.008(3)	0.075(8)
O104	0.446(4)	0.276(2)	0.293(4)	0.115(12)
C101	0.205(4)	0.145(2)	0.320(4)	0.066(11)
C102	0.106(4)	0.362(2)	0.308(4)	0.069(12)
C103	0.066(4)	0.248(2)	0.113(4)	0.055(10)
C104	0.335(4)	0.269(2)	0.314(4)	0.056(10)
N1	0.166(3)	0.120(2)	0.620(3)	0.050(7)
N2	−0.145(3)	0.124(2)	0.489(3)	0.046(7)
C1	0.073(3)	0.149(2)	0.696(3)	0.049(9)
C2	−0.072(3)	0.115(2)	0.641(3)	0.047(8)
C3	−0.293(4)	0.086(2)	0.429(4)	0.063(11)
C4	−0.292(4)	0.001(2)	0.437(4)	0.061(10)
C5	−0.207(4)	−0.040(2)	0.349(4)	0.056(10)
C91	0.301(4)	0.162(2)	0.666(4)	0.031(7)
C92	−0.165(3)	0.206(2)	0.463(3)	0.043(8)
C11	0.223(2)	0.322(1)	0.727(2)	0.043(8)
C12	0.298(2)	0.325(1)	0.874(2)	0.054(9)
C13	0.264(2)	0.377(1)	0.975(2)	0.067(11)
C14	0.156(2)	0.426(1)	0.927(2)	0.063(10)
C15	0.081(2)	0.423(1)	0.780(2)	0.073(12)
C16	0.115(2)	0.372(1)	0.680(2)	0.052(9)
C21	0.457(2)	0.295(1)	0.652(2)	0.037(7)
C22	0.574(2)	0.253(1)	0.712(2)	0.046(8)
C23	0.708(2)	0.287(1)	0.756(2)	0.066(11)
C24	0.725(2)	0.363(1)	0.741(2)	0.055(10)
C25	0.608(2)	0.405(1)	0.681(2)	0.069(11)
C26	0.474(2)	0.371(1)	0.637(2)	0.058(10)
C31	−0.197(2)	0.318(1)	0.278(2)	0.036(7)
C32	−0.232(2)	0.366(1)	0.384(2)	0.044(8)
C33	−0.307(2)	0.430(1)	0.348(2)	0.068(11)
C34	−0.348(2)	0.447(1)	0.206(2)	0.069(11)
C35	−0.314(2)	0.400(1)	0.101(2)	0.058(10)
C36	−0.238(2)	0.335(1)	0.137(2)	0.050(9)
C41	−0.209(2)	0.162(1)	0.169(2)	0.044(8)
C42	−0.354(2)	0.165(1)	0.122(2)	0.066(11)
C43	−0.436(2)	0.112(1)	0.009(2)	0.091(15)
C44	−0.371(2)	0.056(1)	−0.056(2)	0.093(15)
C45	−0.225(2)	0.054(1)	−0.009(2)	0.121(19)
C46	−0.144(2)	0.107(1)	0.104(2)	0.080(13)

[a] $U_{eq} = (1/3)\Sigma_i \Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$.

Atomic coordinates for **1** and **2** are given in Tables 5 and 6, respectively. Lists of anisotropic thermal parameters, torsion angles and hydrogen atom coordinates have been deposited with the Cambridge Crystallographic Data Centre. Tables of structure factors are available from the authors.

Acknowledgment

We thank the Research Council of the Republic of Croatia for financial support.

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