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Five-co-ordinate cobalt(II) and nickel(II) complexes of 1,4,8,11-tetrakis-(diphenylphosphinomethyl)-1,4,8,11-tetraazacyclotetradecane (tpta), [MCl(tpta)]X [X = ClO<sub>4</sub>, BF<sub>4</sub>, PF<sub>6</sub> and B(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>]. Crystal structures of [CoCl(tpta)]ClO<sub>4</sub>·C<sub>6</sub>H<sub>6</sub> and [NiCl(tpta)]ClO<sub>4</sub>·C<sub>6</sub>H<sub>6</sub><sup>†</sup>

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A series of five-co-ordinate cobalt(II) and nickel(II) complexes with 1,4,8,11-tetrakis(diphenylphosphinomethyl)-1,4,8,11-tetraazacyclotetradecane (tpta) has been prepared and characterized. The complexes are high-spin paramagnetic substances, 1:1 electrolytes, consistent with the general formula [MCl(tpta)]X [M = Co or Ni;  $X = ClO_4$ , BF<sub>4</sub>, PF<sub>6</sub> or B(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>]. A binuclear cobalt(II) complex of formula [(CoCl<sub>2</sub>)<sub>2</sub>(tpta)]·H<sub>2</sub>O has also been isolated. The crystal and molecular structures of [CoCl(tpta)]ClO<sub>4</sub>·C<sub>6</sub>H<sub>6</sub> and [NiCl(tpta)]ClO<sub>4</sub>·C<sub>6</sub>H<sub>6</sub> have been determined. The complexes have a distorted square-pyramidal geometry around the metal which is co-ordinated by four nitrogen atoms from the tpta ligand and an apical chlorine atom bound on the side of the four pendant chains of the macrocyclic ring. The distortions are greater in the cobalt complexes and are of the trigonal-bipyramidal type.

The significance of tetraazamacrocyclic ligands and their transition-metal complexes lies, mainly, in the resemblance of these systems to the natural products, such as metalloporphyrins, vitamin B<sub>12</sub> or chlorophylls. Related to this is the current interest in functionalized tetraazamacrocycles the potential for metal-ion recognition of which may be influenced by a match between the size of the ligand hole and a particular metal ion as well as by the nature of the substituents.<sup>1,2</sup>

1,4,8,11-Tetrakis(diphenylphosphinomethyl)-1,4,8,11-tetraazacyclotetradecane (tpta) with its eight donor atoms provides a variety of modes of co-ordination. Recently, we reported the synthesis and structural characterization of a number of chromium(0), molybdenum(0) and tungsten(0) complexes with this macrocyclic ligand.<sup>3-5</sup> In both types of species, *i.e.* in the binuclear  $[{M(CO)_4}_2(tpta)]$  and tetranuclear  $[{M(CO)_5}_4-$ (tpta)] complexes, the ligand is co-ordinated to the metal through phosphorus donors from the pendant arms. The metal atoms are not incorporated into the macrocyclic ring because of a greater affinity of these soft metals for phosphorus and the steric requirements of the ligand. By extension of our study to the complexes of other transition metals we expected a different way of co-ordination. Here we report the synthesis of a series of cobalt(II) and nickel(II) complexes having the general formula [MCl(tpta)]X,  $X = ClO_4$ ,  $BF_4$ ,  $PF_6$  or  $B(C_6H_5)_4$ , and also of a binuclear cobalt(II) complex, [(CoCl<sub>2</sub>)<sub>2</sub>(tpta)]·H<sub>2</sub>O. The complexes were characterized for their magnetic, spectroscopic,



† Non-SI unit employed:  $\mu_B \approx 9.27 \times 10^{-24} \mbox{ J } T^{-1}.$ 



**Scheme 1** Five possible configurations of the co-ordinated tetraaza macrocycles, as introduced by Bosnich *et al.*,<sup>6</sup> *trans* **I**–**IV** and *cis* **V**. The signs + and - indicate whether the hydrogen atoms on the nitrogens would lie above or below the plane of the flattened macrocycle

conductometric and structural properties. Crystal and molecular structures were determined for  $[CoCl(tpta)]ClO_4 \cdot C_6H_6$  and  $[NiCl(tpta)]ClO_4 \cdot C_6H_6$ , which showed the ligand to be coordinated to the metal through nitrogen atoms of the macrocyclic ring.

It is known that the parent 14-membered tetraazamacrocycle, *i.e.* 1,4,8,11-tetraazacyclotetradecane (cyclam), can adopt five different configurations in metal complexes, trans I-IV and cis V (Scheme 1, nomenclature given by Bosnich et al.<sup>6</sup>), the most stable being the trans-III configuration. The first-row transition-metal complexes having trans-III configuration are thus square planar or trans-octahedral, with a coplanar set of four nitrogen donor atoms. However, tetraazamacrocycles with tertiary nitrogen atoms in the ring, 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (tmc) for example, very often assume trans-I configuration and show a marked propensity towards five-co-ordination, a fifth unidentate ligand coordinating on the side of the four N-methyl groups of the macrocycle. In such a way the metal atom is pulled out of the macrocyclic plane and the complex is forced to adopt either a square-pyramidal or trigonal-bipyramidal geometry. Different types of intermediate structures along with the two regular

#### Table 1 Microanalytical data for the new complexes

		Analysis (%) *					
Co	omplex	Colour	С	Н	Metal	Cl	
1	[(CoCl <sub>2</sub> ) <sub>2</sub> (tpta)]·H <sub>2</sub> O	Blue	59.45 (59.45)	5.50 (5.45)	9.40 (9.40)	11.25	(11.30)
2a	[CoCl(tpta)]ClO <sub>4</sub>	Light lilac	62.25 (62.75)	5.85 (5.75)	4.95 (4.95)	3.05	(3.00)
3a	[NiCl(tpta)]ClO <sub>4</sub>	Yellow	62.35 (62.75)	5.60 (5.80)	4.60 (4.95)	2.75	(3.00)
2b	[CoCl(tpta)]ClO <sub>4</sub> ·C <sub>6</sub> H <sub>6</sub>	Lilac	64.40 (64.55)	5.85 (5.90)	4.70 (4.65)	2.80	(2.80)
3b	[NiCl(tpta)]ClO <sub>4</sub> ·C <sub>6</sub> H <sub>6</sub>	Green-yellow	64.65 (64.55)	5.95 (5.90)	4.60 (4.65)	2.75	(2.80)
4a	[CoCl(tpta)]BF <sub>4</sub>	Light lilac	62.95 (63.40)	5.60 (5.85)	4.95 (5.00)	3.45	(3.00)
5a	[NiCl(tpta)]BF <sub>4</sub>	Yellow	63.10 (63.45)	5.60 (5.85)	4.80 (5.00)	3.15	(3.00)
4b	[CoCl(tpta)]BF <sub>4</sub> ·C <sub>6</sub> H <sub>6</sub>	Lilac	65.35 (65.20)	6.10 (5.95)	4.60 (4.70)	2.80	(2.85)
5b	[NiCl(tpta)]BF <sub>4</sub> ·C <sub>6</sub> H <sub>6</sub>	Green-yellow	65.00 (65.20)	5.85 (5.95)	4.60 (4.70)	2.70	(2.85)
6	[CoCl(tpta)]PF <sub>6</sub>	Light lilac	59.90 (60.40)	5.70 (5.55)	4.70 (4.80)	3.05	(2.90)
7	[NiCl(tpta)]PF <sub>6</sub>	Yellow	60.05 (60.45)	5.35 (5.55)	4.60 (4.75)	2.75	(2.90)
8	$[CoCl(tpta)][B(C_6H_5)_4]$	Lilac	72.95 (73.45)	6.50 (6.30)	4.20 (4.20)	2.35	(2.50)
9	$[NiCl(tpta)][B(C_6H_5)_4]$	Green-yellow	73.90 (73.44)	6.10 (6.30)	3.85 (4.15)	2.25	(2.50)
* Calculated values are given in parentheses.							

<b>Table 2</b> Magnetic moments, molar conductivities and infrared spectral data for the com
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			Infrared (cm <sup>-1</sup> )		
Complex	$\mu_{eff}/\mu_B$	$\Lambda/\Omega^{-1}  \mathrm{cm^2}  \mathrm{mol^{-1}}$	ν(M–Cl) <sup>b</sup>	Anion( $ClO_4^-, BF_4^-, PF_6^-$ ) vibrations <sup>c</sup>	
1	4.80	19.14	318s, 280m	_	
2a	4.93	18.94	281m	1092vs, 620s	
3a	3.11	24.83	275w	1090vs, 618s	
2b	4.90	21.32	277m	1102vs, 624s	
3b	3.01	20.17	269w	1098vs, 623s	
4a	4.85	19.15	282m	1052vs	
5a	3.62	19.73	273w	1050vs	
4b	4.87	20.75	273m	1063vs	
5b	3.26	20.08	268m	1060vs	
6	5.12	19.81	283m	835vs, 555s	
7	3.35	23.46	275w	834vs, 555s	
8	5.18	14.96	300m	d	
9	3.41	15.95	295m	d	

<sup>a</sup> In nitrobenzene. <sup>b</sup> Polyethylene pellets. <sup>c</sup> KBr pellets. <sup>d</sup> Overlapped by the phenyl vibration bands of the ligand.

Table 3 Electronic spectral data for the complexes \*

Complex	$\lambda_{\rm max}/{\rm nm}~(\epsilon/{\rm dm^3~mol^{-1}~cm^{-1}})$
1	515 (sh), 536 (sh, 76), 592 (444), 635 (sh, 229), 666 (428), 697 (429), 1258 (36)
reflectance	518 (sh), 537, 594, 640 (sh), 665, 707, 1200
2a	518 (61), 577 (39), 666 (sh), 809 (19), 969 (12)
reflectance	512, 584, 800
<b>4a</b>	517 (41), 591 (34), 661 (sh), 724 (sh), 793 (14), 965 (10)
6	519 (66), 583 (45), 660 (sh), 725 (sh), 822 (20), 949 (13)
8	522 (76), 583 (54), 666 (sh), 728 (sh), 827 (22), 967 (sh)
3a	435 (196), 529 (sh), 603 (sh), 733 (65), 883 (sh)
reflectance	360, 438, 531 (sh), 609 (sh), 731
<b>3b</b> reflectance	430, 520 (sh), 620 (sh), 738
5a	433 (197), 523 (sh), 600 (sh), 727 (64), 874 (sh)
7	438 (197), 530 (sh), 604 (sh), 740 (68), 883 (sh)
9	440 (306), 532 (sh), 608 (sh), 741 (102), 890 (sh)

\* In benzene solutions (or solid reflectance, where stated).

geometries were found in metal complexes, depending on the metal and on the nature of the additional ligand.  $^{7-15}$ 

The results obtained here are discussed and correlated with the data available in the literature. This showed tpta to coordinate to Co and Ni in a similar manner to that of tmc. The present study is, however, one of the rare ones in which five-coordinate complexes of functionalized tetraazamacrocycles have been characterized both structurally and spectroscopically.

# **Results and Discussion**

### **Preparation and properties**

The analytical data for complexes 1-9 prepared in this study are

summarized in Table 1 and some of their physical properties are given in Tables 2 and 3.

By mixing the ethanolic solutions of  $CoCl_2 \cdot 6H_2O$  and tpta in a molar ratio of  $\approx 2:1$ , at room temperature, a blue microcrystalline product analysing as  $[(CoCl_2)_2(tpta)] \cdot H_2O$  **1** precipitated after stirring for a short time. In nitrobenzene it behaves as a 1:1 electrolyte (Table 2). In principle, either [CoCl(tpta)]- $[CoCl_3(H_2O)]$  or  $[Co(tpta)][CoCl_4] \cdot H_2O$  {or conceivably  $[Co(H_2O)(tpta)][CoCl_4]$ } would satisfy the above requirements. Single crystals of **1** suitable for X-ray diffraction measurements could not be obtained. The compound was used in the preparation of cobalt complexes in the series **2–9** (below). It is to be noted that the reaction of nickel(II) chloride hexahydrate and tpta, performed under the same experimental conditions as for Co, failed to give an analogous binuclear nickel(II) complex.

Mixing of the appropriate amounts of  $CoCl_2 \cdot 6H_2O$  (or  $NiCl_2 \cdot 6H_2O$ ), tpta and an additional metal or ammonium salt containing the corresponding anion in absolute ethanol, with stirring of the reaction mixture in air and at room temperature, resulted in crystalline compounds satisfying the formula [MCl(tpta)]X [M = Co or Ni; X =  $ClO_4$ , BF<sub>4</sub>, PF<sub>6</sub> or B(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>]. The complexes displayed conductivities, in nitrobenzene, typical of 1:1 electrolytes (Table 2). Somewhat lower values of molar conductivities obtained for [CoCl(tpta)][B(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>] **8** and [NiCl(tpta)][B(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>] **9** may be due to the bulkiness of the tetraphenylborate anion. All cobalt complexes, [CoCl(tpta)]X, could also be obtained by a reaction of **1** and an appropriate metal or ammonium salt.

In the solid state the complexes are fairly stable in air at room temperature. Owing to low solubility in all common organic solvents, recrystallization of the complexes was not possible and prior to elemental analyses the purity was checked by the X-ray powder diffraction and infrared spectral data. In dimethyl sulfoxide (dmso) and dimethylformamide (dmf) they dissolve with a change in colour as a result of decomposition. However, the complexes of both metals dissolved in benzene which is associated with the formation of the solvates [MCl-(tpta)]X·C<sub>6</sub>H<sub>6</sub>. Once these solvate species have formed they cannot be redissolved in benzene. Single crystals of the perchlorate and tetrafluoroborate compounds of both metals were obtained by crystallization from benzene in quantities sufficient for carrying out the complete analyses (Table 1, compounds 2b, 3b, 4b and 5b). The hexafluorophosphate and tetraphenylborate derivatives crystallize poorly and rather slowly and their benzene solvates were not fully analysed.

According to the X-ray powder diffraction patterns the perchlorate, tetrafluoroborate and hexafluorophosphate complexes of both metals {[MCl(tpta)]X (M = Co or Ni; X = ClO<sub>4</sub>, BF<sub>4</sub> or PF<sub>6</sub>)} are all isostructural but different from the corresponding benzene solvate derivatives [MCl(tpta)]X·C<sub>6</sub>H<sub>6</sub>, (M = Co or Ni; X = ClO<sub>4</sub>, BF<sub>4</sub> or PF<sub>6</sub>) which are mutually isostructural as well. It is not unexpected that the tetraphenylborate compounds (**8** and **9**) with the very bulky B(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub><sup>-</sup> anion are not isostructural with the other complexes.

### Spectroscopic and magnetic measurements

Infrared and electronic spectra are indicative of a five-coordinate metal centre present in the [MCl(tpta)]<sup>+</sup> cation.

Selected infrared spectral data of the complexes are given in Table 2 and in Fig. 1. Co-ordination of the ligand to the metal through nitrogen atoms caused the distinctive three-band pattern for the :N(CH<sub>2</sub>)<sub>3</sub> moiety<sup>16</sup> present in the spectrum of the tpta ligand at 2800, 2770 and 2735 cm<sup>-1</sup> to disappear completely in the spectra of complexes. The characteristic bands of the perchlorate, tetrafluoroborate and hexafluorophosphate anions appear in all cases without splitting, indicating that these groups act only as counter ions. All compounds exhibit a weak to medium far-infrared band in the range 270-300 cm<sup>-1</sup>, assigned as a M-Cl stretching vibration.17 In the far-IR spectrum of complex 1 two absorptions, at 318 and 280  $\text{cm}^{-1}$ , are assigned as Co-Cl stretching vibrations. This spectrum displays also weak infrared bands around 3400 and 1600 cm<sup>-1</sup> assignable to the vibrations of the water molecule (O-H stretching and H-O-H bending, respectively).

The UV/VIS absorption maxima of the new complexes, obtained from benzene solutions and solid-reflectance spectra, are reported in Table 3. Some characteristic spectral patterns are shown in Figs. 2 and 3. The electronic spectrum of the binuclear cobalt(II) complex **1** is predominantly that of a tetrahedral cobalt(II) species.<sup>18-21</sup> The spectra of **2–9** can be assigned as consistent with five-co-ordination,<sup>18,22-24</sup> and are in accord with the crystal structure analyses of **2b** and **3b**.



**Fig. 1** The IR spectra of (*a*) the tpta ligand, (*b*) the binuclear cobalt(II) complex [(CoCl<sub>2</sub>)<sub>2</sub>(tpta)]·H<sub>2</sub>O **1** and (*c*) the mononuclear cobalt(II) complex [CoCl(tpta)]PF<sub>6</sub> **6** 



Fig. 2 Electronic absorption spectra of (a)  $[CoCl(tpta)]ClO_4$  2a  $(2 \times 10^{-3} \text{ mol dm}^{-3} \text{ in benzene})$  and (b)  $[(CoCl_2)_2(tpta)] \cdot H_2O$  1  $(10^{-3} \text{ mol dm}^{-3} \text{ in benzene})$ 



**Fig. 3** Electronic absorption spectra of (*a*) [NiCl(tpta)]BF<sub>4</sub> **5a** ( $10^{-3}$  mol dm<sup>-3</sup> in benzene) and (*b*) [NiCl(tpta)]ClO<sub>4</sub> **3a** (solid reflectance)

#### Table 4Selected bond lengths (Å), angles (°) and torsion angles (°) for complexes 2b (M = Co) and 3b (M = Ni)

0	0	0	1 , ,	. ,	
	2b	3b		2b	3b
M-Cl(1)	2.296(2)	2.306(1)	M-N(3)	2.241(4)	2.191(3)
M-N(1)	2.279(4)	2.214(4)	M-N(4)	2.121(4)	2.109(3)
M-N(2)	2.130(4)	2.124(3)			
N(1)-M-N(2)	82.64(14)	84.44(13)	C(10)-N(1)-M	113.1(3)	111.9(2)
N(1)-M-N(3)	168.4(2)	172.35(12)	C(91)-N(1)-M	111.8(3)	113.8(2)
N(1) - M - N(4)	91.50(14)	92.38(13)	C(2)-N(2)-M	107.7(3)	105.2(2)
N(2)-M-N(3)	92.46(14)	92.46(13)	C(3)–N(2)–M	117.4(3)	115.7(3)
N(2)-M-N(4)	140.1(2)	147.79(13)	C(92)–N(2)–M	101.9(3)	106.1(2)
N(3)–M–N(4)	85.48(14)	86.51(13)	C(5)–N(3)–M	111.6(3)	110.8(2)
N(1)-M-Cl(1)	96.81(11)	94.63(9)	C(6)–N(3)–M	100.8(3)	101.4(2)
N(2)–M–Cl(1)	111.76(11)	107.76(10)	C(93)–N(3)–M	117.2(3)	117.7(2)
N(3)–M–Cl(1)	94.83(11)	92.98(9)	C(7)–N(4)–M	105.3(3)	103.4(2)
N(4)–M–Cl(1)	108.15(12)	104.44(9)	C(8)–N(4)–M	115.8(3)	113.3(2)
C(1)–N(1)–M	102.8(3)	103.4(2)	C(94)–N(4)–M	108.3(3)	111.7(2)
C(10)-N(1)-C(1)-C(2)	79.5(5)	80.1(4)	C(5)-N(3)-C(6)-C(7)	76.9(5)	76.8(4)
N(1)-C(1)-C(2)-N(2)	57.2(5)	57.7(5)	N(3)-C(6)-C(7)-N(4)	58.2(5)	60.4(4)
C(1)-C(2)-N(2)-C(3)	-167.0(4)	-165.9(3)	C(6)-C(7)-N(4)-C(8)	-163.1(4)	-162.4(3)
C(2)-N(2)-C(3)-C(4)	173.4(4)	170.7(4)	C(9)-C(8)-N(4)-C(7)	174.4(4)	172.9(4)
N(2)-C(3)-C(4)-C(5)	-67.0(6)	-65.6(5)	N(4)-C(8)-C(9)-C(10)	-70.2(6)	-70.1(5)
C(3)-C(4)-C(5)-N(3)	73.4(6)	72.7(5)	C(8)-C(9)-C(10)-N(1)	70.8(6)	70.3(5)
C(4)-C(5)-N(3)-C(6)	-170.6(4)	-174.8(4)	C(1)-N(1)-C(10)-C(9)	-170.2(4)	-173.2(4)

Average bond lengths and angles within the tpta ligand (m = 1-4; r = macrocyclic ring atom; Ph = phenyl ring atoms)

3b
1.499(1)
1.509(1)
113.2(1)
107.9(3)
110.0(1)
114.8(1)

Average bond lengths and angles within the phenyl rings (n = 1-8)

	2b	3b
C(n1)-C(n2), C(n1)-C(n6)	1.389	1.384(1)
C(n2)-C(n3), C(n5)-C(n6)	1.389	1.386(1)
C(n3)-C(n4), C(n4)-C(n5)	1.364	1.363(1)
C(n2)-C(n1)-C(n6)	118.0	117.9(3)
C(n1)-C(n2)-C(n3), C(n1)-C(n6)-C(n5)	120.6	120.8(4)
C(n2)-C(n3)-C(n4), C(n4)-C(n5)-C(n6)	120.5	120.4(4)
C(n3)-C(n4)-C(n5)	119.9	119.7(2)

The cobalt(II) complexes exhibit room-temperature magnetic moments between  $\mu_{eff} = 4.8$  and 5.2  $\mu_B$  and the nickel(II) complexes between  $\mu_{eff} = 3.0$  and 3.6  $\mu_B$  (Table 2), indicative of high-spin d<sup>7</sup> and d<sup>8</sup> electron configurations, respectively.<sup>18</sup>

#### Crystal structures of complexes 2b and 3b

Single crystals of  $[CoCl(tpta)]ClO_4 \cdot C_6H_6$  **2b** and  $[NiCl(tpta)]-ClO_4 \cdot C_6H_6$  **3b**, suitable for X-ray analysis, were formed by slow evaporation of benzene solutions of **2a** and **3a**, respectively.

Complexes **2b** and **3b** were found to be isostructural. The crystal structures consist of  $[MCl(tpta)]^+$  cations (M = Co in **2b** and Ni in **3b**), perchlorate anions and benzene molecules (Fig. 4). The oxygen atoms from the perchlorate anion are too far away to form any interaction with the metal, and the benzene solvent molecules form only van der Waals contacts.

The structure of the  $[MCl(tpta)]^+$  cation is shown in Fig. 5. Selected bond distances, angles and torsion angles are listed in Table 4. The metal atom is co-ordinated by four nitrogen atoms from the tpta macrocycle and an apical chlorine atom forming a distorted square pyramid. The distortion is greater in **2b** and is towards a trigonal-bipyramidal arrangement with the Cl(1) atom in equatorial position and N(1) and N(3) in apical positions. The chlorine atom is bonded to the metal on the side of the four pendant diphenylphosphinomethyl groups and inside the cavity they form. The configuration of the macrocycle can



Fig. 4 Packing diagram of complexes [CoCl(tpta)]ClO<sub>4</sub>·C<sub>6</sub>H<sub>6</sub> 2b and [NiCl(tpta)]ClO<sub>4</sub>·C<sub>6</sub>H<sub>6</sub> 3b

be characterized as *trans*-**I** using the Bosnich notation<sup>6</sup> or R, S, R, S. It can be seen in the view of the [MCl(tpta)]<sup>+</sup> cation given in the packing diagram in Fig. 4 that the four diphenyl-phosphinomethyl groups point upward at the same side of the macrocyclic ring. This stereoisomer is kinetically stable although it is not the most thermodynamically stable one.<sup>25</sup>

The *trans* M–N distances are either both long [M–N(1) and M–N(3) of 2.279(4) and 2.241(4) Å in **2b**; 2.214(4) and 2.191(3) Å in **3b**] or short [M–N(2) and M–N(4) of 2.130(4) and 2.121(4) Å in **2b**; 2.124(3) and 2.109(3) Å in **3b**]. The difference in the



Fig. 5 Structure of [NiCl(tpta)]<sup>+</sup> in complex 3b. The [CoCl(tpta)]<sup>+</sup> cation in 2b is isostructural and has the same atom numbering scheme. The thermal ellipsoids are at the 50% probability level

bond lengths of these two sets of values is much less pronounced for 3b although it is still significant. The long set of bond distances is significantly longer in 2b than in 3b and represents the greatest difference between these two complexes. The bond angles N(1)-M-N(3) associated with the long set of distances are  $168.4(2)^{\circ}$  for Co and  $172.4(1)^{\circ}$  for Ni, while the bending away from Cl is much greater for the shorter set, N(2)-M-N(4) is 140.1(2)° for Co and 147.8(1)° for Ni. The four tpta N atoms are not planar and the distortion is of a tetrahedral nature, N(1) and N(3) being above and N(2) and N(4) below the least-squares plane by approximately 0.2 Å. The Co and Ni atoms are displaced above this plane by 0.477(2) and 0.366(2) Å, respectively.

It is interesting to make comparison with complexes of similar tetraazamacrocyclic ligands. The only examples of fiveco-ordination where the structures of both cobalt and nickel complexes were determined are those with N3- in the apical position, and methyl groups as substituents at N,  $[Co(N_3) (tmc)]ClO_4^{11}$  and  $[Ni(N_3)(tmc)]ClO_4^{.8}$  The structure of  $[Co-(N_3)(tmc)]^+$  also has two short Co–N distances [2.106(5) and 2.130(5) Å] and two long ones [2.213(5) and 2.247(5) Å], with the angle associated with the long distances being larger  $[167.8(2)^{\circ}]$  than the other one  $[140.8(2)^{\circ}]$ . The authors describe it as intermediate between square-pyramidal and trigonalbipyramidal (with the azide ion in equatorial position). The angles and the short bond lengths are similar as in 2b, but the long ones are significantly shorter than in **2b**. In [Ni(N<sub>3</sub>)(tmc)] the Ni-N bond lengths are shorter [2.102(8) and 2.105(8) Å] and there are no significant differences among them nor among the trans N-Ni-N angles since the crystallographic plane of symmetry passes through atoms C(4) and C(9) (the labelling of the macrocycle is the same as in the present structures) and the four tmc N atoms are coplanar. The co-ordination is distorted square pyramidal. The origin of the structural difference between the complexes of Co and Ni was assigned to the difference in the d-electron configuration.<sup>11</sup> We can conclude that the difference between **2b** and **3b**, as well as the difference between the tpta and tmc complexes, is influenced not only by electronic but also by steric effects. The diphenylphosphinomethyl group represents the bulkiest nitrogen substituent in all of the structures of 14-membered tetraazamacrocycle complexes. The steric interactions of the phenyl rings prevent closer approach of N(1) and N(3) atoms and cause lengthening of the corresponding M-N distances and further deformation of the square-pyramidal co-ordination in both 2b and 3h

Distorted square-pyramidal co-ordination is also found in some porphyrin complexes containing the CoN<sub>4</sub>Cl structural unit.<sup>26</sup> The authors suggest that the out-of-plane displacements could not be attributed to a variation in size of the N<sub>4</sub> core but mainly to the presence of chlorine in the fifth co-ordination site.26

The zinc(11) complexes [ZnX(tmc)]ClO<sub>4</sub> were found as deformed square pyramidal when  $X = Cl^{10}$  or deformed trigonal bipyramidal when  $X = O_2 COCH_3$ .<sup>27</sup> The origin of this difference is possibly the different X ligand. All of the mentioned tmc complexes have the trans-I configuration of the macrocycle. It is also found in  $[NiX(tmc)]^+$ ,  $X = O_2COCH_3$ , (CH<sub>3</sub>)<sub>2</sub>NCHO or CH<sub>3</sub>CN<sup>28</sup> and in [Cu(H<sub>2</sub>O)(tmc)]<sup>+</sup>.<sup>1</sup>

# Experimental

### Materials

1,4,8,11-Tetrakis(diphenylphosphinomethyl)-1,4,8,11-tetraazacyclotetradecane was prepared as previously described,<sup>29</sup> including the reaction of 1,4,8,11-tetraazacyclotetradecane and diphenylphosphine, which were used as received. All other chemicals, i.e. CoCl<sub>2</sub>·6H<sub>2</sub>O, NiCl<sub>2</sub>·6H<sub>2</sub>O, Co(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O, Ni(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O, NaClO<sub>4</sub>·H<sub>2</sub>O, NaBF<sub>4</sub>, NH<sub>4</sub>PF<sub>6</sub> and NaB-(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>, were of reagent grade and used as supplied. The solvents were purified and dried by standard methods.

#### **Physical measurements**

Elemental analyses for C, H, Cl, Co and Ni were obtained from the Central Analytical Service of Ruder Bošković Institute. Infrared spectra were recorded on a Perkin-Elmer model 580B spectrophotometer on KBr pellets in the region 4000-200 cm<sup>-1</sup> and on polyethylene pellets in the region  $400-200 \text{ cm}^{-1}$ . The electrical conductivity of 10<sup>-3</sup> mol dm<sup>-3</sup> solutions in nitrobenzene was measured on a Tacussel conductivity bridge, type Cd 7, at 25 °C. Magnetic susceptibility measurements were performed at room temperature, by the Gouy method, using CuSO<sub>4</sub>·5H<sub>2</sub>O as calibrant. Electronic spectra were measured on a UV-VIS-NIR Cary-5 spectrometer. Solution spectra were run in C<sub>6</sub>H<sub>6</sub> using 1 cm silica cells. For solid-state spectra, Nujol mulls of the complexes were soaked into Filtrak No.391 filterpaper with Nujol soaked filter-paper as the reference.

### **Preparation of complexes**

In general, the complexes were prepared by mixing appropriate amounts of the reacting components (*i.e.* tpta,  $CoCl_2 \cdot 6H_2O$  or NiCl<sub>2</sub>·6H<sub>2</sub>O and a corresponding counter ion salt) in absolute ethanol and by stirring the resulting suspension for the required period of time, in air and at room temperature. The cobalt complexes, [CoCl(tpta)]X,  $X = ClO_4$ ,  $BF_4$ ,  $PF_6$  or  $B(C_6H_5)_4$ , could also be obtained by starting from compound 1. In that case a higher excess of the corresponding counter ion salt and a longer stirring time were needed for completion of the reaction. As an illustration, for tetrafluoroborate and tetraphenylborate derivatives (4a and 8) both procedures are described below, and only one procedure is given for the other compounds.

[(CoCl<sub>2</sub>)<sub>2</sub>(tpta)]·H<sub>2</sub>O 1. A mixture of tpta (0.198 g, 0.20 mmol), CoCl<sub>2</sub>·6H<sub>2</sub>O (0.107 g, 0.45 mmol) and absolute ethanol (15 cm<sup>3</sup>) was stirred in air, at room temperature, for 3 h. The blue microcrystalline precipitate of 1 was then filtered off, washed with a few cm<sup>3</sup> of absolute ethanol and dried in vacuo. The yield was 0.215 g (85%).

[CoCl(tpta)]ClO<sub>4</sub> 2a. The compound tpta (0.110 g, 0.11 mmol) and CoCl<sub>2</sub>·6H<sub>2</sub>O (0.060 g, 0.25 mmol) were mixed in absolute ethanol (13 cm<sup>3</sup>) and stirred for 3 h. Then, without

#### Table 5 Crystal data, data collection and structure refinement parameters for complexes 2b and 3b \*

	2b	3b
Empirical formula	C <sub>69</sub> H <sub>74</sub> Cl <sub>9</sub> CoN4O4P4	CeoH74CloN4NiO4P4
M	1265.02	1264.80
a/Å	13.468(4)	13.459(3)
b/Å	16.752(5)	16.735(4)
c/Å	17.325(6)	17.383(5)
$\alpha /^{\circ}$	67.19(1)	67.05(1)
β/°	69.41(1)	69.22(1)
$\gamma/^{\circ}$	68.62(1)	68.48(1)
$U/Å^3$	3253(2)	3250(1)
λ/Å	0.710 73	1.541 86
$\mu/cm^{-1}$	4.94	25.13
Transmission factor range		0.74-0.95
<i>F</i> (000)	1326	1328
Crystal size/mm	0.06  imes 0.26  imes 0.28	0.12 imes 0.22 imes 0.25
Scan type	ω	$\theta$ -2 $\theta$
$\theta$ Range for data collection/°	2.16-27.04	2.85-60.02
Index ranges	$-15 \le h \le 13, -19 \le k \le 19,$	$-14 \le h \le 14, -17 \le k \le 18,$
5	$0 \le l \le 21$	$0 \le l \le 19$
No. reflections collected	11 340	9740
No. independent reflections $(R_{int})$	10 284 (0.049)	9526 (0.057)
No. observed reflections <sup><i>b</i></sup>	3692	6150
No. parameters	640	740
$R^{b,c}$	0.0684	0.0631
$R'^{b,d}$	0.0821	0.1569
g in w <sup>e</sup>	0.0275	0.1295
Goodness of fit on $F^{2b}$	1.184	1.050
Largest difference peak and hole/e ${\rm \AA^{-3}}$	0.322, -0.285	0.828, f - 0.525
Largest difference peak and hole/e Å <sup><math>-3</math></sup>	0.322, -0.285	$0.828,^{f} - 0.525$

<sup>*a*</sup> Details in common: triclinic, space group  $P\bar{l}$ ; Z = 2;  $D_c = 1.292$  g cm<sup>-3</sup>; maximum  $\Delta/\sigma$  0.001. <sup>*b*</sup> Criterion  $I > 2\sigma(I)$ . <sup>*c*</sup>  $R = \Sigma ||F_o| - |F_c||/\Sigma |F_o|$ . <sup>*d*</sup>  $R' = [\Sigma w (F_o^2 - F_c^2)^2 / \Sigma w (F_o^2)^2]^2$ . <sup>*e*</sup>  $w = 1/\{\sigma^2 (F_o^2) + [g(F_o^2 + 2F_c^2)/3]^2\}$ . <sup>*f*</sup> 1.02 Å from Ni.

separating the precipitate,  $Co(ClO_4)_2$ .6H<sub>2</sub>O (0.110 g, 0.30 mmol) was added and the reaction mixture stirred for 3 h. The resulting light lilac solid of **2a** was filtered off, washed with a small quantity of absolute ethanol and dried *in vacuo* over molecular sieves. The yield was 0.100 g (76%).

The same compound in similar yield was obtained by using  $NaClO_4$ ·H<sub>2</sub>O instead of Co(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O.

**[CoCl(tpta)]BF<sub>4</sub> 4a.** *Procedure (a).* A mixture of tpta (0.149 g, 0.15 mmol),  $CoCl_2 \cdot 6H_2O$  (0.048 g, 0.20 mmol) and  $NaBF_4$  (0.044 g, 0.40 mmol) in absolute ethanol (12 cm<sup>3</sup>) was stirred at room temperature for 4 h. The resulting light lilac precipitate (0.135 g, 77%) was filtered off, washed with a small amount of absolute ethanol and dried *in vacuo* over molecular sieves.

*Procedure (b).* A mixture of complex **1** (0.095 g, 0.075 mmol), NaBF<sub>4</sub> (0.033 g, 0.30 mmol) and absolute ethanol (10 cm<sup>3</sup>) was stirred at room temperature overnight. The precipitate (yield 0.058 g, 66%) was filtered off, washed and dried as above.

**[CoCl(tpta)]PF<sub>6</sub> 6.** A mixture of tpta (0.099 g, 0.10 mmol),  $CoCl_2 \cdot 6H_2O$  (0.040 g, 0.17 mmol) and  $NH_4PF_6$  (0.029 g, 0.18 mmol) was stirred in absolute ethanol (10 cm<sup>3</sup>) for 4 h. The resulting light lilac precipitate was filtered off and dried as usual. The yield was 0.095 g (77%).

**[CoCl(tpta)][B(C**<sub>6</sub>**H**<sub>5</sub>)<sub>4</sub>] **8.** *Procedure* (*a*). A mixture of tpta (0.110 g, 0.11 mmol),  $CoCl_2 \cdot 6H_2O$  (0.048 g, 0.20 mmol) and  $NaB(C_6H_5)_4$  (0.075 g, 0.22 mmol) in absolute ethanol (10 cm<sup>3</sup>) was stirred for 4 h. The lilac fine-crystalline product was filtered off, washed with dry ethanol and dried *in vacuo*. The yield was 0.118 g (76%).

*Procedure (b).* The salt NaB( $C_6H_5$ )<sub>4</sub> (0.188 g, 0.55 mmol) was added to a suspension of complex **1** (0.140 g, 0.11 mmol) in absolute ethanol (15 cm<sup>3</sup>) and the reaction mixture was stirred overnight. The lilac precipitate was filtered off, washed and dried as above. The yield was 0.074 g (48%).

[NiCl(tpta)]ClO<sub>4</sub> 3a. A mixture of tpta (0.099 g, 0.10 mmol),

NiCl<sub>2</sub>·6H<sub>2</sub>O (0.036 g, 0.15 mmol) and Ni(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.062 g, 0.17 mmol) was stirred in absolute ethanol (10 cm<sup>3</sup>) at room temperature for 2 h. The resulting yellow precipitate, yield 0.085 g (72%), was filtered off, washed out with absolute ethanol and dried *in vacuo* over molecular sieves.

**[NiCl(tpta)]BF<sub>4</sub> 5a.** Absolute ethanol (10 cm<sup>3</sup>) was added to a mixture of tpta (0.130 g, 0.13 mmol), NiCl<sub>2</sub>·6H<sub>2</sub>O (0.040 g, 0.17 mmol) and NaBF<sub>4</sub> (0.029 g, 0.26 mmol) and the suspension stirred in air at room temperature. The yellow crystalline precipitate that resulted after stirring for 2 h was separated, washed and dried as above. The yield was 0.090 g (59%).

**[NiCl(tpta)]PF<sub>6</sub> 7.** The compound tpta (0.099 g, 0.10 mmol), NiCl<sub>2</sub>·6H<sub>2</sub>O (0.036 g, 0.15 mmol) and NH<sub>4</sub>PF<sub>6</sub> (0.026 g, 0.16 mmol) were mixed and stirred in absolute ethanol (10 cm<sup>3</sup>) at room temperature for 3 h. The yellow precipitate of **7** was then filtered off, washed and dried as usual. The yield was 0.092 g (75%).

**[NiCl(tpta)][B(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>] 9.** A mixture of tpta (0.130 g, 0.13 mmol), NiCl<sub>2</sub>·6H<sub>2</sub>O (0.048 g, 0.20 mmol) and NaB(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub> (0.096 g, 0.28 mmol) was stirred in absolute ethanol (15 cm<sup>3</sup>) at room temperature for 4 h. The green-yellow precipitate that resulted was filtered off, washed with dry solvent and dried *in vacuo* over molecular sieves. The yield was 0.144 g (78%).

# Crystallography

**Crystal data and data collection parameters.** X-Ray data were collected at room temperature on the Philips PW1100 diffractometer (upgraded by Stoe). The unit-cell parameters and details of data collection are given in Table 5. Unit-cell dimensions were obtained by least-squares refinement of 28 reflections,  $21.3 < 2\theta < 29.8^{\circ}$  for complex **2b** and  $20.7 < 2\theta < 57.6^{\circ}$  for **3b**. Standard reflections monitored every 90 min indicated no significant change of the intensities for **2b** and a drop amounting to 8% for **3b**. An empirical absorption correction was applied for **3b**.

Structure solution and refinement. The structure of complex 2b was solved by the heavy-atom method. Subsequent full-matrix least-squares refinement on  $F^2$  and Fourier difference maps revealed all non-hydrogen atoms. The positions of the heavy atom and the macrocyclic ring atoms were used as a starting model in 3b. Owing to the small number of collected data (small crystal) in relation to the number of parameters the phenyl atoms were refined as rigid groups in **2b**. First the atoms were fitted by a regular hexagon, but much better results were obtained by defining a fragment with the bond lengths and angles in the phenyl rings obtained in our previous study of a chromium(0) complex with tpta.<sup>5</sup> A decrease of the endocyclic angle  $\alpha$  is caused by the  $\sigma$ -electron release from phosphorus and a difference also occurs in the bond lengths. The values used are given in Table 4. Hydrogen atom positions were included using a riding model. Anisotropic  $U_{ij}$  were used for all non-hydrogen atoms and the hydrogen atoms were assigned values of 1.2 U of their parent atom. The structure solution, refinement and molecular graphics computing was performed on an IBM PC/ AT-compatible microcomputer using SHELXS 86,<sup>30</sup> SHELXL 96,<sup>31</sup> ORTEP 92,<sup>32</sup> and PLUTON <sup>33</sup> programs.

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