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_4, BF_4, PF_6 and $B(C_6H_5)_4$]. Crystal structures of [CoCl(tpta)]$ClO_4\cdot C_6H_6$ and [NiCl(tpta)]$ClO_4\cdot C_6H_6$ †

Pavica Planinić,*[a] Dubravka Matković-Čalogović[b] and Henrika Meider[a]

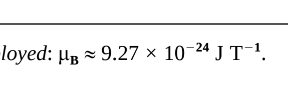
[a] *Department of Physical Chemistry, Ruđer Bošković Institute, Bijenička 54, 10000 Zagreb, Croatia*

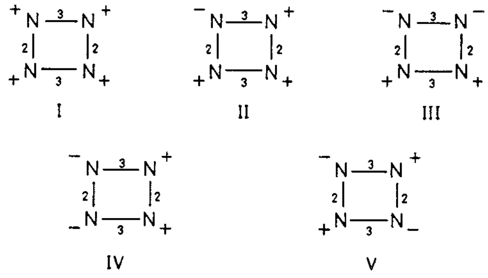
[b] *Laboratory of General and Inorganic Chemistry, Faculty of Science, University of Zagreb, Zvonimirova 8, 10000 Zagreb, Croatia*

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_4, PF_6 or $B(C_6H_5)_4$]. A binuclear cobalt(II) complex of formula [$(CoCl_2)_2$(tpta)]$\cdot H_2O$ has also been isolated. The crystal and molecular structures of [CoCl(tpta)]$ClO_4\cdot C_6H_6$ and [NiCl(tpta)]$ClO_4\cdot C_6H_6$ 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_{12} 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.[1,2]

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.[3–5] 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, [$(CoCl_2)_2$(tpta)]$\cdot H_2O$. The complexes were characterized for their magnetic, spectroscopic, 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 co-ordinated to the metal through nitrogen atoms of the macrocyclic ring.





Scheme 1 Five possible configurations of the co-ordinated tetraaza macrocycles, as introduced by Bosnich *et al.*,[6] *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

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.*[6]), 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 co-ordinating 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

---

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

Table 1 Microanalytical data for the new complexes

		Analysis (%)*			
Complex	Colour	C	H	Metal	Cl
1 $[(CoCl_2)_2(tpta)]\cdot H_2O$	Blue	59.45 (59.45)	5.50 (5.45)	9.40 (9.40)	11.25 (11.30)
2a $[CoCl(tpta)]ClO_4$	Light lilac	62.25 (62.75)	5.85 (5.75)	4.95 (4.95)	3.05 (3.00)
3a $[NiCl(tpta)]ClO_4$	Yellow	62.35 (62.75)	5.60 (5.80)	4.60 (4.95)	2.75 (3.00)
2b $[CoCl(tpta)]ClO_4\cdot C_6H_6$	Lilac	64.40 (64.55)	5.85 (5.90)	4.70 (4.65)	2.80 (2.80)
3b $[NiCl(tpta)]ClO_4\cdot C_6H_6$	Green-yellow	64.65 (64.55)	5.95 (5.90)	4.60 (4.65)	2.75 (2.80)
4a $[CoCl(tpta)]BF_4$	Light lilac	62.95 (63.40)	5.60 (5.85)	4.95 (5.00)	3.45 (3.00)
5a $[NiCl(tpta)]BF_4$	Yellow	63.10 (63.45)	5.60 (5.85)	4.80 (5.00)	3.15 (3.00)
4b $[CoCl(tpta)]BF_4\cdot C_6H_6$	Lilac	65.35 (65.20)	6.10 (5.95)	4.60 (4.70)	2.80 (2.85)
5b $[NiCl(tpta)]BF_4\cdot C_6H_6$	Green-yellow	65.00 (65.20)	5.85 (5.95)	4.60 (4.70)	2.70 (2.85)
6 $[CoCl(tpta)]PF_6$	Light lilac	59.90 (60.40)	5.70 (5.55)	4.70 (4.80)	3.05 (2.90)
7 $[NiCl(tpta)]PF_6$	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.

Table 2 Magnetic moments, molar conductivities[a] and infrared spectral data for the complexes

			Infrared (cm^{-1})	
Complex	μ_{eff}/μ_B	Λ/Ω^{-1} cm^2 mol^{-1}	ν(M−Cl)[b]	Anion(ClO_4^-,BF_4^-,PF_6^-) vibrations[c]
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*

[a] In nitrobenzene. [b] Polyethylene pellets. [c] KBr pellets. [d] Overlapped by the phenyl vibration bands of the ligand.

Table 3 Electronic spectral data for the complexes*

Complex	λ_{max}/nm (ε/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
4a	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
3b 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 ≈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_4, PF_6 or $B(C_6H_5)_4$]. The complexes displayed conductivities, in nitrobenzene, typical of 1:1 electrolytes (Table 2). Somewhat lower values of molar conductivities obtained for [CoCl(tpta)][$B(C_6H_5)_4$] **8** and [NiCl(tpta)][$B(C_6H_5)_4$] **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$\cdot C_6H_6$. 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_4, BF_4 or PF_6)} are all isostructural but different from the corresponding benzene solvate derivatives [MCl(tpta)]X$\cdot C_6H_6$, (M = Co or Ni; X = ClO_4, BF_4 or PF_6) which are mutually isostructural as well. It is not unexpected that the tetraphenylborate compounds (**8** and **9**) with the very bulky $B(C_6H_5)_4{}^-$ anion are not isostructural with the other complexes.

Spectroscopic and magnetic measurements

Infrared and electronic spectra are indicative of a five-co-ordinate metal centre present in the [MCl(tpta)]$^+$ 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 $:N(CH_2)_3$ moiety[16] present in the spectrum of the tpta ligand at 2800, 2770 and 2735 cm^{-1} 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^{-1}, assigned as a M–Cl stretching vibration.[17] In the far-IR spectrum of complex **1** two absorptions, at 318 and 280 cm^{-1}, are assigned as Co–Cl stretching vibrations. This spectrum displays also weak infrared bands around 3400 and 1600 cm^{-1} 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.[18–21] The spectra of **2**–**9** can be assigned as consistent with five-co-ordination,[18,22–24] and are in accord with the crystal structure analyses of **2b** and **3b**.

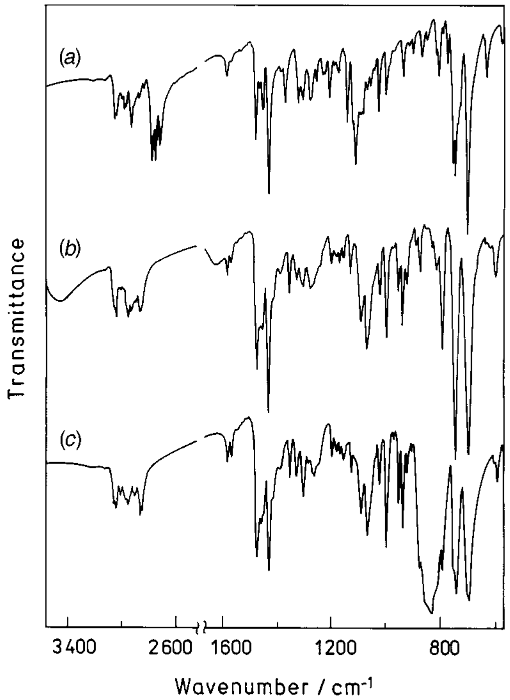


Fig. 1 The IR spectra of (*a*) the tpta ligand, (*b*) the binuclear cobalt(II) complex [$(CoCl_2)_2$(tpta)]$\cdot H_2O$ **1** and (*c*) the mononuclear cobalt(II) complex [CoCl(tpta)]PF_6 **6**

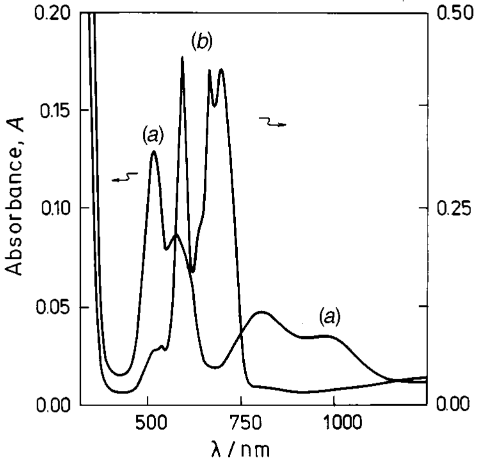


Fig. 2 Electronic absorption spectra of (*a*) [CoCl(tpta)]ClO_4 **2a** (2×10^{-3} mol dm^{-3} in benzene) and (*b*) [$(CoCl_2)_2$(tpta)]$\cdot H_2O$ **1** (10^{-3} mol dm^{-3} in benzene)

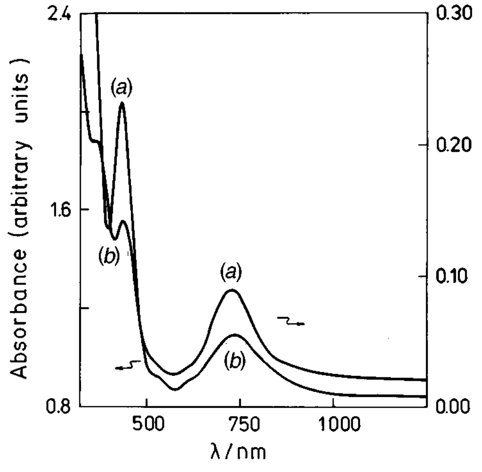


Fig. 3 Electronic absorption spectra of (*a*) [NiCl(tpta)]BF_4 **5a** (10^{-3} mol dm^{-3} in benzene) and (*b*) [NiCl(tpta)]ClO_4 **3a** (solid reflectance)

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

	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)

	2b	**3b**		**2b**	**3b**
P−C(9*m*)	1.874(2)	1.868(2)	N−C(r)	1.491(1)	1.499(1)
P−C (Ph)	1.826(1)	1.833(1)	C(r)−C(r)	1.509(1)	1.509(1)
C (Ph)−P−C (Ph)	102.7(2)	102.6(3)	N−C(r)−C(r)	113.7(1)	113.2(1)
C (Ph)−P−C(9*m*)	100.7(1)	100.6(1)	C(r)−N−C(r)	108.0(1)	107.9(3)
N−C(9*m*)−P	116.9(2)	116.3(3)	C(r)−N−C(9*m*)	110.0(1)	110.0(1)
C (Ph)−C (Ph)−P	120.9(1)	121.0(1)	C(r)−C(r)−C(r)	115.4(1)	114.8(1)

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

	2b	**3b**
C(*n*1)−C(*n*2), C(*n*1)−C(*n*6)	1.389	1.384(1)
C(*n*2)−C(*n*3), C(*n*5)−C(*n*6)	1.389	1.386(1)
C(*n*3)−C(*n*4), C(*n*4)−C(*n*5)	1.364	1.363(1)
C(*n*2)−C(*n*1)−C(*n*6)	118.0	117.9(3)
C(*n*1)−C(*n*2)−C(*n*3), C(*n*1)−C(*n*6)−C(*n*5)	120.6	120.8(4)
C(*n*2)−C(*n*3)−C(*n*4), C(*n*4)−C(*n*5)−C(*n*6)	120.5	120.4(4)
C(*n*3)−C(*n*4)−C(*n*5)	119.9	119.7(2)

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

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.

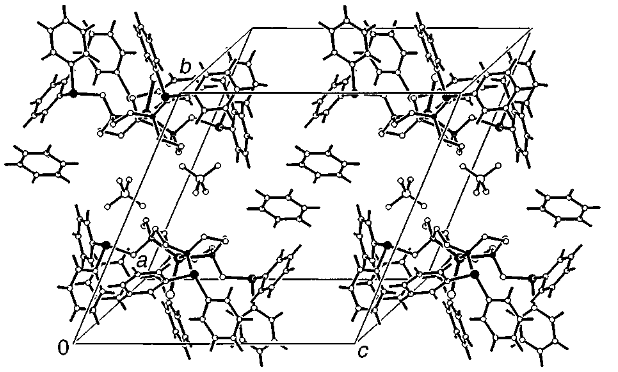


Fig. 4 Packing diagram of complexes $[CoCl(tpta)]ClO_4\cdot C_6H_6$ **2b** and $[NiCl(tpta)]ClO_4\cdot C_6H_6$ **3b**

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 be characterized as *trans*-**I** using the Bosnich notation[6] or *R,S,R,S*. It can be seen in the view of the $[MCl(tpta)]^+$ cation given in the packing diagram in Fig. 4 that the four diphenylphosphinomethyl 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.[25]

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

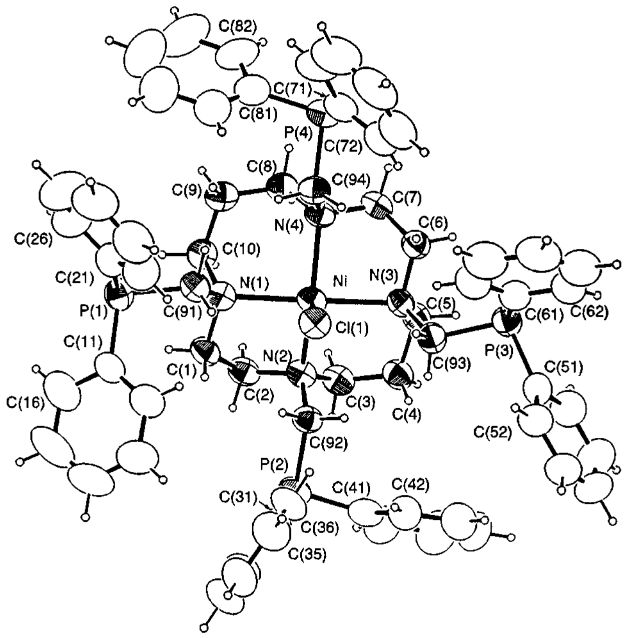


Fig. 5 Structure of [NiCl(tpta)]$^+$ in complex **3b**. The [CoCl(tpta)]$^+$ cation in **2b** is isostructural and has the same atom numbering scheme. The thermal ellipsoids are at the 50% probability level

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)° for Co and 172.4(1)° 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 five-co-ordination where the structures of both cobalt and nickel complexes were determined are those with N_3^- 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)°] than the other one [140.8(2)°]. The authors describe it as intermediate between square-pyramidal and trigonal-bipyramidal (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_3)(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.[11] 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 **3b**.

Distorted square-pyramidal co-ordination is also found in some porphyrin complexes containing the CoN_4Cl structural unit.[26] The authors suggest that the out-of-plane displacements could not be attributed to a variation in size of the N_4 core but mainly to the presence of chlorine in the fifth co-ordination site.[26b]

The zinc(II) complexes [ZnX(tmc)]ClO_4 were found as deformed square pyramidal when X = Cl[10] or deformed trigonal bipyramidal when X = O_2CCH_3.[27] 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_2CCH_3, $(CH_3)_2NCHO$ or CH_3CN[28] and in [Cu(H_2O)(tmc)]$^+$.[12]

Experimental

Materials

1,4,8,11-Tetrakis(diphenylphosphinomethyl)-1,4,8,11-tetraazacyclotetradecane was prepared as previously described,[29] including the reaction of 1,4,8,11-tetraazacyclotetradecane and diphenylphosphine, which were used as received. All other chemicals, *i.e.* $CoCl_2{\cdot}6H_2O$, $NiCl_2{\cdot}6H_2O$, $Co(ClO_4)_2{\cdot}6H_2O$, $Ni(ClO_4)_2{\cdot}6H_2O$, $NaClO_4{\cdot}H_2O$, $NaBF_4$, NH_4PF_6 and $NaB(C_6H_5)_4$, 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 Ruđer Bošković Institute. Infrared spectra were recorded on a Perkin-Elmer model 580B spectrophotometer on KBr pellets in the region 4000–200 cm^{-1} and on polyethylene pellets in the region 400–200 cm^{-1}. The electrical conductivity of 10^{-3} mol dm^{-3} 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 $CuSO_4{\cdot}5H_2O$ as calibrant. Electronic spectra were measured on a UV-VIS-NIR Cary-5 spectrometer. Solution spectra were run in C_6H_6 using 1 cm silica cells. For solid-state spectra, Nujol mulls of the complexes were soaked into Filtrak No.391 filter-paper 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 $NiCl_2{\cdot}6H_2O$ 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.

[$(CoCl_2)_2$(tpta)]·H_2O 1. A mixture of tpta (0.198 g, 0.20 mmol), $CoCl_2{\cdot}6H_2O$ (0.107 g, 0.45 mmol) and absolute ethanol (15 cm^3) 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^3 of absolute ethanol and dried *in vacuo*. The yield was 0.215 g (85%).

[CoCl(tpta)]ClO_4 2a. The compound tpta (0.110 g, 0.11 mmol) and $CoCl_2{\cdot}6H_2O$ (0.060 g, 0.25 mmol) were mixed in absolute ethanol (13 cm^3) and stirred for 3 h. Then, without

Table 5 Crystal data, data collection and structure refinement parameters for complexes **2b** and **3b**[a]

	2b	**3b**
Empirical formula	$C_{68}H_{74}Cl_2CoN_4O_4P_4$	$C_{68}H_{74}Cl_2N_4NiO_4P_4$
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)
α/°	67.19(1)	67.05(1)
β/°	69.41(1)	69.22(1)
γ/°	68.62(1)	68.48(1)
U/Å^3	3253(2)	3250(1)
λ/Å	0.710 73	1.541 86
μ/cm^{-1}	4.94	25.13
Transmission factor range		0.74–0.95
$F(000)$	1326	1328
Crystal size/mm	0.06 × 0.26 × 0.28	0.12 × 0.22 × 0.25
Scan type	ω	θ–2θ
θ Range for data collection/°	2.16–27.04	2.85–60.02
Index ranges	$-15 \leqslant h \leqslant 13, -19 \leqslant k \leqslant 19, 0 \leqslant l \leqslant 21$	$-14 \leqslant h \leqslant 14, -17 \leqslant k \leqslant 18, 0 \leqslant l \leqslant 19$
No. reflections collected	11 340	9740
No. independent reflections (R_{int})	10 284 (0.049)	9526 (0.057)
No. observed reflections[b]	3692	6150
No. parameters	640	740
R[b,c]	0.0684	0.0631
R'[b,d]	0.0821	0.1569
g in w[e]	0.0275	0.1295
Goodness of fit on F^2[b]	1.184	1.050
Largest difference peak and hole/e Å^{-3}	0.322, −0.285	0.828,[f] −0.525

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

separating the precipitate, $Co(ClO_4)_2\cdot 6H_2O$ (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 $NaClO_4\cdot H_2O$ instead of $Co(ClO_4)_2\cdot 6H_2O$.

[CoCl(tpta)]BF$_4$ 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^3) 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), $NaBF_4$ (0.033 g, 0.30 mmol) and absolute ethanol (10 cm^3) was stirred at room temperature overnight. The precipitate (yield 0.058 g, 66%) was filtered off, washed and dried as above.

[CoCl(tpta)]PF$_6$ 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^3) 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$_6$H$_5$)$_4$] 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^3) 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 $NaB(C_6H_5)_4$ (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^3) 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$_4$ 3a. A mixture of tpta (0.099 g, 0.10 mmol), $NiCl_2\cdot 6H_2O$ (0.036 g, 0.15 mmol) and $Ni(ClO_4)_2\cdot 6H_2O$ (0.062 g, 0.17 mmol) was stirred in absolute ethanol (10 cm^3) 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$_4$ 5a. Absolute ethanol (10 cm^3) was added to a mixture of tpta (0.130 g, 0.13 mmol), $NiCl_2\cdot 6H_2O$ (0.040 g, 0.17 mmol) and $NaBF_4$ (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$_6$ 7. The compound tpta (0.099 g, 0.10 mmol), $NiCl_2\cdot 6H_2O$ (0.036 g, 0.15 mmol) and NH_4PF_6 (0.026 g, 0.16 mmol) were mixed and stirred in absolute ethanol (10 cm^3) 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$_6$H$_5$)$_4$] 9. A mixture of tpta (0.130 g, 0.13 mmol), $NiCl_2\cdot 6H_2O$ (0.048 g, 0.20 mmol) and $NaB(C_6H_5)_4$ (0.096 g, 0.28 mmol) was stirred in absolute ethanol (15 cm^3) 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, $21.3 < 2\theta < 29.8°$ for complex **2b** and $20.7 < 2\theta < 57.6°$ 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.[5] A decrease of the endocyclic angle α is caused by the σ-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,[30] SHELXL 96,[31] ORTEP 92,[32] and PLUTON[33] programs.

CCDC reference number 186/609.

Acknowledgements

We thank the Ministry of Science and Technology of the Republic of Croatia for financial support.

References

1 L. F. Lindoy, *The Chemistry of Macrocyclic Ligand Complexes*, Cambridge University Press, Cambridge, 1990; R. D. Hancock, in *Perspective in Coordination Chemistry*, eds. A. F. Williams, C. Floriani and A. E. Merbach, Verlag Helvetica Chimica Acta, Basel, 1992.
2 D. Parker and J. A. G. Williams, *J. Chem. Soc., Dalton Trans.*, 1996, 3613 and refs. therein.
3 D. Matković-Čalogović, H. Meider and P. Planinić, *J. Organomet. Chem.*, 1993, **461**, 117.
4 P. Planinić, H. Meider and D. Matković-Čalogović, *J. Organomet. Chem.*, 1994, **483**, 205.
5 H. Meider, D. Matković-Čalogović and P. Planinić, *J. Organomet. Chem.*, 1996, **506**, 265.
6 B. Bosnich, C. K. Poon and M. L. Tobe, *Inorg. Chem.*, 1965, **4**, 1102.
7 E. K. Barefield and F. Wagner, *Inorg. Chem.*, 1973, **12**, 2435.
8 M. J. D'Aniello, jun., M. T. Mocella, F. Wagner, E. K. Barefield and I. C. Paul, *J. Am. Chem. Soc.*, 1975, **97**, 192.
9 K. D. Hodges, R. G. Wollmann, E. K. Barefield and D. N. Hendrickson, *Inorg. Chem.*, 1977, **16**, 2746.
10 N. W. Alcock, N. Herron and P. Moore, *J. Chem. Soc., Dalton Trans.*, 1978, 1282.
11 S. Reimer, M. Wicholas, B. Scott and R. D. Willett, *Acta Crystallogr., Sect. C*, 1989, **45**, 1694.
12 T.-J. Lee, T.-Y. Lee, C.-Y. Hong, D.-T. Wu and C.-S. Chung, *Acta Crystallogr., Sect. C*, 1986, **42**, 999.
13 R. A. Bauer, W. R. Robinson and D. W. Margerum, *J. Chem. Soc., Chem. Commun.*, 1973, 289.
14 N. Herron and P. Moore, *Inorg. Chim. Acta*, 1979, **36**, 89.
15 S. Bürki and T. A. Kaden, *J. Chem. Soc., Dalton Trans.*, 1991, 805.
16 K. Nakanishi, *Infrared Absorption Spectroscopy*, Nankodo Company Limited, Tokyo, 1964.
17 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley, New York, 1978.
18 A. B. P. Lever, *Inorganic Electronic Spectroscopy*, Elsevier, Amsterdam, 1968.
19 L. W. Gosser and G. W. Parshall, *Inorg. Chem.*, 1974, **13**, 1947; O. K. Kireeva, B. M. Bulychev, N. R. Streltsova, V. K. Belski and A. G. Dunin, *Polyhedron*, 1992, **11**, 1981.
20 L. I. Katzin and E. Gebert, *J. Am. Chem. Soc.*, 1950, **72**, 5464; D. A. Fine, *J. Am. Chem. Soc.*, 1962, **84**, 1139; D. H. Brown, K. P. Forrest, R. H. Nuttall and D. W. A. Sharp, *J. Chem. Soc. A*, 1968, 2146; R. D. Farina and J. H. Swinehart, *J. Am. Chem. Soc.*, 1969, **91**, 568; K. Sawada and T. Suzuki, *J. Inorg. Nucl. Chem.*, 1981, **43**, 2301.
21 M. Scrocco and A. M. Paoletti, *J. Electon Spectrosc. Relat. Phenom.*, 1995, **74**, 231.
22 L. Sacconi, R. Morassi and S. Midollini, *J. Chem. Soc. A*, 1968, 1510.
23 M. Ciampolini and G. P. Speroni, *Inorg. Chem.*, 1966, **5**, 45; M. Di Vaira and P. L. Orioli, *Chem. Commun.*, 1965, 590.
24 G. A. Kalligeros and E. L. Blinn, *Inorg. Chem.*, 1972, **11**, 1145; F. Luo, R. L. Webb, C. Kelly, M. L. Mino, B. Woodworth and E. L. Blinn, *Inorg. Chim. Acta*, 1995, **234**, 75; M. R. Oberholzer, M. Neuburger, M. Zehnder and T. A. Kaden, *Helv. Chim. Acta*, 1995, **78**, 505.
25 F. Wagner and E. K. Barefield, *Inorg. Chem.*, 1976, **15**, 408.
26 (*a*) O. P. Anderson and D. K. Lavallee, *J. Am. Chem. Soc.*, 1977, **99**, 1404; (*b*) S. De Angelis, E. Solari, C. Floriani, A. Chiesi-Villa and C. Rizzoli, *J. Am. Chem. Soc.*, 1994, **116**, 5702.
27 M. Kato and T. Ito, *Inorg. Chem.*, 1985, **24**, 509.
28 M. Kato and I. Ito, *Bull. Chem. Soc. Jpn.*, 1986, **59**, 285; S. F. Lincoln, T. W. Hambley, D. L. Pisaniello and J. H. Coates, *Aust. J. Chem.*, 1984, **37**, 713; I. S. Crick, B. F. Hoskins and P. A. Tregolan, *Inorg. Chim. Acta*, 1986, **114**, L33.
29 H. Hope, M. Viggiano, B. Moezzi and P. P. Power, *Inorg. Chem.*, 1984, **23**, 2550.
30 G. M. Sheldrick, SHELXS 86, Program for the Automatic Solution of Crystal Structures, University of Göttingen, 1986.
31 G. M. Sheldrick, SHELXL 96, Program for the Refinement of Crystal Structures, University of Göttingen, 1996.
32 I. Vicković, ORTEP 92, *J. Appl. Crystallogr.*, 1994, **27**, 437.
33 A. L. Spek, PLUTON, University of Utrecht, 1993.

Received 13*th March* 1997; *Paper* 7/01913K