

interpretation of the NMR spectra of related ruthenium(II) compounds containing this ligand (Hage, Haasnoot, Reedijk & Vos, 1986). The Ru<sup>III</sup>-N(1') distance of 2.073 Å is slightly longer than the metal-nitrogen bonds observed in [Ru(bpy)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup> (average 2.05 Å). This might originate from the presence of acetonitrile *trans* to the pyridine group. The Ru-N(11) distance of 2.034 Å is the shortest metal-ligand bond in the molecule.

The octahedral geometry is not regular, because of the bite angle of the ligand (78.8°). Interestingly, this angle is the same as that observed for bpy in [Ru(bpy)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup> (Eggleston, Goldsby, Hogson & Meyer, 1985). The Cl atoms constitute a mutual meridional arrangement around the central Ru atom. The Ru<sup>III</sup>-Cl bond lengths of 2.330, 2.343 and 2.345 Å are up to 0.024 Å longer than the Ru-Cl distances in the structure of [Ru(bpy)<sub>2</sub>Cl<sub>2</sub>]Cl·H<sub>2</sub>O (Eggleston, Goldsby, Hogson & Meyer, 1985), approximately equal to the Ru-Cl distance in [Ru(NH<sub>3</sub>)<sub>5</sub>-Cl]Cl<sub>2</sub> (Prout & Powell, 1962) and 0.01–0.04 Å shorter than the Ru-Cl distances in the structure of [RuCl<sub>3</sub>(NO){P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>]<sub>2</sub> (Haymore & Ibers, 1975).

The differences in the Ru-Cl distances for the various ruthenium compounds can be attributed to bipyridine and especially NO<sup>+</sup> and PPh<sub>3</sub> having stronger π-acceptor properties than 1Mepytr. Acetonitrile, which has rather strong σ-donor properties, is also expected to influence the Ru-Cl distances.

A projection of the unit cell is given in Fig. 3. No stacking between the molecules is observed. The shortest intermolecular distance found in this structure

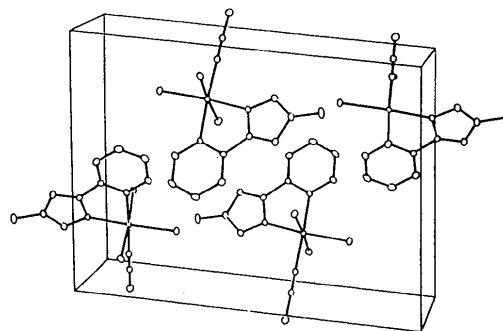


Fig. 3. Projection of the unit cell of *mer*-Ru(1Mepytr)(CH<sub>3</sub>CN)Cl<sub>3</sub>.

is between H(35) and H(36) and is 2.62 Å. Also, a number of short chlorine-hydrogen distances in the range 2.67–3.16 Å are observed in this structure.

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## Structure of 4,4,6,6-Tetrachloro-2-[ferrocenyl(hydroxy)methyl]-2-isopropyl-1,3,5,2λ<sup>5</sup>,4λ<sup>5</sup>,6λ<sup>5</sup>-triazatriphosphorine

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**Abstract.** C<sub>14</sub>H<sub>18</sub>Cl<sub>4</sub>FeN<sub>3</sub>OP<sub>3</sub>, *M<sub>r</sub>* = 534.9, monoclinic, *I*2/*a*, *a* = 21.72 (1), *b* = 8.581 (1), *c* = 23.377 (4) Å, β = 101.68 (3)°, *V* = 4267 (2) Å<sup>3</sup>, *Z* =

8, *D<sub>x</sub>* = 1.665 g cm<sup>-3</sup>, Mo Kα, λ = 0.71073 Å, μ = 14.4 cm<sup>-1</sup>, *F*(000) = 2160, *T* = 130 K, *R* = 0.029 for 3759 observed reflections with *I* > 2.5σ(*I*). The N<sub>3</sub>P<sub>3</sub> six-membered ring has an envelope conformation. The ferrocenyl group is attached to the isopropyl-substituted

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P atom by an asymmetric  $-C(OH)H-$  unit. Mean bond lengths are  $P-N = 1.620$  (3),  $1.559$  (3) [segment  $P(\text{organic substituent})-N-PCl_2$ ] and  $1.585$  (2) Å (segment  $PCl_2-N-PCl_2$ ). Endocyclic angles at  $P(\text{organic substituent})$  and  $PCl_2$  are  $115.7$  (1) and  $119.6$  (1)° (mean value), respectively. Two significantly different endocyclic angles at N are observed,  $119.7$  (1) and  $122.1$  (3)° (mean value). The ferrocenyl moiety with the Cp rings in an almost eclipsed conformation displays normal symmetry. Two types of hydrogen bonding are observed,  $O-H \cdots N = 2.59$  (2) and  $C-H \cdots O = 2.57$  (2) Å.

**Introduction.** Recently we described the reaction of  $(NPCl_2)_3$  with alkyl Grignard reagents in the presence of  $[Bu_3PCuI]_4$  followed by the addition of aldehydes or ketones and subsequent acid hydrolysis to yield *gem*-alkylhydroxyalkyltetrachlorocyclotriphosphazenes (Buwalda & van de Grampel, 1986). In the scope of our investigations into organometallic derivatives of P, N, S heterocycles the title compound was prepared according to this procedure. A full structure determination was carried out to gather insight into the effects of the substituents on the geometry of the ring skeleton. Moreover this determination enables us to study the influence of the organic groups on the overall bonding properties of the ring.

**Experimental.** Suitable orange coloured crystals obtained by recrystallization from petroleum ether (60–80°C). Crystal ( $0.07 \times 0.25 \times 0.50$  mm) was glued on the top of a glass fibre and transferred into the cold-nitrogen stream of the low-temperature unit on an Enraf-Nonius CAD-4F diffractometer interfaced to a PDP-11/23. Graphite-monochromated Mo *K* $\alpha$  radiation used to obtain 9247 reflections ( $h$  0–27,  $k$  –10–10,  $l$  –29–29);  $1.17 < \theta < 27.0^\circ$ ;  $\omega/2\theta$  scan,  $\Delta\omega = (0.90 + 0.35 \tan\theta)^\circ$ . Three reference reflections measured every 208 min ( $6\bar{3}\bar{5}$ : r.m.s.d. 1.6%; 950: r.m.s.d. 1.6%; 606: r.m.s.d. 1.2%) showed no indication of crystal decomposition during the 253 h of X-ray exposure time. Cell dimensions from setting angles of 25 reflections ( $8.57 < \theta < 15.35^\circ$ ). Reduced-cell calculations did not indicate any higher lattice symmetry (Le Page, 1982). \* Intensities corrected for scale variation and for Lorentz and polarization effects. Absorption correction applied (Spek, 1983); min. and max. correction factors being 1.11 and 1.44 on  $I$ , respectively. Variance  $\sigma^2(I)$  calculated based on counting statistics plus a term  $(PI)^2$ , where  $P (=0.026)$  is the

Table 1. Final atomic coordinates and equivalent isotropic thermal parameters for non-H atoms with their *e.s.d.*'s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}$ (Å <sup>2</sup> )*
Fe(1)	0.35539 (2)	0.03380 (4)	0.14662 (1)	0.0180 (1)
Cl(1)	0.29177 (3)	–0.14518 (7)	0.35593 (3)	0.0259 (2)
Cl(2)	0.32130 (3)	0.05520 (8)	0.46696 (3)	0.0297 (2)
Cl(3)	0.52959 (3)	0.14020 (9)	0.46096 (3)	0.0375 (2)
Cl(4)	0.52800 (3)	–0.04933 (8)	0.34898 (3)	0.0376 (2)
P(1)	0.38001 (3)	0.28840 (6)	0.32917 (2)	0.0131 (2)
P(2)	0.34715 (3)	0.03254 (7)	0.38975 (2)	0.0145 (2)
P(3)	0.47097 (3)	0.08309 (7)	0.38637 (3)	0.0168 (2)
O(1)	0.30301 (8)	0.3553 (2)	0.23056 (7)	0.0316 (6)
N(1)	0.32834 (8)	0.1830 (2)	0.35277 (8)	0.0141 (5)
N(2)	0.41777 (9)	–0.0268 (2)	0.40119 (8)	0.0175 (6)
N(3)	0.45227 (8)	0.2328 (2)	0.34935 (8)	0.0167 (6)
C(1)	0.3747 (1)	0.4871 (2)	0.3530 (1)	0.0181 (6)
C(2)	0.3913 (1)	0.4944 (3)	0.4197 (1)	0.0266 (6)
C(3)	0.4175 (1)	0.5927 (3)	0.3261 (1)	0.0280 (6)
C(4)	0.3624 (1)	0.2840 (3)	0.24903 (9)	0.0180 (6)
C(5)	0.3691 (1)	0.1206 (3)	0.22914 (9)	0.0173 (6)
C(6)	0.3240 (1)	–0.0021 (3)	0.22269 (9)	0.0198 (6)
C(7)	0.3536 (1)	–0.1392 (3)	0.2064 (1)	0.0225 (6)
C(8)	0.4165 (1)	–0.1021 (3)	0.2037 (1)	0.0226 (6)
C(9)	0.4264 (1)	0.0574 (3)	0.2176 (1)	0.0196 (6)
C(10)	0.3335 (1)	0.2139 (3)	0.0882 (1)	0.033 (1)
C(11)	0.2825 (1)	0.1126 (4)	0.0840 (1)	0.034 (1)
C(12)	0.3012 (2)	–0.0373 (3)	0.0696 (1)	0.039 (1)
C(13)	0.3659 (2)	–0.0251 (4)	0.0649 (1)	0.040 (1)
C(14)	0.3845 (1)	0.1297 (4)	0.0765 (1)	0.034 (1)

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

instability constant as derived from the excess variance in the reference reflections (McCandlish, Stout & Andrews, 1975). Data set averaged in a set of 4629 unique reflections. Structure solved by direct methods (Sheldrick, 1986) and refined on  $F$  by block-diagonal least-squares techniques with anisotropic thermal parameters for non-H atoms. H atoms located on a difference Fourier map and included in the final refinement with isotropic temperature factors. Convergence reached at  $R = 0.029$ ,  $wR = 0.032$ ,  $w = 1/\sigma^2(F)$ ,  $S = 1.863$ ; 3759 observed reflections with  $I > 2.5\sigma(I)$ ; 309 parameters refined; maximum  $\Delta/\sigma = 0.0015$ . Minimum and maximum residual densities in final Fourier map  $-0.62$  and  $0.50 e \text{ \AA}^{-3}$ . Correction for isotropic secondary extinction applied (Zachariasen, 1967),  $g = 0.27$  (3)  $\times 10^{-4}$ . Final fractional atomic coordinates and equivalent isotropic thermal parameters for the non-H atoms are given in Table 1.\* Scattering factors from Cromer & Mann (1968). Anomalous-dispersion factors were taken from Cromer & Liberman (1970). All calculations carried out on the CDC-Cyber 170/760 computer of the University of Groningen with the program packages *XTAL* (Stewart

\* The conventional space group is  $C2/c$ . Transformation:

$$\begin{aligned} (a') & & (-10-1) (a) \\ (b') & = & (011) (b) \\ (c')_{(C2/c)} & & (-100) (c)_{(I2/a)} \end{aligned}$$

$$a' = 28.507, b' = 8.581, c' = 21.720 \text{ \AA}, \beta' = 126.58^\circ.$$

\* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and bond lengths and angles involving H and an *ORTEP* plot (Johnson, 1965) have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44373 (32 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

& Hall, 1983), *EUCLID* (Spek, 1982; calculation of geometric data) and locally modified version of *PLUTO* (Meetsma, 1986; Motherwell & Clegg, 1978; preparation of illustrations).

**Discussion.** As visualized in Fig. 1, the molecular structure can be divided into two main parts: the phosphazene ring and the ferrocenyl group, connected by the asymmetric  $-C(OH)H-$  bridge. The ferrocenyl part is located over the ring in a nearly symmetrical position:  $C(6)\cdots N(1) = 3.415(3)$ ,  $C(6)\cdots Cl(1) = 3.547(3)$ ,  $C(9)\cdots N(3) = 3.371(3)$  and  $C(9)\cdots Cl(4) = 3.542(3)$  Å. These intramolecular contacts are larger than the sum of the van der Waals radii,  $C\cdots N = 3.25$  and  $C\cdots Cl = 3.45$  Å (Bondi, 1964). The intramolecular  $C\cdots Cl$  distances arise obviously by a rotation of the  $sp^3$  bonding tetrahedra at P(2) and P(3) about the P(2)–N(1) and P(3)–N(3) bond, respectively. As a consequence, the P–Cl bonds are no longer in a symmetrical position with respect to the plane formed by the atoms P(1), P(2), P(3), N(1) and N(3). The angles of P(2)–Cl(1), P(2)–Cl(2), P(3)–Cl(4) and P(3)–Cl(3) with this plane being  $45.04(5)$ ,  $54.76(5)$ ,  $45.35(5)$  and  $54.72(5)^\circ$ , respectively. Moreover, N(2) is positioned out of the aforementioned plane by  $0.161(6)$  Å, giving the ring an envelope conformation. Puckering parameters are:  $Q = 0.118(1)$  Å,  $\theta = 111.6(5)^\circ$ ,  $\varphi = 1.1(8)^\circ$  (Cremer & Pople, 1975). The isopropyl group is also located over the ring. Both the position of the ferrocenyl moiety and the position of the isopropyl group give the molecule a compact shape. The P–N bonds (Table 2) in the phosphazene ring are not equal but show the usual trend; in a P–N–P segment the smallest P–N bond length is observed adjacent to the P atom bearing

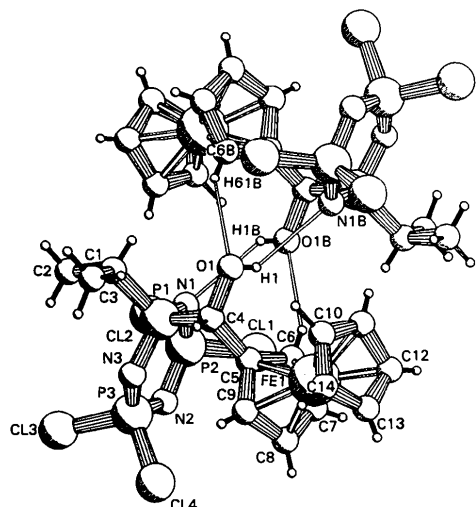


Fig. 1. *PLUTO* drawing of  $(NPCl_2)_2NP'PrCpFeCp$  illustrating the puckering and the adopted numbering scheme. Two molecules are connected by the hydrogen bonds  $O(1)-H(1)\cdots N(1B)$  and  $C(6B)-H(61B)\cdots O(1)$ .

Table 2. Selected data on the geometry

Bond distances (Å)			
Cl(1)–P(2)	2.003 (1)	C(5)–C(9)	1.432 (3)
Cl(2)–P(2)	2.005 (1)	C(6)–Fe(1)	2.053 (2)
Cl(3)–P(3)	2.001 (1)	C(6)–C(7)	1.429 (4)
Cl(4)–P(3)	2.007 (1)	C(7)–Fe(1)	2.045 (3)
P(1)–N(1)	1.623 (2)	C(7)–C(8)	1.417 (3)
P(1)–N(3)	1.617 (2)	C(8)–Fe(1)	2.046 (3)
P(2)–N(1)	1.561 (2)	C(8)–C(9)	1.413 (4)
P(2)–N(2)	1.587 (2)	C(9)–Fe(1)	2.034 (2)
P(3)–N(2)	1.583 (2)	C(10)–Fe(1)	2.053 (3)
P(3)–N(3)	1.556 (2)	C(10)–C(11)	1.396 (4)
C(1)–P(1)	1.805 (2)	C(10)–C(14)	1.395 (4)
C(1)–C(2)	1.529 (3)	C(11)–Fe(1)	2.042 (3)
C(1)–C(3)	1.522 (3)	C(11)–C(12)	1.410 (4)
C(4)–C(5)	1.494 (4)	C(12)–Fe(1)	2.035 (3)
C(4)–P(1)	1.835 (2)	C(12)–C(13)	1.435 (6)
C(4)–O(1)	1.414 (3)	C(13)–Fe(1)	2.033 (3)
C(5)–Fe(1)	2.033 (2)	C(13)–C(14)	1.399 (5)
C(5)–C(6)	1.425 (3)	C(14)–Fe(1)	2.045 (3)
Bond angles (°)			
C(4)–P(1)–N(1)	108.7 (1)	N(2)–P(3)–Cl(4)	107.47 (8)
C(4)–P(1)–N(3)	106.3 (1)	N(3)–P(3)–Cl(3)	109.32 (8)
C(4)–P(1)–C(1)	108.8 (1)	N(3)–P(3)–Cl(4)	109.86 (8)
N(1)–P(1)–N(3)	115.7 (1)	Cl(3)–P(3)–Cl(4)	100.27 (5)
N(1)–P(1)–C(1)	109.3 (1)	P(1)–N(1)–P(2)	121.8 (1)
N(3)–P(1)–C(1)	107.9 (1)	P(2)–N(2)–P(3)	119.7 (1)
N(1)–P(2)–Cl(1)	110.00 (8)	P(1)–N(3)–P(3)	122.3 (1)
N(1)–P(2)–Cl(2)	109.18 (8)	P(1)–C(1)–C(2)	109.7 (1)
N(1)–P(2)–N(2)	119.6 (1)	P(1)–C(1)–C(3)	110.6 (2)
Cl(1)–P(2)–Cl(2)	100.01 (5)	C(2)–C(1)–C(3)	111.1 (2)
Cl(1)–P(2)–N(2)	107.76 (8)	C(5)–C(4)–P(1)	108.9 (2)
Cl(2)–P(2)–N(2)	108.46 (8)	C(5)–C(4)–O(1)	116.8 (2)
N(2)–P(3)–N(3)	119.6 (1)	P(1)–C(4)–O(1)	107.0 (1)
N(2)–P(3)–Cl(3)	108.61 (8)		
Torsion angles (°)			
N(3)–P(1)–N(1)–P(2)	–3.2 (2)	N(2)–P(3)–N(3)–P(1)	4.7 (2)
N(1)–P(1)–N(3)–P(3)	3.0 (2)	C(2)–C(1)–P(1)–C(4)	–178.2 (1)
N(2)–P(2)–N(1)–P(1)	–4.3 (2)	C(3)–C(1)–P(1)–C(4)	–55.3 (2)
N(1)–P(2)–N(2)–P(3)	12.3 (2)	C(5)–C(4)–P(1)–C(1)	177.9 (1)
N(3)–P(3)–N(2)–P(2)	–12.5 (2)	C(4)–C(5)–Fe(1)–C(10)	3.0 (2)

the more electronegative substituents (Winter, van de Grampel, de Boer, Meetsma & Spek, 1987). Hence in the segments P(organic substituent)–N–PCl<sub>2</sub> the P(organic substituent)–N bond length [1.620(3) Å, mean value\*] is larger than the PCl<sub>2</sub>–N bond length [1.559(3) Å, mean value]. In the segment PCl<sub>2</sub>–N–PCl<sub>2</sub> the P–N bond lengths are equal within the experimental error [1.587(2) and 1.583(2) Å]. The ferrocenyl moiety displays normal geometry [C(5)–C(9) = 1.424(3), C(10)–C(14) = 1.404(6), C–Fe = 2.042(7) Å, and C–C–C = 108.0(6)°, mean values]. The cyclopentadienyl rings have an almost eclipsed conformation [torsion angle C(4)–C(5)–Fe(1)–C(10) = 3.0(2)°] and are nearly parallel [the dihedral angle between the rings is 1.3(1)°]. These data are in agreement with corresponding data for ferrocene (Seiler & Dunitz, 1979), 2,2-dicyanovinylferrocene (Krukoniš, Silverman & Yannoni, 1972) and ferrocene derivatives of (NPCl<sub>2</sub>)<sub>3</sub> (Allcock, Lavin, Riding & Whittle, 1984). The monoclinic unit cell contains eight molecules of the

\* Throughout this paper the mean values and their standard errors have been calculated using the formulae given by Domenicano, Vacigo & Coulson (1979).

title compound. These molecules are ordered in pairs of enantiomers, between which weak hydrogen bonding (Berkovitch-Yellin & Leiserowitz, 1984) is observed:  $N(1)\cdots H(1)$  ( $\frac{1}{2}-x, \frac{1}{2}-y, \frac{1}{2}-z$ ) = 2.59 (2) and  $O(1)\cdots H(61)$  ( $\frac{1}{2}-x, \frac{1}{2}-y, \frac{1}{2}-z$ ) = 2.57 (2) Å [sum of the van der Waals radii is 2.75 and 2.72 Å, respectively (Bondi, 1964)]. The angles  $N(1)\cdots H(1)-O(1)$  and  $O(1)\cdots H(61)-C(6)$  are 132 (2) and 150 (2)°, respectively.

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*Acta Cryst.* (1988). **C44**, 61–63

## Hexacarbonyl-tris( $\mu$ -diphenylphosphido)-bis( $\mu_3$ -hydrido)-triangulo-trirhenium

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**Abstract.**  $[\text{Re}_3(\text{CO})_6(\mu_3\text{-H})_2\{\text{P}(\text{C}_6\text{H}_5)_2\}_3]\cdot 0.72\text{CCl}_4$ ,  $M_r = 1395.0$ , triclinic,  $P\bar{1}$ ,  $a = 11.058$  (2),  $b = 12.505$  (3),  $c = 18.122$  (6) Å,  $\alpha = 99.77$  (2),  $\beta = 90.13$  (2),  $\gamma = 109.66$  (2)°,  $U = 2321.0$  Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.995$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 80.2$  cm<sup>-1</sup>,  $F(000) = 1310.6$ ,  $T = 298$  (1) K, final  $R = 0.0541$  for 3918 unique reflections. The central fragment of the molecule consists of a triangular Re ring edge-bridged by diphenylphosphido groups and triply bridged by two hydrides. The Re–Re bonds [ $r(\text{Re}–\text{Re}) = 2.730$  (1) Å] indicate a multiple-bond character.

**Introduction.** The family of triangular  $M_3$  cluster compounds ( $M$  = transition metal) reaches a saturated valence electron configuration with 48 electrons (CVE) in the presence of  $\pi$  acceptor ligands (Lauher, 1978). Numerous compounds of this and three with CVE number 46, including the recently described complex anion  $[\text{Re}_3(\text{CO})_9\{\text{P}(\text{C}_6\text{H}_5)_3\}(\mu\text{-H})_4]^-$  (Beringhelli, D'Alfonso, Freni, Ciani, Sironi & Molinari, 1986), are

structurally known. The neutral title compound with different bridging of the  $\text{Re}_3$  core is the first example with an unsaturated 44 CVE number. Its molecular determination is necessary for a molecular-orbital description to characterize the multiple Re–Re bond supported by bridging ligands.

A further important aspect of this structural determination is connected with our attempt to find the positional parameters of the two triply-bridged hydrides – earlier proved by <sup>1</sup>H NMR measurements – because the title substance illustrates a profitable hydrogen-bonding pattern for an unsaturated triangular  $M_3$  metal atom arrangement at the surface of metals in heterogeneous catalytic hydrogenation reactions.

**Experimental.** The orange crystals were prepared by reaction of  $[\text{Re}_2(\text{CO})_8\{\text{P}(\text{C}_6\text{H}_5)_3\}_2]$  with hydrogen at 493 K (Haupt, Flörke & Balsaa, 1988). Crystal size 0.06 × 0.08 × 0.25 mm, Nicolet R3m/V diffractometer,  $\omega$ – $2\theta$  scan, scan speed 1.5–9.7° min<sup>-1</sup>, graphite-monochromated Mo  $K\alpha$ ; lattice parameters refined