Table 5. *Selected stability constants*

The number to the left in each case is log *K* for the complexation of M^{2+} by L^{4-}, while the number to the right is log *K* for protonation of the complex ion ML^{2-}. Values are taken from Martell & Smith (1974).

Metal	egta^{4-}	edta^{4-}
Cu^{2+}	17·6/4·3	18·8/3·0
Mn^{2+}	12·2/4·1	13·9/3·1
Mg^{2+}	5·2/7·6	8·8/3·9

egta^{4-} ligand utilizes both amine N atoms in coordinating to Cu^{II} in solution. Preferential crystallization of (2) must be attributed to the low solubility of the neutral dinuclear species, and to the adoption of an especially favorable coordination environment about the Cu^{II} ion. The equilibrium constant for the formation of the dinuclear Cu^{II} complex has been measured [$Cu^{2+} + Cu(egta)^{2-} \rightleftharpoons Cu_2(egta)$, $\log K = 4{\cdot}31$ (Ohzeki, Saruhashi & Kambara, 1980)].

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Structure of Monoaquabis(isocyanato)(2,2′:6′,2″-terpyridyl)nickel(II)

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Abstract. [Ni(C$_{15}$H$_{11}$N$_3$)(H$_2$O)(NCO)$_2$], $M_r = 394{\cdot}0$, monoclinic, $P2_1/n$, $a = 9{\cdot}488\ (7)$, $b = 13{\cdot}735\ (4)$, $c = 13{\cdot}985\ (17)$ Å, $\beta = 107{\cdot}82\ (5)°$, $V = 1735\ (5)$ Å^3, $Z = 4$, $D_m = 1{\cdot}60\ (3)$, $D_x = 1{\cdot}51$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 1{\cdot}22$ mm^{-1}, $F(000) = 808$, room temperature, $R = 0{\cdot}047$ ($wR = 0{\cdot}053$) for 3211 reflections with $I \geq 2{\cdot}5\sigma(I)$. The Ni ion displays distorted octahedral coordination, with the three N atoms of 2,2′:6′,2″-terpyridine and the N atom of one NCO

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ligand in the equatorial plane [largest deviation from N(1), N(2), N(3), N(5) mean plane −0·004 (4) Å for N(2)]. The Ni atom is 0·087 (2) Å out of this plane, while the N atom of the second NCO ligand and a water molecule occupy the apical sites.

Introduction. The ligand 2,2′:6′,2″-terpyridine (hereafter terpy) forms two types of metallic complexes. The bis(terpyridine) complexes corresponding to the metal to terpy ratio of 1:2 are always discrete molecules (Allmann, Henke & Reinen, 1978; Arriortua, Rojo, Amigó, Germain & Declercq, 1982). However, mono(terpyridine) complexes (ratio 1:1), especially with the Cu^{II} ion, can give rise to mononuclear (Rojo, Vlasse & Beltran, 1983; Allmann, Kremer & Kucharzcyk, 1984) and polynuclear species (Anderson, Packard & Wicholas, 1976; Rojo, Arriortua, Ruiz, Darriet, Villeneuve & Beltran-Porter, 1987).

The coordination chemistry of the cyanato anion $(NCO)^-$ has already been considered extensively (Norbury, 1975; Kohout, Hvastijova & Gazo, 1978; Kepert, Kucharski & White, 1980). However, less attention has been paid to the study of (cyanato)-nickel(II) complexes.

In previous papers, we have reported the crystal structures of two mono(terpyridine)nickel(II) complexes with chloride and nitrite ligands (Cortés, Arriortua, Rojo, Solans, Miravitlles & Beltran, 1985; Cortés, Arriortua, Rojo, Solans & Beltran, 1986). In order to appreciate the ligand behavior of pseudohalide anions in this kind of compound, we have determined the crystal structure of the title compound.

Experimental. $[Ni(NCO)_2(terpy)(H_2O)]$ was prepared by mixing the complex $[NiCl(terpy)(H_2O)_2]Cl.H_2O$ (Cortés, Arriortua, Rojo, Solans, Miravitlles & Beltran, 1985) with an excess of sodium cyanate in aqueous solution. Green prisms were obtained by slow evaporation of an aqueous/ethanolic solution containing the resulting compound. Density was measured by flotation in bromoform/acetone mixture.

Preliminary cell dimensions and space-group symmetry were obtained from Weissenberg and oscillation photographs. A prism-shaped crystal (0·27 × 0·52 × 0·87 mm) was used for the measurement. Philips PW 1100 diffractometer, graphite-monochromatized Mo *Kα*; cell parameters from 25 reflections ($6 \leq \theta \leq 10°$); *ω*-scan technique, scan width 1°, scan speed 0·03° s^{-1}. Three intensities measured every 2 h, no significant differences. 4501 unique reflections ($2 \leq \theta \leq 30°$). $R_{int} = 0·041$. 3211 with $I \geq 2·5\sigma(I)$; *h*, *k*, *l* range ±12, 19, 12. The structure was solved by direct methods with *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Full-matrix least-squares refinement with *SHELX*76 (Sheldrick, 1976). The function minimized was $\sum w[|F_o| - |F_c|]^2$, with $w = [\sigma^2|F_o| + 0·011|F_o^2|]^{-1}$. Two independent refinements with O(1), N(4), O(2) and N(5) positions interchanged. Final localization was decided from the 'best' value of *R* and anisotropic refinements. H from $\Delta\rho$ and refined with an overall isotropic temperature factor, the remaining atoms refined anisotropically. 287 parameters refined. Final $R = 0·047$ ($wR = 0·053$) for all observed reflections. Max. shift/e.s.d. = 0·31 for *y* of O(*w*) and 0·78 for *z* of H(4). Max. and min. peak in final $\Delta\rho$ map 0·4 e $Å^{-3}$ at 0·97 Å from H(14) and −0·3 e $Å^{-3}$, respectively. IBM 3083 computer. The scattering factors were taken from *International Tables for X-ray Crystallography* (1974).*

An infrared (IR) spectrum was obtained with a Perkin–Elmer spectral photometer 1420. Magnetic susceptibility measurements were performed with a Faraday-type magnetic microbalance between 77 and 300 K.

Discussion. The atomic positional and equivalent isotropic thermal parameters are listed in Table 1. Bond lengths and angles are given in Table 2. The structure of the compound is shown in Fig. 1 together with the atomic numbering system. Fig. 2 shows the packing of the molecules in the unit cell.

The Ni^{II} ion displays distorted octahedral coordination with the three atoms of 2,2′:6′,2″-terpyridine and the N atom of one NCO in the equatorial plane [largest deviation from N(3), N(2), N(1), N(5) mean plane −0·004 (4) Å for N(2)]. The Ni^{II} ion is 0·087 (2) Å out of this plane, while the N atom of the second NCO and a water molecule occupy the apical sites. The Ni—N(terpy) bond lengths range from 2·047 (3) Å for N(2) to an average value of 2·158 (8) Å for the remaining N atoms. The steric effect of terpy produces a decrease in N—Ni—N [average value 77·5 (2)°] and C(11)—N(3)—Ni and C(5)—N(1)—Ni angles [114·2 (3)°] and an enlargement of N(3)—Ni—N(5) and N(1)—Ni—N(5) [average value 102 (1)°] and C(15)—N(3)—Ni and C(1)—N(1)—Ni angles [126·2 (4)°], while the C(6)—N(2)—Ni bond angles are 119·5 (2)°. The C_2N_2Ni five-membered rings have an envelope form with C(11) and C(5) atoms out of the plane defined by the remaining four atoms. The Ni^{II} ion is nearly in the plane defined by N(5), C(17) and O(2) atoms [Ni—N(5)—C(17)—O(2) torsion angle is 170·5 (4)°, Ni—N(4)—C(16)—O(1) torsion angle is −138·4 (4)°]. This explains the shortening of the Ni—N(5) bond length, which is 0·073 Å shorter than that obtained for the Ni—N(4) bond. This suggests that there is more *π*-donor character in the Ni—N(5) bond, which is in agreement with the shorter N(5)—C(17) bond length.

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44803 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional coordinates* ($\times 10^4$; Ni$\times 10^5$) *and equivalent isotropic temperature factors* (Å^2) *with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{8}{3}\pi^2(U_{11} + U_{22} + U_{33}).$$

	x	y	z	B_{eq}
Ni	3760 (3)	11162 (2)	24830 (3)	2·59 (2)
O(w)	−1728 (3)	1163 (1)	1198 (2)	3·84 (10)
N(1)	92 (3)	2665 (2)	2571 (2)	3·12 (10)
N(2)	−888 (2)	1218 (1)	3432 (2)	2·66 (9)
N(3)	−35 (2)	−394 (1)	2753 (2)	2·91 (8)
C(1)	696 (3)	3361 (2)	2116 (3)	3·72 (12)
C(2)	623 (4)	4359 (2)	2336 (3)	4·69 (15)
C(3)	−109 (4)	4631 (2)	3029 (3)	4·82 (16)
C(4)	−748 (4)	3922 (2)	3484 (3)	4·11 (14)
C(5)	−635 (3)	2935 (2)	3230 (2)	3·03 (11)
C(6)	−1296 (3)	2113 (2)	3677 (2)	2·95 (10)
C(7)	−2251 (3)	2210 (2)	4268 (3)	3·74 (13)
C(8)	−2776 (4)	1368 (3)	4613 (3)	4·10 (14)
C(9)	−2326 (3)	441 (2)	4380 (3)	3·86 (14)
C(10)	−1371 (3)	393 (2)	3779 (2)	2·86 (10)
C(11)	−819 (3)	−530 (2)	3422 (2)	2·91 (10)
C(12)	−1094 (3)	−1463 (2)	3743 (3)	3·75 (13)
C(13)	−517 (4)	−2278 (2)	3381 (3)	4·40 (14)
C(14)	292 (4)	−2148 (2)	2701 (3)	4·38 (14)
C(15)	494 (3)	−1188 (2)	2389 (3)	3·62 (13)
N(4)	2363 (3)	1210 (2)	3690 (2)	3·77 (11)
C(16)	3065 (3)	1796 (2)	4250 (2)	3·75 (13)
O(1)	3845 (3)	2387 (3)	4821 (3)	8·32 (18)
N(5)	1458 (3)	983 (2)	1433 (3)	4·20 (13)
C(17)	1770 (3)	753 (2)	719 (3)	3·38 (13)
O(2)	2142 (2)	534 (2)	−18 (2)	6·62 (17)

Table 2. *Bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Ni—N(1)	2·152 (2)	C(5)—N(1)	1·361 (4)
Ni—N(2)	2·047 (3)	C(5)—C(6)	1·516 (4)
Ni—N(3)	2·165 (2)	C(6)—C(7)	1·408 (4)
Ni—N(4)	2·115 (3)	C(7)—C(8)	1·401 (5)
Ni—N(5)	2·042 (3)	C(8)—C(9)	1·413 (5)
Ni—O(w)	2·241 (3)	C(9)—C(10)	1·413 (4)
N(4)—C(16)	1·177 (4)	C(10)—N(2)	1·366 (3)
C(16)—O(1)	1·218 (4)	N(2)—C(6)	1·364 (3)
C(17)—O(2)	1·224 (4)	C(10)—C(11)	1·513 (4)
N(5)—C(17)	1·169 (4)	C(11)—C(12)	1·409 (4)
N(1)—C(1)	1·368 (4)	C(12)—C(13)	1·408 (4)
C(1)—C(2)	1·411 (5)	C(13)—C(14)	1·404 (5)
C(2)—C(3)	1·404 (6)	C(14)—C(15)	1·420 (4)
C(3)—C(4)	1·398 (5)	C(15)—N(3)	1·362 (3)
C(4)—C(5)	1·413 (3)	C(11)—N(3)	1·374 (4)

N(1)—Ni—N(2)	77·7 (1)	Ni—N(1)—C(5)	114·0 (2)
N(1)—Ni—N(3)	154·8 (1)	Ni—N(1)—C(1)	125·9 (2)
N(1)—Ni—N(4)	89·5 (1)	Ni—N(2)—C(6)	119·5 (2)
N(1)—Ni—N(5)	103·3 (1)	Ni—N(3)—C(11)	114·4 (2)
N(1)—Ni—O(w)	85·5 (1)	Ni—N(4)—C(16)	139·3 (2)
N(2)—Ni—N(3)	77·3 (1)	Ni—N(5)—C(17)	162·5 (3)
N(2)—Ni—N(4)	92·0 (1)	N(4)—C(16)—O(1)	177·3 (4)
N(2)—Ni—N(5)	174·6 (1)	N(5)—C(17)—O(2)	177·7 (3)
N(2)—Ni—O(w)	87·9 (1)	Ni—N(3)—C(15)	126·5 (2)
N(3)—Ni—N(4)	94·8 (1)		
N(3)—Ni—N(5)	101·3 (1)		
N(3)—Ni—O(w)	90·2 (1)		
N(4)—Ni—N(5)	93·3 (1)		
N(4)—Ni—O(w)	174·6 (1)		
N(5)—Ni—O(w)	86·9 (1)		

It is relevant to note that the cyanate C—O distance is similar to those found (Anderson, Brown & Finney, 1979; Kepert, Kucharski & White, 1980) in terminally N-bonded transition-metal systems, but the C—N distance is significantly longer.

Table 3 lists the cyanate dimensions of other structurally characterized cyanate-containing molecules. These terminally N-bonded systems fall into two groups based on their MNC angles and N—C distances, as illustrated by a plot of MNC *vs* d_{NC} shown in Fig. 3. For those molecules where the MNC angle approaches 120°, the C—N distance tends toward what would be expected for a C=N double bond. On the other hand, when the MNC angle approaches 180° the C—N distance is short, indicative of a C≡N triple bond. Practically all of the terminally bound transition-metal

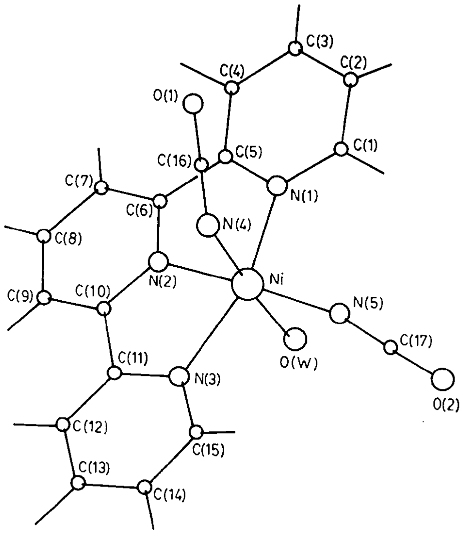

Fig. 1. Molecular structure of the [Ni(NCO)$_2$(terpy)(H$_2$O)] complex showing the atom numbering.

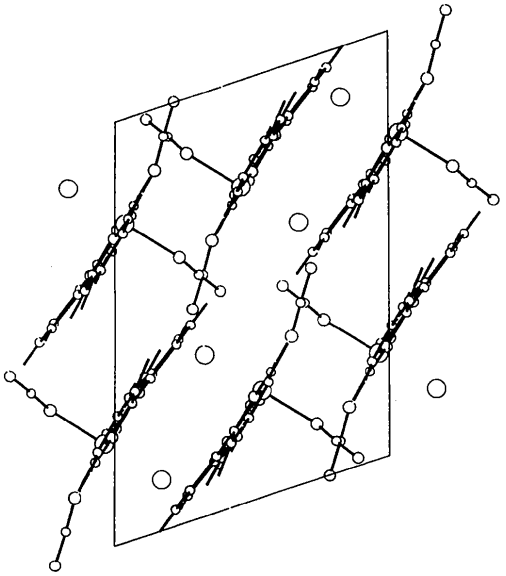

Fig. 2. Packing of the [Ni(NCO)$_2$(terpy)(H$_2$O)] molecules in the unit cell viewed down the b axis, a/c axis vertical.

Table 3. *Dimensions of terminally* N-*bonded cyanates*

	Ligand	N–C(Å)	C–O(Å)	*M*NC(°)	References
HNCO		1·207 (10)	1·170 (10)	128·1	(*a*)
H_3NCO		1·19 (3)	1·18 (3)	140	(*b*)
H_3SiNCO		1·150	1·179	~ 180	(*c*)
H_3GeNCO		1·190 (7)	1·182 (7)	141·3 (4)	(*d*)
$[Cp_2Ti(NCO)_2]$	(NCO)(1)	1·151 (5)	1·192 (5)	171·8 (3)	(*e*)
	(NCO)(2)	1·157 (5)	1·184 (5)	175·7 (3)	
$[Cp_2Zr(NCO)_2]$	(NCO)(1)	1·140 (5)	1·176 (6)	172·6 (3)	(*e*)
	(NCO)(2)	1·156 (5)	1·175 (5)	177·5 (3)	
$[CpCr(NO_2)(NCO)]$		1·126 (5)	1·179 (6)	180·0 (4)	(*f*)
$[CpMo(CO)(PPh_3)_2(NCO)]$		1·118 (14)	1·238 (16)	178·3 (9)	(*g*)
$[Co(terpy)(NCO)_2]$	(NCO)(1)	1·126 (9)	1·197 (9)	160·9 (8)	(*h*)
	(NCO)(2)	1·126 (9)	1·197 (9)	160·9 (8)	
$[(CH_3)_4NAg(NCO)_2]$	(NCO)(1)	1·076 (19)	1·200 (17)	170·0 (13)	(*i*)
	(NCO)(2)	1·111 (18)	1·129 (18)	172·1 (12)	
$[Ni(NCO)_2(terpy)(H_2O)$	(NCO)(1)	1·177 (4)	1·218 (4)	139·3 (2)	(*j*)
	(NCO)(2)	1·169 (4)	1·224 (4)	162·5 (3)	

Abbreviations: Cp_2 = bis(η-cyclopentadienyl); $(PPh_3)_2$ = bis(triphenylphosphine); terpy = 2,2′:6′,2″-terpyridine.

References: (*a*) Jones, Shoolery, Shulman & Yost (1950); (*b*) Curl, Rao, Sastry & Hodgeson (1963), (*c*) Gerry, Thompson & Sugden (1966); (*d*) Murdoch & Rankin (1972); (*e*) Anderson, Brown & Finney (1979); (*f*) Bush & Sim (1970); (*g*) McPhail, Knox, Robertson & Sim (1971); (*h*) Kepert, Kucharski & White (1980); (*i*) Aarflot & Åse (1974); (*j*) this work.

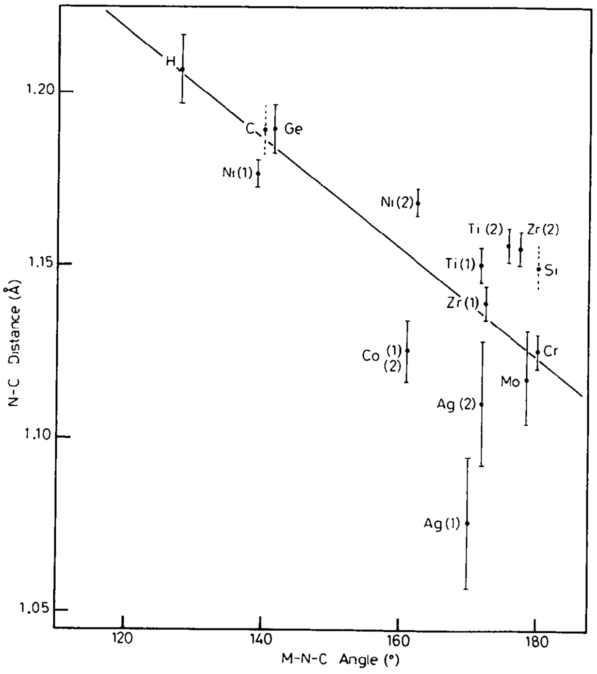

Fig. 3. Plot of C–N bond distance *vs M*NC bond angle for a series of terminally N-bonded cyanate complexes. Approximate error bars are indicated and dashed lines are used when no error values were reported. Labels identify the *M* group of the molecules listed in Table 3.

cyanate systems investigated to date fall in this latter category. It is curious then that the C–N distances of both cyanate ligands in $[Ni(NCO)_2(terpy)(H_2O)]$ fall in the range of the C=N double bond, despite the Ni–N(5)–C(17) angle of 162·5 (3)°.

The distortion from octahedral towards trigonal prismatic geometry was calculated by quantification of the Muetterties & Guggenberger (1974) model (Cortés, Arriortua, Rojo, Solans, Miravitlles & Beltran, 1985). The value of the distortion observed ($\Delta = 0{\cdot}05$) for the title compound is smaller than that for the hexacoordinated terpyridine complexes (Cortés, Arriortua, Rojo, Solans, Miravitlles & Beltran, 1985) and indicates that the $[NiN_5O]$ polyhedron is close to octahedral.

An abundance of IR data is recorded for cyanate compounds when the NCO ion is N-bonded. However, there are very few data reported for O-cyanate complexes, none of which have been confirmed by X-ray crystallography studies (Nelson & Nelson, 1969; Norbury, 1975). In the present complex, the ν_a absorption is split into two frequencies (2170, 2230 cm^{-1}). This splitting is better attributed to the presence of two cyanate ions than to symmetry or lattice effects. The symmetric stretching vibration ν_s is at 1304 cm^{-1}, in the range for N-bonded cyanates. The splitting observed in the δ (NCO) vibration (602 and 592 cm^{-1}) is probably due to lattice effects and appears in complexes containing terminally bonded NCO.

Susceptibility measurements over a temperature range (77–300 K) show paramagnetic behavior. The effective magnetic moment at room temperature is 3·2 BM ($1BM = 9{\cdot}274078 \times 10^{-24} JT^{-1}$).

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Structure du Trihydrogéno Hydroxy-1 Ethanedi(phosphonate)-1,1 de Rubidium Dihydrate

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Abstract. [$Rb\{C(CH_3)(OH)(P_2O_6H_3)\}].2H_2O$, $M_r = 326{\cdot}52$, triclinic, $P\bar{1}$, $a = 6{\cdot}627\,(5)$, $b = 7{\cdot}592\,(5)$, $c = 11{\cdot}066\,(3)$ Å, $\alpha = 79{\cdot}82\,(4)$, $\beta = 80{\cdot}69\,(4)$, $\gamma = 71{\cdot}24\,(5)°$, $V = 516\,(5)$ Å^3, $Z = 2$, $D_m = 2{\cdot}090$, $D_x = 2{\cdot}103$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 5{\cdot}00$ mm^{-1}, $F(000) = 324$, room temperature, $R = 0{\cdot}030$ for 1491 independent reflections. Each Rb is seven-coordinated. It is bound to one tridentate, one bidentate and two monodentate ligands. This arrangement is a layer structure parallel to the *ab* plane where the diphosphonate ions are linked together by a very strong and symmetric hydrogen bond O(4)···O(5) = 2·415 Å. These layers are connected by a chain of two water molecules which act as both hydrogen-bond donors and acceptors.

Introduction. Le complexe $RbCH_3C(OH)(PO_3H_2)(PO_3H).2H_2O$ s'obtient sous forme de monocristaux incolores prismatiques par décomposition du carbonate de rubidium dans une solution aqueuse à 30% d'acide hydroxyéthyldiphosphonique (HEDP) avec le rapport moléculaire $HEDP{:}Rb_2CO_3 = 2$ suivie d'une évaporation lente de la solution à température ambiante.

Ce travail entre dans le cadre d'une étude structurale systématique des complexes pouvant se former entre cations métalliques et acides organophosphorés à fonction hydroxydiphosphonique.[†]

Partie expérimentale. Densité expérimentale évaluée par flottaison dans un mélange diiodométhane/phtalate d'éthyle; cristal de dimensions 0,650 × 0,350 × 0,400 mm; intensités collectées sur diffractomètre Enraf–Nonius CAD-4 équipé d'un monochromateur en graphite, paramètres de la maille affinés par moindres carrés en utilisant 25 réflexions dans le domaine $16 \leq 2\theta \leq 24°$; $\theta_{\max} = 25°$; $-7 \leq h \leq 7$, $-9 \leq k \leq 9$, $0 \leq l \leq 13$; correction de Lorentz et de polarisation; correction empirique d'absorption à partir de mesures azimutales (North, Phillips & Mathews, 1968), valeur extrême de l'absorption: 0,719; trois réflexions de contrôle d'intensité testées toutes les heures: correction linéaire de la décroissance de 0,26% par heure; 1977 réflexions mesurées, dont 1899 indépendantes et 1491

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[†] Etude intégrée dans une 'Action de Recherche Coordonnée' pluridisciplinaire soutenue par le PIRSEM – CNRS et l'AFME portant sur la synthèse et la mise au point de nouveaux extractants hydroxydiphosphonés à hautes performances.

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