

**Discussion.** In  $\text{Zn}(\text{dotaH}_2)$  (Fig. 2) the metal ion is surrounded by the four nitrogens of the macrocycle and by two carboxylate oxygens, so that a distorted *cis*-octahedral geometry results. The two nitrogens  $\text{N}(2)$  and  $\text{N}(2)'$  (*trans* to each other in the macrocycle) and the two oxygens  $\text{O}(1)$  and  $\text{O}(1)'$  stemming from the acetate groups attached at  $\text{N}(2)$  and  $\text{N}(2)'$  form a plane in which the metal ion is also situated. The other two nitrogens  $\text{N}(1)$  and  $\text{N}(1)'$  are axially coordinated and complete the octahedron. The macrocycle is folded along the  $\text{N}(1)$ – $\text{N}(1)'$  axis and assumes the *cis*-I configuration (Bosnich, Poon & Tobe, 1965). The  $\text{Zn}^{2+}$  is situated on the  $C_2$  axis which bisects the  $\text{O}(1)$ – $\text{Zn}$ – $\text{O}(1)'$  angle. The other two carboxylates are protonated and not involved in coordination. They form hydrogen bonds  $\text{O}(4)$ – $\text{H}(13)\cdots\text{O}(2)$  to a second molecule, the  $\text{O}(4)$ – $\text{O}(2)$  distance being 2.62 (8) Å and the  $\text{O}$ – $\text{H}$ – $\text{O}$  angle 162 (5)°. The  $\text{Zn}$ – $\text{N}$  and  $\text{Zn}$ – $\text{O}$  bonds are somewhat longer than those of the corresponding  $\text{Ni}^{2+}$  complex (Riesen, Zehnder & Kaden, 1986), but the angles are similar. The  $\text{N}(1)$ – $M$ – $\text{N}(1)'$  angle is 153.9° for  $M = \text{Zn}^{2+}$ , compared to 153.9 and 158.6° for  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$ , respectively, and is distinctly smaller than that expected for the octahedron (180°). This is due to the strain inherent in the 12-membered macrocycle, which does not allow the nitrogens to occupy the ideal position.

The structure of  $\text{Zn}(\text{tetaH}_2)\cdot 4\text{H}_2\text{O}$ , shown in Fig. 3, indicates that the metal ion in a *trans*-octahedral arrangement of the four amino nitrogens of the macrocycle and two carboxylate oxygens. Since the  $\text{Zn}^{2+}$  sits on an inversion centre it is in the plane defined by the four nitrogens with  $\text{Zn}$ – $\text{N}$  bond

lengths of 2.110 and 2.253 Å. The  $\text{Zn}$ – $\text{O}$  bonds are 2.127 Å long, so that the octahedron is somewhat elongated along the  $\text{N}(2)$ – $\text{Zn}$ – $\text{N}(2)$  axis. This is in contrast to the geometry found for the  $\text{Cu}(\text{teta})^{2-}$  species (Riesen, Zehnder & Kaden, 1988), which is elongated along the  $\text{O}$ – $\text{Cu}$ – $\text{O}$  axis. The angles around the  $\text{Zn}^{2+}$  are close to 90°, the  $\text{O}(1)$ – $\text{Zn}$ – $\text{N}(1)$  angle being the smallest at 80.9°. The macrocycle is in the *trans*-III configuration according to the nomenclature of Bosnich, Poon & Tobe (1965). The two carboxylates not involved in coordination are protonated and form hydrogen bonds, from  $\text{O}(3)$ – $\text{H}(15)$  to  $\text{OW}(1)'$ , which itself forms hydrogen bonds to  $\text{O}(2)$  and  $\text{OW}(2)'$ . This last water is also hydrogen bonded to  $\text{O}(1)$ . The  $\text{O}$ – $\text{O}$  distances range from 2.61 to 2.78 Å with  $\text{O}$ – $\text{H}$ – $\text{O}$  angles from 161 to 177°.

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## Structure of a Monocyclopentadienyl Niobium(III) Phosphine Adduct

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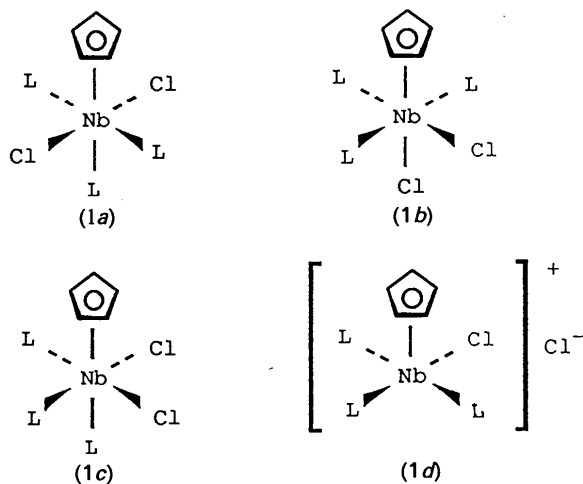
**Abstract.** Dichloro( $\eta^5$ -cyclopentadienyl)tris(trimethylphosphine)niobium(III),  $[\text{NbCl}_2(\text{C}_5\text{H}_5)-$

$\{\text{P}(\text{CH}_3)_3\}_3]$ ,  $M_r = 457.15$ , monoclinic,  $P2_1/n$ ,  $a = 18.900$  (9),  $b = 12.696$  (7),  $c = 18.820$  (8) Å,  $\beta = 113.11$  (4)°,  $V = 4153$  Å<sup>3</sup>,  $Z = 8$ ,  $D_x = 1.462$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 10.3$  cm<sup>-1</sup>,  $F(000) =$

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1888, room temperature,  $R = 0.036$  for 2617 observations. The structure exhibits a pseudo-octahedral environment for the metal, with the chlorine in a *cis* position. Two crystallographically independent molecules having comparable interatomic distances are found in the unit cell. The crystals were obtained by reduction of CpNbCl<sub>4</sub> with two equivalents of sodium amalgam in toluene in the presence of the phosphine ligand.

**Introduction.** The chemistry of the monocyclopentadienyl-derivative complexes of the Group V elements, niobium and tantalum has received little attention compared with their bis(cyclopentadienyl) counterparts. Low-valency monocyclopentadienyl derivatives stabilized by ligands such as phosphine could be convenient precursors, but knowledge of their structure remains limited. The reduction of ( $\eta^5$ -Cp)NbCl<sub>4</sub> with two equivalents of sodium amalgam in the presence of excess PMe<sub>3</sub> afforded crystals of a diamagnetic compound, analysed as ( $\eta^5$ -Cp)NbCl<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub>. The synthesis of this niobium(III) compound by an alternative route has been reported recently (Alt & Engelhardt, 1989) and thus prompts us to report its X-ray structural determination. X-ray characterization has been carried out, since several structures, three molecular complexes (1*a*), (1*b*) and (1*c*), which differ in the geometrical distribution of the chlorine and phosphine ligands, as well as an ionic four-legged piano-stool isomer (1*d*), must be considered.



**Experimental.** *Synthesis.* CpNbCl<sub>4</sub> (0.98 g, 3.32 mmol) was allowed to react with sodium amalgam (0.15 Na/0.8 ml Hg) in 5 ml toluene in the presence of PMe<sub>3</sub> (1.7 ml, 15 mmol). After 6 h of reaction time, filtration over a celite pad was achieved. The brown-red filtrate was concentrated to about 25 ml. Crystallization at 243 K gave red

Table 1. *Summary of crystallographic data for* ( $\eta^5$ -Cp)NbCl<sub>2</sub>(PMe<sub>3</sub>)<sub>3</sub>

Compound	C <sub>14</sub> H <sub>32</sub> Cl <sub>2</sub> P <sub>3</sub> Nb
Colour	Brown-red
Molecular weight	457.15
Crystal system	Monoclinic
Space group	<i>P2<sub>1</sub>/n</i>
<i>a</i> (Å)	18.900 (9)
<i>b</i> (Å)	12.696 (7)
<i>c</i> (Å)	18.820 (8)
$\beta$ (°)	113.11 (4)
<i>V</i> (Å <sup>3</sup> )	4153 (2)
<i>Z</i>	8
Density (calc.) (g cm <sup>-3</sup> )	1.462
Crystal dimensions (mm)	0.08 × 0.18 × 0.22
<i>F</i> (000)	1888
Diffractometer	Enraf-Nonius CAD-4
Radiation	Mo <i>K</i> $\alpha$
Linear absorption coefficient (cm <sup>-1</sup> )	10.3
Scan type	$\omega/2\theta = 1$
<i>hkl</i> limits	0, 22; 0, 15; -22, 22
Data collected	7460
Unique data used [ $F_o^2 > 4\sigma(F_o^2)$ ]	2617
<i>R</i> <sub>int</sub>	0.024
Number of parameters refined	182
<i>R</i>	0.037
<i>wR</i>	0.036
<i>S</i>	1.09

crystals (1.5 g, 59%), slightly soluble in toluene, more soluble in CH<sub>2</sub>Cl<sub>2</sub>, while decomposition occurred in CHCl<sub>3</sub>. Analysis: Calculated for C<sub>14</sub>H<sub>32</sub>Cl<sub>2</sub>NbP<sub>3</sub>: C: 36.76; H: 7.06; Cl: 15.54; P: 20.35. Found: C: 33.63; H: 6.21; Cl: 15.90; P: 17.50.

The monocrystal was introduced under argon into a sealed Lindemann capillary and mounted on an automatic diffractometer. The cell parameters were obtained by fitting a set of 25 high- $\theta$  reflections. The crystal parameters and basic information on data collection and structure refinement are shown in Table 1. The data collection [ $2\theta_{\max} = 50^\circ$ , scan  $\omega/2\theta = 1$ ,  $t_{\max} = 60$  s, intensity controls without appreciable decay (0.4%)] gave 7460 reflections of which 2617 were independent ( $R_{\text{int}} = 0.024$ ) with  $I > 4\sigma(I)$ .

After Lorentz and polarization corrections the structure was solved with a Patterson map which revealed the two Nb atoms. The remaining non-H atoms were found after a scale-factor refinement and a Fourier difference map. After isotropic ( $R = 0.09$ ) refinement, an absorption correction with *DIFABS* (Walker & Stuart, 1983) was made.  $T_{\max} = 1.26$ ,  $T_{\min} = 0.82$ . After an anisotropic ( $R = 0.056$ ) refinement of all the non-H atoms, many H atoms were located by a Fourier difference map, the remainder being set in calculated positions. The whole structure was refined by the full-matrix least-squares technique {use of *F* magnitudes;  $x, y, z, \beta_{ij}$  for Nb, Cl, P and C atoms,  $x, y, z$  fixed for H atoms, 1589 observations;  $w = [\sigma^2(I) + (0.04F_o^2)^2]^{-1/2}$ } with the resulting  $R = 0.037$ ,  $wR = 0.036$  and  $S = 1.09$  (residual  $0.34 \text{ e } \text{\AA}^{-3}$ ).  $(\Delta/\sigma)_{\max} = 0.265$ . Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV). All calculations were performed on a Digital PDP 11/60 computer with the *SDP* package (Frenz, 1985). Final positional param-

Table 2. Positional and thermal parameters for  $(\eta^5\text{-Cp})\text{NbCl}_2(\text{PMe}_3)_3$ 

	x	y	z	B(Å <sup>2</sup> )
Nb1	0.76128 (5)	0.16777 (7)	0.63430 (5)	2.40 (2)
Nb11	0.36200 (4)	0.23942 (6)	0.73056 (4)	2.57 (2)
Cl1	0.8249 (1)	0.3449 (2)	0.6689 (1)	3.73 (6)
Cl2	0.6681 (1)	0.2640 (2)	0.6845 (1)	3.99 (6)
Cl11	0.3158 (1)	0.0654 (2)	0.6629 (1)	3.47 (6)
Cl12	0.3052 (1)	0.1531 (2)	0.8211 (1)	4.46 (6)
P1	0.8830 (2)	0.1590 (2)	0.6020 (2)	3.91 (6)
P2	0.6866 (2)	0.2747 (2)	0.5062 (2)	3.56 (6)
P3	0.8379 (1)	0.1418 (2)	0.7844 (1)	2.98 (6)
P11	0.3918 (1)	0.2397 (2)	0.6067 (1)	3.18 (6)
P12	0.4821 (2)	0.1161 (2)	0.8047 (2)	4.21 (7)
P13	0.2149 (1)	0.2837 (2)	0.6521 (1)	3.33 (6)
C1	0.7789 (7)	-0.0133 (8)	0.6219 (6)	4.8 (3)
C2	0.7307 (7)	0.0309 (8)	0.5503 (6)	4.8 (3)
C3	0.6614 (6)	0.0587 (9)	0.5571 (7)	5.1 (3)
C4	0.6680 (6)	0.0325 (8)	0.6327 (7)	4.4 (3)
C5	0.7382 (6)	-0.0101 (8)	0.6712 (6)	4.5 (3)
C6	0.7780 (7)	0.116 (1)	0.8382 (6)	5.4 (3)
C7	0.8922 (6)	0.2541 (9)	0.8395 (6)	4.4 (3)
C8	0.9092 (6)	0.0366 (9)	0.8215 (6)	4.8 (3)
C9	0.9751 (6)	0.161 (1)	0.6840 (7)	6.2 (3)
C10	0.9003 (7)	0.047 (1)	0.5504 (8)	7.7 (4)
C11	0.8989 (6)	0.264 (1)	0.5427 (6)	5.4 (3)
C12	0.7228 (7)	0.3996 (9)	0.4892 (7)	5.6 (3)
C13	0.6667 (9)	0.214 (1)	0.4138 (7)	7.4 (4)
C14	0.5895 (7)	0.315 (1)	0.4940 (7)	6.4 (4)
C21	0.3880 (6)	0.4166 (8)	0.7174 (6)	4.3 (3)
C22	0.4564 (6)	0.3655 (8)	0.7618 (6)	4.3 (3)
C23	0.4481 (6)	0.3397 (9)	0.8342 (6)	4.5 (3)
C24	0.3767 (7)	0.3737 (9)	0.8281 (6)	5.0 (3)
C25	0.3392 (6)	0.4224 (8)	0.7588 (6)	5.2 (3)
C26	0.1612 (6)	0.319 (1)	0.7097 (7)	6.1 (3)
C27	0.1540 (5)	0.1782 (9)	0.5946 (7)	5.1 (3)
C28	0.1865 (7)	0.3925 (9)	0.5836 (7)	5.4 (3)
C29	0.3099 (6)	0.2280 (9)	0.5165 (5)	4.4 (3)
C30	0.4396 (6)	0.3501 (9)	0.5822 (6)	4.9 (3)
C31	0.4514 (6)	0.1354 (9)	0.5937 (6)	5.3 (3)
C32	0.4907 (6)	-0.011 (1)	0.7637 (7)	5.9 (3)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as:  $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$ .

eters and isotropic thermal parameters are listed in Table 2.\*

**Discussion.** Crystals of  $(\eta^5\text{-Cp})\text{NbCl}_2(\text{PMe}_3)_3$  suitable for X-ray analysis were grown from the reaction medium resulting from the reduction of  $(\eta^5\text{-Cp})\text{NbCl}_4$  with sodium amalgam in toluene in the presence of an excess of  $\text{PMe}_3$ . The atom labelling is defined in Fig. 1, which represents one of the two crystallographically independent molecules found in the asymmetric unit cell. Selected bond distances and angles for these two slightly different molecules are collected in Table 3. The coordination sphere of this 18-electron complex may be described as a distorted octahedron with the Cl atoms in *cis* positions. The structure in the solid state thus corresponds to isomer (1*b*). The Nb—Cl bond lengths [2.513 (3) to 2.607 (3) Å] are quite long, even for trivalent niobium, the longest terminal Nb—Cl bond reported so

\* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and a full list of bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53536 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Selected bond lengths (Å) and angles (°) of  $(\eta^5\text{-Cp})\text{NbCl}_2(\text{PMe}_3)_3$ 

Nb1—Cl1	2.513 (3)	Nb11—Cl11	2.528 (2)
Nb1—Cl2	2.607 (3)	Nb11—Cl12	2.588 (3)
Nb1—P1	2.603 (3)	Nb11—P11	2.603 (3)
Nb1—P2	2.641 (3)	Nb11—P12	2.657 (3)
Nb1—P3	2.641 (2)	Nb11—P13	2.646 (2)
Nb1—C1	2.347 (11)	Nb11—C21	2.337 (10)
Nb1—C2	2.266 (11)	Nb11—C22	2.295 (10)
Nb1—C3	2.332 (10)	Nb11—C23	2.363 (9)
Nb1—C4	2.452 (11)	Nb11—C24	2.440 (11)
Nb1—C5	2.452 (11)	Nb11—C25	2.458 (11)
Cl1—Nb1—Cl2	79.00 (9)	Cl11—Nb11—Cl12	79.11 (9)
Cl1—Nb1—P1	73.8 (1)	Cl11—Nb11—P11	72.76 (9)
Cl1—Nb1—P2	78.84 (8)	Cl11—Nb11—P12	78.75 (8)
Cl1—Nb1—P3	80.13 (8)	Cl11—Nb11—P13	79.90 (8)
Cl2—Nb1—P1	152.84 (9)	Cl12—Nb11—P11	151.84 (9)
Cl2—Nb1—P2	83.97 (9)	Cl12—Nb11—P12	83.96 (9)
Cl2—Nb1—P3	80.52 (8)	Cl12—Nb11—P13	80.81 (8)
P1—Nb1—P2	90.76 (9)	P11—Nb11—P12	91.75 (9)
P1—Nb1—P3	94.64 (9)	P11—Nb11—P13	92.82 (8)
P2—Nb1—P3	155.87 (9)	P12—Nb11—P13	155.74 (9)

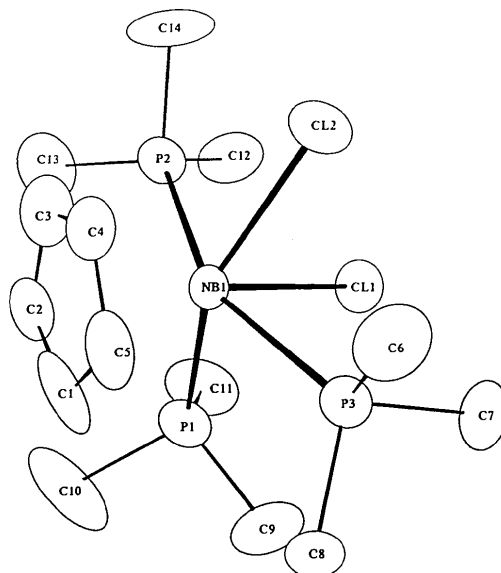


Fig. 1. ORTEP drawing of  $(\eta^5\text{-Cp})\text{NbCl}_2(\text{PMe}_3)_3$  showing the atom-labelling scheme.

far being 2.505 (4) Å (Aspinall, Robert & Lippard, 1984; Cotton, Duraj & Roth, 1984). The Nb—Cl(2) distance is especially long, probably as a result of some *trans* effect exerted by the  $\text{PMe}_3(\text{P1})$  ligand for which the Nb—P bond length is also the shortest. The mean Nb—C(Cp) bond distance for the two molecules is 2.37 Å and is thus in agreement with data reported in the literature for either mono- or biscyclopentadienyl derivatives (Holloway & Melnik, 1986); however, large variations in these Nb—C distances [2.266 (11) to 2.458 (11) Å] were observed. An examination of the C—C bond distances also reveals a spread [1.350 (14)–1.42 (2) Å] consistent with a distorted  $\eta^5$ -coordination mode of the cyclopentadienyl moiety. As for  $(\eta^5\text{-Cp})\text{Ta}(\eta^2\text{C}_2\text{H}_4)\text{Cl}_2(\text{PMe}_2\text{Ph})_2$  (Atwood, Honan & Rogers, 1982), steric problems appear to be the likely origin of this

distortion. Steric congestion around the metal is also evidenced by the small Cl(1)—Nb—Cl(2) and Cl(1)—Nb—P(1) angles (79 and 73.8°, respectively). The Nb—PMe<sub>3</sub> distances are of two types depending on the ligand in the *trans* position; they are shorter than those observed in Nb<sub>4</sub>Cl<sub>10</sub>(PMe<sub>3</sub>)<sub>6</sub> (Cotton & Shang, 1988), one of the few niobium–phosphine adducts structurally characterized. The lability of the phosphine ligand and/or metathesis reactions opens synthetic routes to other monocyclopentadienyl derivatives.

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## Tricarbonyl[(1,2,3,4- $\eta$ )-2,3-dimethylbutadiene]cobalt Acetonitriletrichloroferrate(1-)

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**Abstract.** [Co(C<sub>6</sub>H<sub>10</sub>)(CO)<sub>3</sub>][Fe(Cl)<sub>3</sub>(C<sub>2</sub>H<sub>3</sub>N)], *M*<sub>r</sub> = 428.35, monoclinic, *P*2<sub>1</sub>/*a*, *a* = 11.259 (10), *b* = 12.043 (4), *c* = 12.727 (7) Å,  $\beta$  = 97.53 (6)°, *V* = 1710.8 Å<sup>3</sup>, *Z* = 4, *D*<sub>x</sub> = 1.663 Mg m<sup>-3</sup>, Mo *K* $\alpha$ ,  $\lambda$  = 0.71069 Å,  $\mu$  = 2.291 mm<sup>-1</sup>, *F*(000) = 856, *T* = 291 (1) K, *R* = 0.032 for 1383 independent observed reflections. The title compound, an archetypal Co<sup>I</sup> species, was studied in the hope of gaining further information about [7,7,7-(CO)<sub>3</sub>-7-CoB<sub>10</sub>H<sub>12</sub>]<sup>-</sup>, which had previously been described formally as a Co<sup>III</sup> complex. Comparison of Co—CO distances and C—O IR stretching frequencies lends support to this conclusion.

**Introduction.** Recently (Macgregor, Yellowlees & Welch, 1990) we reported that analysis of the structure of the anion [7,7,7-(CO)<sub>3</sub>-7-CoB<sub>10</sub>H<sub>12</sub>]<sup>-</sup> (1) implied that the {B<sub>10</sub>H<sub>12</sub>} moiety in this species could best be described as the *arachno* fragment {B<sub>10</sub>H<sub>12</sub>}<sup>4-</sup>, and therefore that the formal oxidation state of the Co atom was +3.

In an attempt to gain further information on this system we describe here the results of a structural study of the cation [(CO)<sub>3</sub>Co(dmbd)]<sup>+</sup> (2) [dmbd = 2,3-dimethylbutadiene,  $\eta$ -CH<sub>2</sub>C(Me)C(Me)CH<sub>2</sub>]. This species has been selected for comparison with the cobaltaborane anion since (i) it contains a

directly analogous metal coordination sphere (a tricarbonyl unit and an acyclic  $\eta^4$ -bonded ligand) and (ii) the oxidation state of cobalt in the title compound is clearly known (+1). Spectroscopic evidence for the cation [(CO)<sub>3</sub>Co(dmbd)]<sup>+</sup> was first furnished in 1974 (Chauldry & Paulson, 1974), but no bulk preparation and characterization was carried out. Here we report the isolation of (2) as its [FeCl<sub>3</sub>(NCMe)]<sup>-</sup> salt.

**Experimental.** Compound prepared as the [FeCl<sub>3</sub>(NCMe)]<sup>-</sup> salt by oxidation of a CH<sub>2</sub>Cl<sub>2</sub> solution of [Co(CO)<sub>2</sub>(dmbd)]<sub>2</sub> with FeCl<sub>3</sub>, removal of solvent *in vacuo*, and extraction of the resultant solid into acetonitrile; identity checked by IR spectroscopy (KBr disc,  $\nu_{C-O}$  = 2130, 2100 and 2080 cm<sup>-1</sup>), and established by diffraction study; marine blue crystal, 0.2 × 0.2 × 0.3 mm, mounted on an Enraf–Nonius CAD-4 diffractometer (Mo *K* $\alpha$  radiation, graphite monochromator); cell parameters and orientation matrix from least-squares refinement of the setting angles (9 <  $\theta$  < 12°) of 25 centred reflections; data collection by  $\omega$ -2 $\theta$  scans in 96 steps with  $\omega$  scan width (0.8 + 0.34tan $\theta$ )°; data (*h*: 0 to 10, *k*: 0 to 11, *l*: -12 to 12) measured for 1 ≤  $\theta$  ≤ 20° over 18 X-ray hours; corrections for Lorentz and polarization effects applied (Gould & Smith, 1986); 1699 indepen-