

# Chromium carbonyl complexes containing 1,4,8,11-tetrakis-(methyldiphenylphosphino)-1,4,8,11-tetraazacyclotetradecane (TPTA): the synthesis and characterization of $[\text{Cr}(\text{CO})_4]_2\text{TPTA}$ and $[\text{Cr}(\text{CO})_5]_4\text{TPTA}$

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## Abstract

Two chromium carbonyl complexes containing 1,4,8,11-tetrakis(methyldiphenylphosphino)-1,4,8,11-tetraazacyclotetradecane (TPTA) have been prepared: the binuclear species  $[\text{Cr}(\text{CO})_4]_2\text{TPTA}$  (1) and the tetranuclear species  $[\text{Cr}(\text{CO})_5]_4\text{TPTA}$  (2). The crystal structure of 2 has been determined.

**Keywords:** Chromium; Carbonyl; Tetraaza ligand; Crystal structure; Macrocycle

## 1. Introduction

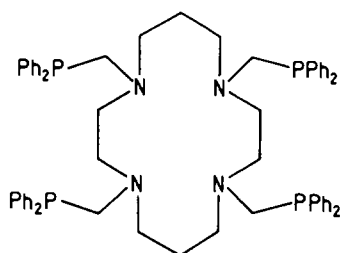
The design and synthesis of polyazamacrocycles and their metal complexes have been the focus of research in recent years because of their possible relevance for the recognition of particular metal ions and in the modelling of metalloproteins. Spectroscopic and magnetic properties of polynuclear macrocyclic complexes have also been widely studied, as well as the potential application of such complexes in extraction and catalysis [1–4].

Among the polyazamacrocyclic ligands most studied are tetraazacycloalkanes. Of particular interest are those bearing functionalized side chains. Depending on the bonding strength of the ligating groups and the size of the cavity of the ring, they can combine with metal ions selectively. Various functional groups such as amine, hydroxyl, amide, carboxyl or nitrile have been attached to the side chains of nitrogen donors [5–9]. In addition, various substituents such as phenol, pyridyl, catechol,

imidazole or amine have been attached to the carbon atoms of macrocyclic framework [10,11]. Some of these donor groups greatly change the properties of the complexes or affect the coordination geometry of the metal ions.

For some time we have been interested in the coordination chemistry of polydentate ligands [12–15]. Recently we reported the synthesis and characterization [14,15] of several molybdenum and tungsten complexes containing 1,4,8,11-tetrakis(methyldiphenylphosphino)-1,4,8,11-tetraazacyclotetradecane (TPTA), a tetraaza macrocyclic ligand with phosphorus donors in the pendant arms (Scheme 1). This compound has great potential for coordination with metal ions. Surprisingly, our work has provided the only information on the coordination chemistry of this ligand, which was first prepared in 1984 [16]. This may, at least in part, be due to the sensitivity of this ligand towards most of the common solvents, which means that great care is needed in handling it. In extension of our programme we describe below the preparation and spectroscopic characterization of the two chromium carbonyl complexes with this ligand,  $[\text{Cr}(\text{CO})_4]_2\text{TPTA}$  (1) and  $[\text{Cr}(\text{CO})_5]_4\text{TPTA}$  (2), and the crystal structure of the latter.

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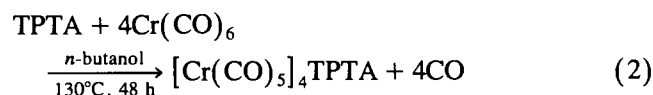
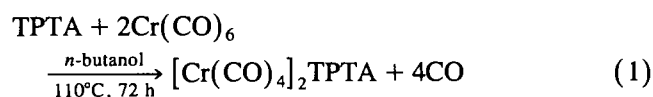


Scheme 1. 1,4,8,11-tetrakis(methyldiphenylphosphino)-1,4,8,11-tetraazacyclotetradecane (TPTA).

## 2. Results and discussion

### 2.1. Preparation and properties

Reactions between TPTA and  $\text{Cr}(\text{CO})_6$ , leading to a binuclear complex  $[\text{Cr}(\text{CO})_4]_2\text{TPTA}$  (**1**) and a tetranuclear complex  $[\text{Cr}(\text{CO})_5]_4\text{TPTA}$  (**2**), took place in hot *n*-butanol under argon in a sealed Carius tube, according to Eqs. 1 and 2.



The outcome of the reaction is very sensitive to the ligand-to-metal ratios, the reaction temperature, and the heating and cooling rates. Inappropriate ratios or tem-

peratures can result in a mixture of **1** and **2** and some unchanged starting materials may be present, while use of a slightly higher temperature results in decomposition of the ligand by the cleavage of P–C bonds. However, when properly carried out, the reactions gave yellow crystals of **1** or **2**, which were filtered off and stored under argon. The yield was satisfactory for **2**, but rather poor for **1**, probably because of the somewhat higher solubility of the binuclear complex.

When stored in air, both compounds gradually deteriorate. They are only sparingly soluble in all common polar and non-polar solvents and readily decompose in solution, which prevented from recording some spectroscopic data. For the same reason the complexes could not be recrystallized, but the products were usually pure as isolated and gave satisfactory elemental analyses. Magnetic susceptibility measurements confirmed that the complexes are diamagnetic, as expected for the Cr(0) state. Both are non-electrolytes in nitrobenzene.

The available information, including the IR data, indicated that both chromium complexes, the binuclear  $[\text{Cr}(\text{CO})_4]_2\text{TPTA}$  and the tetranuclear complex  $[\text{Cr}(\text{CO})_5]_4\text{TPTA}$ , have the same type of structure as the previously described binuclear and tetranuclear complexes of molybdenum and tungsten [14,15], with the ligand bound to the metal atoms through the soft phosphorus donors from the pendant arms.

In the case of **2**, in order to confirm the structure unambiguously and to allow comparison with those of the corresponding, molybdenum and tungsten complexes, an X-ray diffraction study was undertaken and single crystals taken from the product obtained by carry-

Table 1  
Selected IR frequencies for the TPTA ligand and for the complexes

IR frequency ( $\text{cm}^{-1}$ ) <sup>a</sup>			Tentative assignments
TPTA	$[\text{Cr}(\text{CO})_4]_2\text{TPTA}$	$[\text{Cr}(\text{CO})_5]_4\text{TPTA}$	
3070 w	3050 w	3060 w	$\nu(\text{C-H})$ aromatic
2950 m	2920 vw	2940 w	$\nu(\text{C-H})$ aliphatic
2800 m, sp	2795 m	2800 vw	$\nu_s \text{CH}_2$ from $\text{N}(\text{CH}_2-)_3$
2770 m, sp			
2735 m, sp			
1960 w	2000 s, sp	2065 s, sp	Overtone and combination
1880 w	1909 vs	1990 m	bands (for the ligand);
1810 w	1891 vs	1930 vs	$\nu(\text{CO})$
1760 w	1873 vs		
1484 s	1482 w	1482 w	$\nu(\text{CC})$ phenyl
1435 vs	1434 s	1435 m	Vibration associated with $=\text{P}-\text{C}_6\text{H}_5$ and $\delta_s \text{CH}_2-\text{CH}_2\text{P}=\text{)}$
1115 s	1110 w	1090 m	Vibration assoc. with $-\text{P}(\text{C}_6\text{H}_5)_2$
740 s	746; 740 m	743 m	C–H out-of-plane bending
695 vs	694 s	694 m	and ring bending
	674 m	673 s	$\delta(\text{Cr}-\text{CO})$
	642 s	652 vs	
	490 m	545 w	$\nu(\text{Cr}-\text{C})$
	418 m	462 m	
	385 w		

<sup>a</sup> KBr pellets.

ing out the reaction in more dilute solutions. In the case of **1**, no crystals of suitable size and quality for single-crystal X-ray determination were obtained in spite of many attempts.

## 2.2. IR spectra

The most characteristic vibrational frequencies for the ligand TPTA and the complexes  $[\text{Cr}(\text{CO})_4]_2\text{TPTA}$  and  $[\text{Cr}(\text{CO})_5]_4\text{TPTA}$  in the  $4000\text{--}200\text{ cm}^{-1}$  region, with tentative assignments, are listed in Table 1. In addition, the IR spectra (KBr pellet) of TPTA, **1** and **2** in the range  $3500\text{--}1500\text{ cm}^{-1}$  are shown in Fig. 1. The spectra clearly indicate the presence of  $\text{Cr}(\text{CO})_4$  and  $\text{Cr}(\text{CO})_5$  units for **1** and **2** respectively and confirm the coordination of the ligand to the metal through phosphorus donors in both complexes.

The IR spectrum of **1** exhibits a four-line pattern of peaks in the terminal CO stretching region, typical of complexes of the type  $\text{cis-}M(\text{CO})_4\text{L}_2$  with  $C_{2v}$  symmetry around the metal atoms. The spectrum of **2** contains a band pattern characteristic of an  $M(\text{CO})_5$  moiety of an idealized  $C_{4v}$  point-group symmetry, which shows  $2A_1 + E$  IR-active carbonyl stretching modes [17]. The CO stretching frequencies of both complexes are significantly higher than those of the corresponding complexes containing nitrogen donors. This is in accord with the observation that ligands bonded through phosphorus

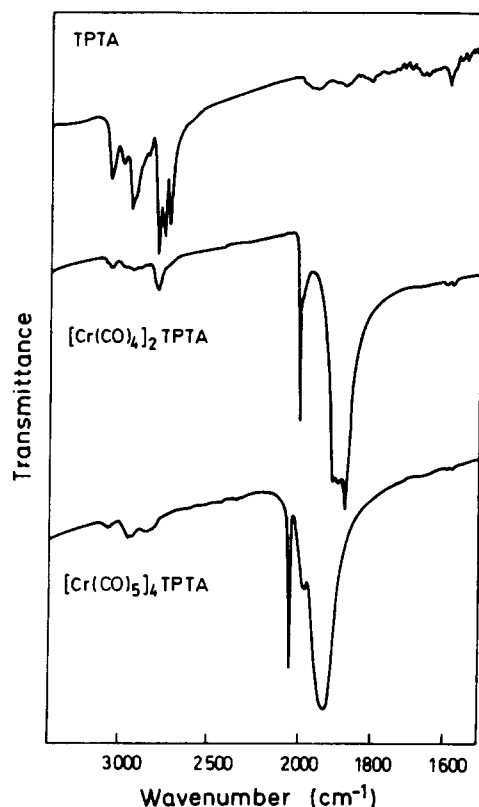
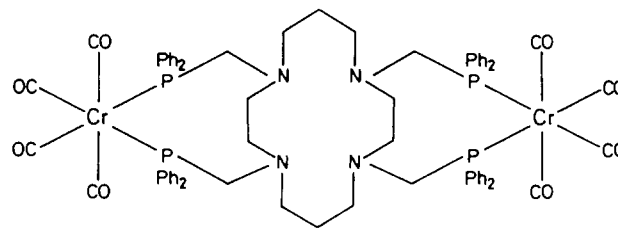


Fig. 1. IR spectra of the ligand TPTA and the complexes.



Scheme 2.

have a greater ‘‘direct donation’’ effect than do those bonded through nitrogen, as is expressed by an increase in the CO stretching frequencies [18–21]. The spectrum of the ligand shows a rather strong band at  $1115\text{ cm}^{-1}$  which can be assigned to the vibrations of the  $-\text{P}(\text{C}_6\text{H}_5)_2$  group [22]. A significant shift in this absorption towards lower frequencies upon complexation (Table 1) is consistent with the bonding of phosphorus to the metal.

The characteristic three-band pattern for the C–H stretching vibrations of  $:\text{N}(\text{CH}_2)_3$  moiety [23] present in the spectrum of TPTA at  $2800, 2770$  and  $2735\text{ cm}^{-1}$  is changed into a single band in the spectrum of **1** (at  $2795\text{ cm}^{-1}$ ) and almost completely disappears in the case of **2**, indicating that this vibration is blocked in the tetranuclear complex. Furthermore, all the other vibrations of the macrocyclic ring [24] are of higher intensity in the spectrum of **1** than in that of **2**, in which some of them are completely missing. This can be associated with a more rigid conformation of the ring in the tetranuclear complex, in which four very bulky chains ( $-\text{CH}_2\text{PPh}_2\text{Cr}(\text{CO})_5$ ) seek to be as widely separated as possible, hence contributing to the rigidity of the ring.

In the light of the analytical and spectroscopic data the structure shown in Scheme 2 can be proposed for  $[\text{Cr}(\text{CO})_4]_2\text{TPTA}$ .

## 2.3. X-ray structure of **2**

The molecular structure of  $[\text{Cr}(\text{CO})_5]_4\text{TPTA}$  is shown in Fig. 2. The bond distances and angles are listed in Table 2. Each of the metal atoms in **2** is coordinated by five carbon atoms from the carbonyl groups and a phosphorus atom from one of the four methyl-diphenylphosphino groups of the TPTA macrocycle, forming a distorted octahedron. The molecule has a crystallographically imposed centre of symmetry. This tetranuclear complex is isomorphous with  $[\text{Mo}(\text{CO})_5]_4\text{TPTA}$  and  $[\text{W}(\text{CO})_5]_4\text{TPTA}$ , with the volume of the unit cell  $65\text{ \AA}^3$  and  $43\text{ \AA}^3$  smaller than those for the Mo and W complexes respectively. The Cr–P distances in **2** are  $0.138$  and  $0.144\text{ \AA}$  shorter than the corresponding Mo–P distances, and  $0.126$  and  $0.129\text{ \AA}$  shorter than the corresponding W–P distances in the related complexes [15]. A similar shortening of  $0.138\text{ \AA}$  of the Cr–P distance relative to that of the Mo–P

distance was found in the case of the isomorphous  $(C_6H_5)_3PCr(CO)_5$  [25] and  $(C_6H_5)_3PMo(CO)_5$  [26] complexes.

In **2** the Cr(1)–P(1) distance of 2.406(1) Å is signifi-

cantly larger than the Cr(2)–P(2) distance of 2.391(1) Å. Since the chemical environments around P(1) and P(2) are the same, the difference in bond length must be the result of steric effects. The phenyl rings C(11)–C(16)

Table 2

Selected bond lengths (Å) and angles (°) with estimated standard deviations in parentheses for  $[Cr(CO)_5]_4TPTA^a$

<i>Bond lengths</i>			
Cr(1)–P(1)	2.406(1)	Cr(2)–P(2)	2.391(1)
Cr(1)–C(51)	1.871(5)	Cr(2)–C(61)	1.864(4)
Cr(1)–C(52)	1.904(6)	Cr(2)–C(62)	1.889(4)
Cr(1)–C(53)	1.874(5)	Cr(2)–C(63)	1.897(4)
Cr(1)–C(54)	1.870(4)	Cr(2)–C(64)	1.907(5)
Cr(1)–C(55)	1.894(4)	Cr(2)–C(65)	1.894(4)
P(1)–C(6)	1.876(3)	P(2)–C(7)	1.859(3)
P(1)–C(11)	1.834(4)	P(2)–C(31)	1.834(3)
P(1)–C(21)	1.826(5)	P(2)–C(41)	1.826(3)
C(51)–O(51)	1.148(6)	C(61)–O(61)	1.148(5)
C(52)–O(52)	1.150(7)	C(62)–O(62)	1.135(5)
C(53)–O(53)	1.146(6)	C(63)–O(63)	1.145(5)
C(54)–O(54)	1.149(6)	C(64)–O(64)	1.130(7)
C(55)–O(55)	1.145(5)	O(65)–C(65)	1.131(5)
N(1)–C(1)	1.467(4)	N(2)–C(7)	1.471(4)
N(1)–C(6)	1.453(5)	C(3)–C(4)	1.519(5)
C(1)–C(2)	1.532(5)	C(4)–C(5)	1.539(5)
C(2)–N(2)	1.473(4)	C(5)–N(1)	1.467(4)
N(2)–C(3)	1.475(4)		
<i>Average bond lengths within the phenyl rings (n = 1, 2, 3, 4)</i>			
Cn(1)–Cn(2), Cn(1)–Cn(6)		1.389(3)	
Cn(2)–Cn(3), Cn(5)–Cn(6)		1.389(3)	
Cn(3)–Cn(4), Cn(4)–Cn(5)		1.364(3)	
<i>Bond angles</i>			
P(1)–Cr(1)–C(51)	175.9(1)	P(2)–Cr(2)–C(61)	177.6(1)
P(1)–Cr(1)–C(52)	98.0(2)	P(2)–Cr(2)–C(62)	86.4(1)
P(1)–Cr(1)–C(53)	91.8(2)	P(2)–Cr(2)–C(63)	94.5(1)
P(1)–Cr(1)–C(54)	88.1(1)	P(2)–Cr(2)–C(64)	89.1(1)
P(1)–Cr(1)–C(55)	88.0(1)	P(2)–Cr(2)–C(65)	91.7(1)
C(51)–Cr(1)–C(52)	85.7(2)	C(61)–Cr(2)–C(62)	92.7(2)
C(51)–Cr(1)–C(53)	90.1(2)	C(61)–Cr(2)–C(63)	87.8(2)
C(51)–Cr(1)–C(54)	88.2(2)	C(61)–Cr(2)–C(64)	91.8(2)
C(51)–Cr(1)–C(55)	90.0(2)	C(61)–Cr(2)–C(65)	86.0(2)
C(52)–Cr(1)–C(53)	89.7(2)	C(62)–Cr(2)–C(63)	90.0(2)
C(52)–Cr(1)–C(54)	173.9(2)	C(62)–Cr(2)–C(64)	175.3(2)
C(52)–Cr(1)–C(55)	92.6(2)	C(62)–Cr(2)–C(65)	87.8(2)
C(53)–Cr(1)–C(54)	89.9(2)	C(63)–Cr(2)–C(64)	91.7(2)
C(53)–Cr(1)–C(55)	177.7(2)	C(63)–Cr(2)–C(65)	173.3(2)
C(54)–Cr(1)–C(55)	87.7(2)	C(64)–Cr(2)–C(65)	91.0(2)
Cr(1)–C(51)–O(51)	179.1(4)	Cr(2)–C(61)–O(61)	179.3(4)
Cr(1)–C(52)–O(52)	175.4(5)	Cr(2)–C(62)–O(62)	178.1(4)
Cr(1)–C(53)–O(53)	178.0(5)	Cr(2)–C(63)–O(63)	174.4(4)
Cr(1)–C(54)–O(54)	176.5(4)	Cr(2)–C(64)–O(64)	178.7(4)
Cr(1)–C(55)–O(55)	176.0(4)	Cr(2)–C(65)–O(65)	175.4(4)
Cr(1)–P(1)–C(6)	112.4(1)	Cr(2)–P(2)–C(7)	117.3(1)
Cr(1)–P(1)–C(11)	110.0(1)	Cr(2)–P(2)–C(31)	119.9(1)
Cr(1)–P(1)–C(21)	123.2(1)	Cr(2)–P(2)–C(41)	110.8(1)
C(6)–P(1)–C(11)	105.0(2)	C(7)–P(2)–C(31)	99.9(1)
C(6)–P(1)–C(21)	100.7(2)	C(7)–P(2)–C(41)	103.4(1)
C(11)–P(1)–C(21)	103.8(2)	C(31)–P(2)–C(41)	103.6(1)
P(1)–C(11)–C(12)	120.3(3)	P(2)–C(31)–C(32)	120.6(2)
P(1)–C(11)–C(16)	120.9(3)	P(2)–C(31)–C(36)	120.9(3)
P(1)–C(21)–C(22)	121.7(3)	P(2)–C(41)–C(42)	122.5(3)
P(1)–C(21)–C(26)	120.8(3)	P(2)–C(41)–C(46)	119.0(2)
P(1)–C(6)–N(1)	114.5(2)	P(2)–C(7)–N(2)	109.7(2)

Table 2 (continued)

Bond angles			
C(6)–N(1)–C(5) <sup>i</sup>	113.5(3)	C(2)–N(2)–C(3)	115.0(3)
C(1)–N(1)–C(5) <sup>i</sup>	115.2(3)	C(2)–N(2)–C(7)	112.7(3)
C(1)–N(1)–C(6)	115.4(3)	C(3)–N(2)–C(7)	112.5(3)
N(1)–C(1)–C(2)	111.6(3)	N(2)–C(3)–C(4)	112.6(3)
C(1)–C(2)–N(2)	115.0(3)	C(3)–C(4)–C(5)	111.2(3)
		C(4)–C(5)–N(1) <sup>i</sup>	114.1(3)
Average bond angles within the phenyl rings (n = 1, 2, 3, 4)			
Cn(2)–Cn(1)–Cn(3)		118.0(4)	
Cn(1)–Cn(2)–Cn(3), Cn(1)–Cn(6)–Cn(5)		120.6(1)	
Cn(2)–Cn(3)–Cn(4), Cn(4)–Cn(5)–Cn(6)		120.5(1)	
Cn(3)–Cn(4)–Cn(5)		119.9(1)	

<sup>a</sup> Symmetry code: (i) 1 – x, 1 – y, 1 – z.

and C(21)–C(26) are at angles of 9.9(2)° and 72.2(2)° respectively to the Cr(1) equatorial carbonyl plane, while the phenyl rings C(31)–C(36) and C(41)–C(46) form angles of 69.3(2)° and 21.2(1)° respectively with the Cr(2) equatorial carbonyl plane. The largest angle involves the C(21)–C(26) ring, and the effect of steric repulsions between the phenyl and CO(52) carbonyl group can be seen in the bond lengths and angles involving these two groups. The hydrogen atom on C(26) is at a distance of 2.35(1) Å from C(52) (2.39(1) Å from O(52)). The close approach causes bending of the CO(52) carbonyl group away from the phenyl, with the P(1)–Cr(1)–C(52) angle of 98.0(2)° showing the largest distortion from ideal octahedral geometry. The steric repulsion causes lengthening of the Cr(1)–P(1) bond and distortion of the P(1) tetrahedron, the Cr(1)–P(1)–C(21) angle being 123.2(1)°. The steric effects on the Cr(2) octahedron are small, since the C(36) and H(36) atoms point between the CO(63) and CO(64) carbonyl groups (Fig. 3).

A correlation of the Cr–P bond lengths and the CO stretching frequency (*E* mode) was suggested by Plastas et al. [25] for compounds of the type LCr(CO)<sub>5</sub>. They observed Cr–P bond lengths of 2.422(1) Å and 2.309(1) Å in (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>PCr(CO)<sub>5</sub> and (C<sub>6</sub>H<sub>5</sub>O)<sub>3</sub>PCr(CO)<sub>5</sub> respectively, and the CO stretching frequencies for these two compounds were found at 1942 cm<sup>-1</sup> and 1960 cm<sup>-1</sup> [27]. The Cr–P bond lengths and the stretching frequency for the present complex do not fit this correlation. From the observed CO stretching frequency of 1930 cm<sup>-1</sup> in **2**, the Cr–P bond lengths should be greater than 2.422(1) Å, but both values are significantly smaller. The unstrained Cr(2)–P(2) bond length is similar to that of 2.389(2) Å in (Ph<sub>2</sub>PC<sub>5</sub>H<sub>4</sub>)<sub>2</sub>Fe[Cr(CO)<sub>5</sub>]<sub>2</sub> [28] and to 2.386(2) Å in Cr(CO)<sub>5</sub>(dpppzO) (dpppzO = 3-diphenylphosphino-6-diphenylphospholyridazine), for which the same CO stretching frequency of 1930 cm<sup>-1</sup> was observed [29]. Both Cr–P bonds in **2** are longer than those in Cr(CO)<sub>5</sub>P(CH<sub>2</sub>CH<sub>2</sub>CN)<sub>3</sub> (*d*(Cr–P) = 2.364(1) Å; *ν*(CO) = 1944 cm<sup>-1</sup>) [26].

The mean Cr–CO<sub>ax</sub> and Cr–CO<sub>eq</sub> distances are 1.868(4) Å and 1.891(5) Å respectively. Shortening of the Cr–C distances *trans* to phosphorus compared with those in the equatorial plane is caused by the greater degree of Cr–C π back bonding resulting from the weaker π acidity of the ligand compared with that of the carbonyl group. The M–C–O angles deviate slightly from linearity and are in the range 174.4(4)–179.3(4)°.

There are no significant differences between corresponding bond lengths and angles in **2** and those in free TPTA or the four complexes [M(CO)<sub>4</sub>]<sub>2</sub>TPTA and [M(CO)<sub>5</sub>]<sub>4</sub>TPTA (M = Mo or W) [14,15]. The conformation of the macrocyclic ring in these complexes was discussed earlier [15].

There is a decrease of the α endocyclic angle in the phenyl rings (average value, 118.0(4)°) caused by the σ-electron release from phosphorus [30].

The molecules are connected only by van der Waals contacts.

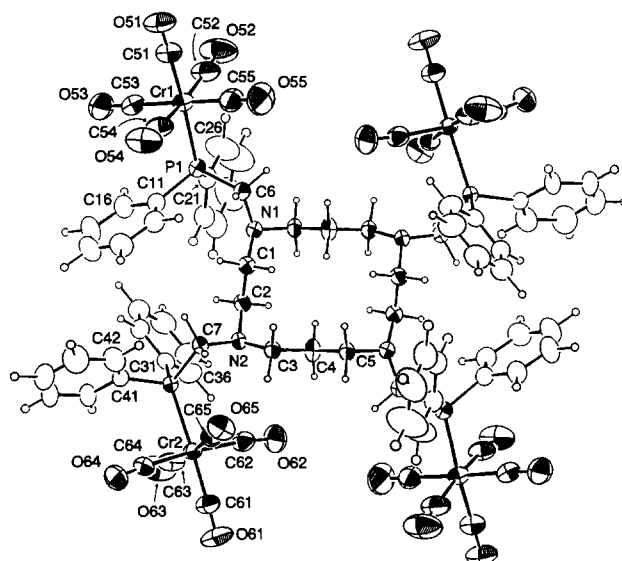


Fig. 2. ORTEP drawing of [Cr(CO)<sub>5</sub>]<sub>4</sub>TPTA with the atom numbering scheme. The thermal ellipsoids are at the 50% probability level.

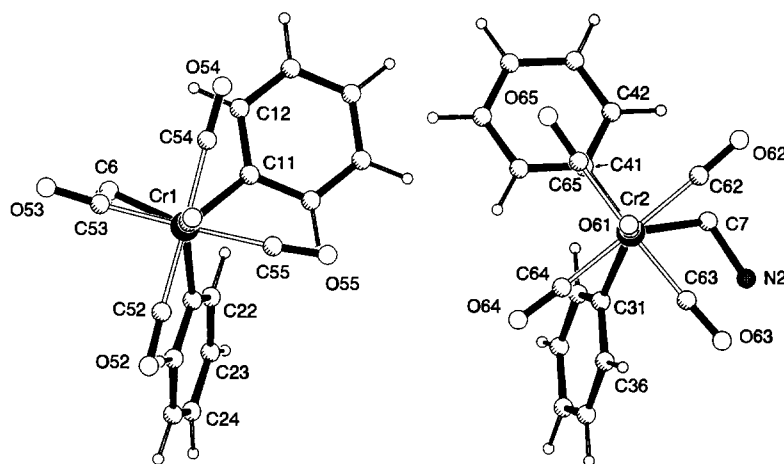


Fig. 3. Views along the Cr(1)–P(1) and Cr(2)–P(2) bonds in 2.

### 3. Experimental details

#### 3.1. Materials

The TPTA was prepared as previously described [16], involving reaction of 1,4,8,11-tetraazacyclotetradecane with diphenylphosphine, both of which were used as received (Fluka). Chromium hexacarbonyl (Merck) was resublimed prior to use. All the solvents were purified and dried by standard methods and distilled under argon before use.

#### 3.2. Physical measurements

Elemental analyses for C, H, N and Cr were carried out at the Central Analytical Service of the Ruđer Bošković Institute. IR spectra on KBr pellets were recorded on a Perkin–Elmer model 580B spectrophotometer in the region 4000–200  $\text{cm}^{-1}$ . The electrical conductivity of  $10^{-3}$  M solutions in nitrobenzene were measured with a Tacussel conductivity bridge, type Cd 7, at 25°C. Magnetic susceptibility data were obtained at 22°C by the Gouy method. The complexes are diamagnetic.

#### 3.3. Preparation of 1 and 2

##### 3.3.1. $[\text{Cr}(\text{CO})_4]_2\text{TPTA}$ (1)

A mixture of 0.055 g (0.25 mmol) of  $\text{Cr}(\text{CO})_6$ , 0.099 g (0.10 mmol) of TPTA and 7  $\text{cm}^3$  of dry *n*-butanol was placed in a 20 cm Carius tube, which was thoroughly degassed and filled with argon; it was then sealed and kept at 110°C for 3 days. The light-yellow crystals of  $[\text{Cr}(\text{CO})_4]_2\text{TPTA}$  were formed with a yield of 22% (0.030 g). They were filtered off, washed with a few cubic centimetres of dry *n*-butanol and dried in vacuo.

Anal. Found: C, 63.58; H, 5.21; N, 4.09; Cr, 7.62.

$\text{C}_{70}\text{H}_{68}\text{Cr}_2\text{N}_4\text{O}_8\text{P}_4$  calc.: C, 63.63; H, 5.19; N, 4.24; Cr, 7.87%.

##### 3.3.2. $[\text{Cr}(\text{CO})_5]_4\text{TPTA}$ (2)

A mixture of 0.099 g (0.45 mmol) of  $\text{Cr}(\text{CO})_6$ , 0.110 g (0.11 mmol) of TPTA and 6  $\text{cm}^3$  of dry *n*-butanol was placed in a 20 cm Carius tube under argon. The

Table 3

Crystal data and details of data collection and refinement for 2

Empirical formula	$\text{Cr}_4\text{C}_{82}\text{H}_{68}\text{N}_4\text{O}_{20}\text{P}_4$
Formula weight	1761.35
Crystal system	Triclinic
Space group	$P\bar{1}$
<i>a</i> (Å)	10.134(3)
<i>b</i> (Å)	13.242(5)
<i>c</i> (Å)	16.320(5)
$\alpha$ (°)	84.37(2)
$\beta$ (°)	76.00(3)
$\gamma$ (°)	77.92(2)
<i>V</i> (Å <sup>3</sup> )	2075(1)
<i>Z</i>	1
$D_{\text{calc}}$ (g $\text{cm}^{-3}$ )	1.409
$F(000)$	904
Face indices, distances	(010), (0 $\bar{1}$ 0) 0.248; (001), (00 $\bar{1}$ )
from centroid (mm)	0.188; (111), ( $\bar{1}\bar{1}\bar{1}$ ) 0.300
$\mu$ ( $\text{cm}^{-1}$ )	6.4
Range of collected data (°)	$4 < \theta < 60$
Scan type	$\omega$
Number of collected reflections	12275
Number of unique reflections with $I > 3\sigma(I)$	5841
Number of parameters refined	519
$R = \sum   F_o  -  F_c   / \sum  F_o $	0.040
$R_w = [\sum w(F_o - F_c)^2 / \sum w(F_o)^2]^{1/2}$	0.043
Weighting scheme <i>w</i>	1.0
Largest final shift/estimated standard deviation	0.002
Maximum final $\Delta\rho$ (electrons $\text{\AA}^{-3}$ )	0.34

Table 4  
Positional parameters and equivalent isotropic thermal parameters, with estimated standard deviation in parentheses for  $[\text{Cr}(\text{CO})_5]_4\text{TPTA}$

	x	y	z	$U_{\text{eq}}^a$ ( $\text{\AA}^2$ )
Cr(1)	-0.25701(6)	0.80581(5)	0.59170(4)	0.0463(1)
Cr(2)	0.52278(5)	0.13793(4)	0.83530(4)	0.0376(1)
P(1)	-0.05413(9)	0.72919(7)	0.64389(5)	0.0375(2)
P(2)	0.32493(8)	0.27040(6)	0.82777(5)	0.0307(2)
N(1)	0.2189(3)	0.6230(2)	0.5861(2)	0.039(1)
C(1)	0.2546(3)	0.5104(2)	0.5998(2)	0.041(1)
C(2)	0.3482(3)	0.4801(2)	0.6627(2)	0.039(1)
N(2)	0.4005(3)	0.3683(2)	0.6733(2)	0.035(1)
C(3)	0.4807(3)	0.3178(2)	0.5951(2)	0.039(1)
C(4)	0.6026(4)	0.3681(3)	0.5509(2)	0.048(1)
C(5)	0.6670(3)	0.3278(3)	0.4619(2)	0.040(1)
C(6)	0.0892(3)	0.6613(3)	0.5602(2)	0.043(1)
C(7)	0.2927(3)	0.3124(2)	0.7211(2)	0.035(1)
C(51)	-0.4210(5)	0.8578(3)	0.5555(3)	0.060(1)
O(51)	-0.5224(3)	0.8886(2)	0.5339(2)	0.082(1)
C(52)	-0.2271(5)	0.9443(4)	0.5749(4)	0.076(1)
O(52)	-0.2168(5)	1.0296(3)	0.5625(3)	0.127(2)
C(53)	-0.1618(5)	0.7808(4)	0.4797(3)	0.073(1)
O(53)	-0.1065(4)	0.7639(4)	0.4110(2)	0.119(2)
C(54)	-0.3033(4)	0.6748(3)	0.6037(3)	0.059(1)
O(54)	-0.3385(4)	0.5967(3)	0.6110(3)	0.092(1)
C(55)	-0.3547(4)	0.8255(3)	0.7054(3)	0.056(1)
O(55)	-0.4191(4)	0.8341(3)	0.7733(2)	0.087(1)
C(11)	-0.0944(3)	0.6285(3)	0.7263(2)	0.041(1)
C(12)	-0.0923(4)	0.5288(3)	0.7044(3)	0.050(1)
C(13)	-0.1354(4)	0.4549(3)	0.7668(3)	0.064(1)
C(14)	-0.1824(5)	0.4803(4)	0.8492(3)	0.071(1)
C(15)	-0.1890(5)	0.5784(4)	0.8710(3)	0.067(1)
C(16)	-0.1450(4)	0.6527(3)	0.8107(2)	0.052(1)
C(21)	0.0410(4)	0.8038(3)	0.6891(2)	0.044(1)
C(22)	0.1313(4)	0.7568(3)	0.7401(2)	0.054(1)
C(23)	0.2114(5)	0.8129(4)	0.7673(3)	0.070(1)
C(24)	0.2046(6)	0.9143(5)	0.7449(4)	0.097(2)
C(25)	0.1196(8)	0.9619(5)	0.6942(5)	0.122(3)
C(26)	0.0371(6)	0.9071(4)	0.6668(4)	0.091(2)
C(61)	0.6720(4)	0.0306(3)	0.8424(3)	0.057(1)
O(61)	0.7629(3)	-0.0362(3)	0.8471(2)	0.089(1)
C(62)	0.4922(4)	0.0856(3)	0.7393(2)	0.046(1)
O(62)	0.4699(4)	0.0548(2)	0.6826(2)	0.070(1)
C(63)	0.6511(4)	0.2126(3)	0.7642(3)	0.054(1)
O(63)	0.7365(3)	0.2503(3)	0.7211(2)	0.085(1)
C(64)	0.5384(5)	0.1972(3)	0.9336(3)	0.061(1)
O(64)	0.5459(5)	0.2312(3)	0.9928(2)	0.100(1)
O(65)	0.3498(4)	-0.0092(2)	0.9407(2)	0.088(1)
C(65)	0.4104(4)	0.0492(3)	0.9027(2)	0.053(1)
C(31)	0.3090(3)	0.3968(2)	0.8700(2)	0.035(1)
C(32)	0.1789(4)	0.4599(3)	0.8960(2)	0.044(1)
C(33)	0.1681(4)	0.5584(3)	0.9221(2)	0.053(1)
C(34)	0.2854(5)	0.5954(3)	0.9228(3)	0.061(1)
C(35)	0.4130(5)	0.5344(3)	0.8969(3)	0.065(1)
C(36)	0.4254(4)	0.4356(3)	0.8703(3)	0.052(1)
C(41)	0.1655(3)	0.2279(2)	0.8842(2)	0.037(1)
C(42)	0.0763(4)	0.1992(3)	0.8430(3)	0.062(1)
C(43)	-0.0370(5)	0.1573(4)	0.8892(4)	0.084(2)
C(44)	-0.0605(5)	0.1442(4)	0.9753(4)	0.077(1)
C(45)	0.0261(5)	0.1729(3)	1.0169(3)	0.064(1)
C(46)	0.1384(4)	0.2150(3)	0.9721(2)	0.050(1)

$$^a U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

tube was sealed, slowly heated to 130°C and kept at this temperature for 48 h; it was then allowed to cool to room temperature. The pale-yellow crystals that separated were filtered off, washed with a few cubic centimetres of dry *n*-butanol and dried in vacuo. The yield was 0.103 g (58%).

Anal. Found: C, 55.93; H, 3.84; N, 3.12; Cr, 11.65.  $\text{C}_{82}\text{H}_{68}\text{Cr}_4\text{N}_4\text{O}_{20}\text{P}_4$  calc.: C, 55.92; H, 3.89; N, 3.18; Cr, 11.81%.

### 3.4. Crystal structure determination

X-ray data were collected at room temperature on a Philips PW1100 diffractometer (modified by STOE) using graphite-monochromated Mo  $\text{K}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Unit-cell parameters were obtained by least-squares refinement of 28 reflections ( $20.2^\circ < 2\theta < 33.6^\circ$ ). Crystal data and details of the data collection and refinement are given in Table 3. Standard reflections monitored every 90 min showed no significant change in intensities. The intensities were corrected for Lorentz and polarization effects but not for absorption or extinction. The small-angle reflections  $\bar{1}01$  and  $0\bar{1}1$  were omitted from calculations in the final cycles.

The positions of the heavy-metal atoms and the macrocyclic ring atoms taken from  $[\text{Mo}(\text{CO})_5]_4\text{TPTA}$  were used as a starting model. Subsequent full-matrix least-squares refinement and difference Fourier maps revealed all non-hydrogen atoms. The hydrogen atom positions were placed in calculated positions (C–H, 1.08 Å, riding model) with grouped isotropic thermal parameters. All non-hydrogen atoms were refined anisotropically. Atomic scattering factors and anomalous dispersion coefficients were taken from the *International Tables for X-ray Crystallography* [31]. Computing was carried out on an IBM PC/AT-compatible computer using SHELX76 [32].

Atomic coordinates are given in Table 4. Lists of anisotropic thermal parameters, hydrogen atom coordinates, and of bond lengths and angles in the phenyl rings have been deposited with the Cambridge Crystallographic Data Centre. Tables of least-squares planar equations are available from the authors.

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