

Table 5. *Environment of the two different -OH groups in Na<sub>2</sub>H<sub>2</sub>SiO<sub>4</sub>.xH<sub>2</sub>O*

Values for x=5 are estimated 'best' values for X-ray and neutron refinements

x=7	←1.69→←2.84→ Si-----O-H···O	←1.64→←2.61→ Si-----O-H···O
	.	.
	.	.
	4H <sub>2</sub> O at 2.84, 2.87, 2.96, 3.03	Na at 2.49 H <sub>2</sub> O at 2.78
x=5	←1.68→←2.88→ Si-----O-H···O	←1.65→←2.61→ Si-----O-H···O
	.	.
	.	.
	2Na at 2.53, 2.53	Na at 2.30 H <sub>2</sub> O at 3.16
x=4	←1.70→←2.72→ Si-----O-H···O	←1.64→←2.75→ Si-----O-H···O
	.	.
	.	.
	2H <sub>2</sub> O at 2.75, 2.82	2Na at 2.38, 2.59

further cross-linked to form the 'net' or puckered sheet shown in Fig. 3(a). This relatively orderly behaviour does not extend to the compound with x=5; although this also contains octahedra linked into sheets, the linkages here are not through edges but

through faces and corners [Fig. 3(c)]. Finally, when x=4, (not illustrated) the coordination number of Na drops to five.

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### The Structure of Hydrated 8'-Hydroxyzearealene, C<sub>18</sub>H<sub>22</sub>O<sub>6</sub>.H<sub>2</sub>O. An Estrogenic Syndrome-Producing Microtoxin\*

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8'-Hydroxyzearealene, C<sub>18</sub>H<sub>22</sub>O<sub>6</sub>, is a microtoxin produced by the fungus *Gibberella zeare* (*Fusarium graminearum*). The material crystallizes in space group *P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>* with cell dimensions *a*=12.81 (4), *b*=16.13 (5) and *c*=8.61 (3) Å with *Z*=4. Counter techniques were used to collect 1611 independent reflections of which 1061 had intensities greater than 3σ(*I*). After renormalization of each parity group, the direct methods program *MULTAN* was used to calculate phases for 445 reflections with *E* values greater than 1.15. All 25 nonhydrogen atoms were located in the *E* map. The structure was refined by full-matrix least-squares techniques to a final *R* of 0.065 for 1061 reflections. The structure consists of a 14-membered lactone ring fused to a benzene ring. Some of the chemistry associated with the 14-membered ring can be rationalized in terms of the conformation. The structure is extensively hydrogen bonded.

#### Introduction

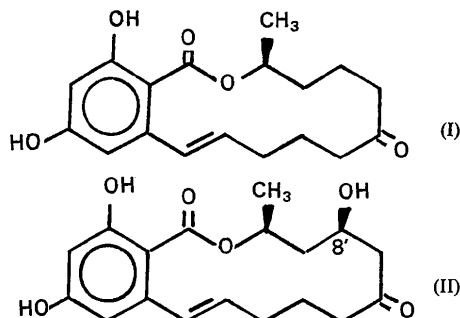
Zearealene is a microtoxin produced by *Gibberella zeare* (*Fusarium graminearum*) when the fungus is allowed to grow on maize under proper conditions of moisture and temperature. Infected grain fed to swine or isolates injected into laboratory animals produce

the estrogenic syndrome which involves primarily the genital system; this appears as vulva hypertrophy, occasional vaginal eversion in the female, preputial enlargement in the castrated male and prominent mammary gland enlargement in both sexes (Stob, Baldwin, Tuite, Andrews & Gillette, 1962; Christensen, Nelson & Mirocha, 1965; Mirocha & Christensen, 1971).

The structure of zearealene (I) was determined by

\* FASTBIOS contribution No. 23.

chemical and spectroscopic techniques to be 6-(10-hydroxy-6-oxo-*trans*-1-undecenyl)- $\beta$ -resorcylic acid lactone (Urry, Wehrmeister, Hodge & Hidy, 1966) and a complete synthesis and assignment of absolute configuration has been reported (Kuo, Taub, Hoffsommer, Wendler, Urry & Mullenbach, 1967; Taub *et al.*, 1968). Chemical reactions and modifications of zearalenone have been reported (Johnston, Sawicki, Windholz & Patchett, 1970; Jensen, Brown, Schmitt, Windholz & Patchett, 1972; Shipchandler, 1975) and comparisons made with estradiol to rationalize the estrogenic activity.



Zearalenone is produced commercially by fermentation and catalytic hydrogenation of the 6' keto

function produces the anabolic agent zearanol. Zearanol is used to improve growth rate and feed efficiency in feed lot cattle (*Fed. Regist.* 1969, 1970) and is being tested clinically for alleviation of menopausal and postmenopausal syndrome (Maqueo & Calderon, 1974; Utian, 1973).

Seven other naturally occurring derivatives of zearalenone were isolated (Mirocha & Christensen, 1971; Mirocha, Christensen & Nelson, 1968; Bolliger & Tamm, 1972), and compound F-5-3 was submitted to the FASTBIOS Laboratory. Chemical and mass spectrometric studies of F-5-3 and F-5-4 showed them to be epimeric 8'-hydroxyzearalenones (Jackson, Fenton, Mirocha & Davis, 1974), and our structural study confirms the assignment of F-5-3 as the 8'(R) epimer (II).

### Experimental

A crystal of dimensions 0.35 × 0.07 × 0.35 mm was mounted with the *c* axis coincident with the rotation axis. The unit cell was found to be orthorhombic and

Table 1. *Crystal data*

$C_{18}H_{22}O_6 \cdot H_2O$ , M.W. 352.4,  $a=12.81$  (4),  $b=16.13$  (5),  $c=8.61$  (3) Å.  $P2_12_12_1$  ( $D_2^h$ , No. 19).  $Z=4$ ,  $F(000)=752$ ,  $V=1779$  Å<sup>3</sup>,  $D_{exp}=1.3$ ,  $D_{cal}=1.315$  g cm<sup>-3</sup>,  $\mu=8.56$  cm<sup>-1</sup>

Table 2. *Atomic parameters* ( $\times 10^4$ ) and *thermal parameters* ( $\times 10^3$ ) for 8'-hydroxyzearalenone

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
C(1)	2439 (6)	964 (5)	75 (10)	35 (4)	34 (4)	36 (5)	4 (3)	-5 (4)	-1 (4)
C(2)	1664 (6)	1566 (5)	-239 (10)	42 (4)	36 (4)	33 (5)	1 (3)	-8 (4)	2 (4)
C(3)	616 (6)	1341 (5)	-402 (10)	42 (4)	41 (4)	34 (5)	2 (4)	-7 (4)	4 (4)
C(4)	317 (6)	537 (5)	-172 (9)	40 (4)	57 (5)	18 (5)	-1 (4)	-1 (4)	4 (4)
C(5)	1062 (6)	-69 (5)	185 (9)	37 (4)	45 (4)	30 (5)	4 (3)	-3 (4)	5 (4)
C(6)	2114 (6)	131 (4)	311 (9)	39 (4)	36 (4)	29 (5)	-5 (3)	1 (4)	2 (4)
O(7)	1881 (5)	2379 (3)	-354 (8)	55 (4)	36 (3)	86 (5)	3 (3)	-7 (4)	4 (3)
O(8)	-701 (4)	290 (4)	-272 (7)	37 (3)	58 (3)	53 (4)	-4 (3)	4 (3)	6 (3)
O(9)	3076 (4)	3675 (3)	1700 (7)	44 (3)	50 (3)	56 (4)	-3 (3)	9 (3)	0 (3)
C(1')	2831 (6)	-567 (4)	689 (10)	39 (5)	31 (4)	44 (5)	-2 (3)	-14 (4)	1 (4)
C(2')	2776 (6)	-1312 (5)	116 (11)	30 (4)	42 (5)	61 (6)	-4 (3)	-14 (4)	12 (5)
C(3')	3408 (6)	-2039 (5)	638 (11)	40 (5)	41 (4)	54 (6)	-6 (4)	-4 (5)	10 (4)
C(4')	3948 (8)	-2531 (5)	-645 (11)	61 (6)	40 (4)	55 (6)	-3 (4)	-28 (5)	-9 (4)
C(5')	4762 (8)	-2023 (5)	-1575 (11)	74 (6)	44 (5)	29 (5)	-8 (5)	-10 (5)	0 (4)
C(6')	5670 (7)	-1730 (5)	-702 (11)	52 (5)	29 (4)	52 (6)	9 (4)	1 (4)	-6 (4)
C(7')	6349 (7)	-1083 (5)	-1494 (12)	56 (6)	44 (5)	60 (6)	12 (4)	17 (5)	0 (5)
C(8)'	5858 (7)	-223 (5)	-1352 (11)	39 (5)	42 (4)	54 (6)	-3 (4)	-2 (4)	7 (4)
C(9')	5940 (6)	131 (4)	223 (10)	35 (4)	33 (4)	42 (5)	-4 (3)	0 (4)	-2 (4)
C(10')	5318 (6)	928 (5)	482 (10)	32 (4)	34 (4)	43 (5)	-6 (3)	-5 (4)	6 (4)
O(11)'	4231 (4)	673 (3)	316 (7)	32 (3)	29 (2)	58 (4)	-2 (2)	-8 (3)	-2 (3)
C(12')	3533 (6)	1254 (5)	92 (10)	44 (5)	37 (4)	45 (6)	4 (4)	5 (4)	-1 (4)
O(13)'	3769 (4)	1968 (3)	-88 (9)	43 (3)	33 (3)	112 (6)	-1 (3)	-6 (4)	16 (3)
C(14')	5479 (7)	1284 (5)	2073 (10)	50 (5)	40 (4)	36 (5)	-12 (4)	-6 (4)	3 (4)
O(15)'	6375 (5)	336 (4)	-2425 (7)	48 (3)	54 (3)	48 (4)	-22 (3)	3 (3)	-1 (3)
O(16)'	5907 (5)	-2001 (3)	598 (8)	64 (4)	49 (3)	55 (4)	-4 (3)	-13 (3)	8 (3)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>		<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
H(10)	1061	-521	870	3.0	H(24')	6667	-1187	-435	3.0
H(11)	455	1875	-870	3.0	H(25')	6667	-1319	-2179	3.0
H(12)	2879	2500	-203	3.0	H(26')	4952	-2604	-2609	3.0
H(17')	5758	1250	0000	3.0	H(27')	4545	-1562	-2179	3.0
H(18')	6300	1596	2174	3.0	H(28')	3536	-2604	-1304	3.0
H(19')	5000	1729	2174	3.0	H(29')	4545	-2917	0000	3.0
H(20')	5152	1038	3261	3.0	H(30')	4091	-1800	1304	3.0
H(21')	5758	-208	1304	3.0	H(31')	3030	-2292	1304	3.0
H(22')	6515	417	435	3.0	H(32')	2212	-1458	-435	3.0
H(23')	5152	-312	-1739	3.0	H(33')	3485	-208	1304	3.0

room-temperature cell dimensions (Table 1) were determined from Weissenberg photographs. The quantity of sample was insufficient for accurate density measurements and the crystal used to collect intensity data was not available for determination of more accurate cell parameters.

The intensity data,  $hk0$  through  $hk7$ , were collected with a Philips Paired diffractometer using equi-inclination geometry, the continuous  $\omega$ -scan technique, Cu  $K\alpha$  radiation ( $\lambda=1.54178$  Å) and a graphite monochromator. A scan range of  $3.4$  to  $6.4^\circ$  and a scan speed of  $2.5^\circ \text{ min}^{-1}$  were used. 1611 independent reflections were measured and 1061 had intensities greater than  $3\sigma(I)$ . The intensities of several reference reflections were monitored during data collection and only statistical variations were observed. Lorentz, polarization and absorption (Stemple, 1969) corrections were applied. Transmission factors ranged from 0.789 to 0.945.

### Structure determination and refinement

The overall temperature and scale factors were determined from a least-squares fitted Wilson curve and normalized structure factors were generated. The *MULTAN* direct methods program (Germain, Main & Woolson, 1971) could not find an appropriate set of reflections to define the origin, and manual selection of origin-defining reflections did not lead to a solution. This is attributed to the small size of certain parity groups in the set of  $|E|$ 's greater than 1.00. Normalized

structure factors were recalculated such that  $\langle E^2 \rangle = 1.0$  for each parity group. The renormalized set contained 445  $|E|$ 's greater than 1.15, and an origin defined by reflections 3,14,1, 11,5,0 and 0,1,4 was selected automatically by *MULTAN* and assigned phases  $\pi/4, \pi/2, \pi/2$ . Reflection 3,14,1 was used to fix the enantiomorph.

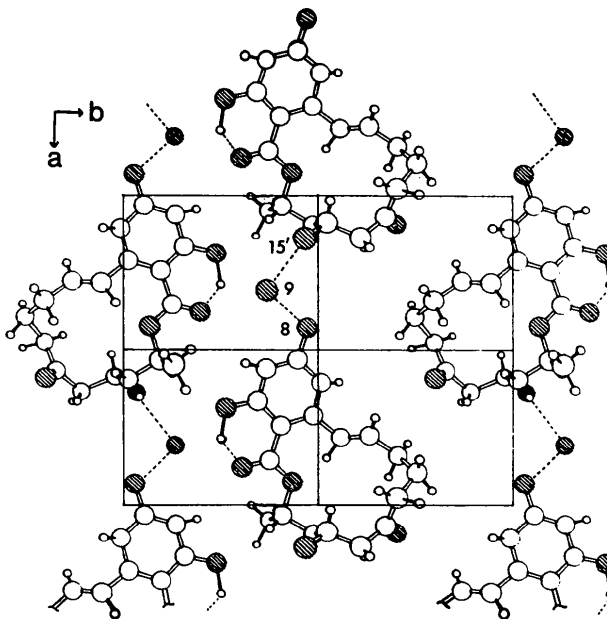


Fig. 1. Two-dimensional network of 8'-hydroxyzearalenone molecules.

Table 3. Bond distances(Å), bond angles and torsion angles( $^\circ$ ) for 8'-hydroxyzearalenone

C(1)–C(2)	1.41 (1)	C(1')–C(2')	1.30 (1)	C(9')–C(10')	1.53 (1)
C(2)–C(3)	1.40 (1)	C(2')–C(3')	1.49 (1)	C(10')–O(11')	1.46 (1)
C(3)–C(4)	1.37 (1)	C(3')–C(4')	1.53 (1)	O(11')–C(12')	1.31 (1)
C(4)–C(5)	1.40 (1)	C(4')–C(5')	1.55 (1)	C(12')–C(1)	1.48 (1)
C(5)–C(6)	1.39 (1)	C(5')–C(6')	1.46 (1)	C(12')–O(13')	1.20 (1)
C(6)–C(1)	1.42 (1)	C(6')–C(7')	1.52 (1)	C(10')–C(14')	1.50 (1)
C(2)–O(7)	1.34 (1)	C(7')–C(8')	1.53 (1)	C(8')–O(15')	1.45 (1)
C(4)–O(8)	1.37 (1)	C(8')–C(9')	1.48 (1)	C(6')–O(16')	1.24 (1)
C(6)–C(1')	1.49 (1)				

#### Possible hydrogen-bonded interactions

O(8)–O(9)*	2.600 (8)	O(7)–O(9)	3.137 (9)	O(16')–O(9)†	2.880 (9)
H(12)–O(7)	1.30	O(15')–O(9)*	2.771 (8)	O(13')–O(9)	3.277 (8)
H(12)–O(13')	1.43	O(7)–O(13')	2.518 (8)	H(12)–O(9)	2.52

1–2–3	121‡	3–4–8	122	4'–5'–6'	116	12'–1–6	125
2–3–4	120	5–4–8	117	5'–6'–7'	117	12'–1–2	117
3–4–5	120	1–6–1'	124	6'–7'–8'	111	7'–8'–15'	109
4–5–6	121	5'–6'–1'	116	7'–8'–9'	113	9'–8'–15'	108
5–6–1	119	6–1'–2'	126	8'–9'–10'	115	9'–10'–14'	113
6–1–2	118	1'–2'–3'	126	9'–10'–11'	104	11'–10'–14'	109
1–2–7	123	2'–3'–4'	116	10'–11'–12'	118	11'–12'–13'	122
3–2–7	116	3'–4'–5'	114	11'–12'–1	115	1–12'–13'	123
		5'–6'–16'	123	7'–6'–16'	120		

#### Internal torsion angles

1–6	–3	3'–4'	118	7'–8'	73	11'–12'	–175
6–1'	–139	4'–5'	64	8'–9'	–171	12'–1	1
1'–2'	–172	5'–6'	–167	9'–10'	65		
2'–3'	–131	6'–7'	80	10'–11'	–163		

\*  $\frac{1}{2} + x, \frac{1}{2} - y, -z$ . Symmetry relationship for intermolecular interaction

†  $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$ .

‡ Standard deviations of bond angles range between  $0.6$  and  $0.8^\circ$ .

Four other reflections were included in the starting set, and of the 256 generated phase sets, two shared the highest absolute figure of merit (1.13). One set had a slightly lower value of  $\psi_0$  and was used to calculate an  $E$  map. All non-hydrogen atoms of the 8'-hydroxyzearalenone molecule as well as a water of hydration were found in the first  $E$  map. Full-matrix isotropic least-squares refinement of the 25 atomic positions reduced  $R$  to 0.098 where  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ . Introduction of anisotropic thermal parameters reduced  $R$  to 0.074. A three-dimensional difference electron density map clearly showed the positions of all H atoms except for those associated with hydroxyl groups O(8) and O(15') and the water molecule. Extensive smearing of electron density was observed around these atoms in the final difference Fourier map, and no assignment of H atom positions could be made.

The contributions of the H atoms were included in a least-squares refinement, but the parameters were not refined. The refinement was terminated at  $R=0.065$  and  $R_w=0.087$ , where  $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ . The function minimized was  $\sum w(F_o - F_c)^2$  where  $w = 1/(\Delta F)^2$  and  $\Delta F = 0.429 + 0.064F_o$ . The scattering factors of Cromer & Waber (1965) were used for C and

O while those of Stewart, Davidson & Simpson (1965) were used for H.

The estimated standard deviations were calculated from the inverse of the normal-equations matrix. All shifts of the parameters during the final cycle were less than 0.05 of the estimated standard deviation. The atomic and thermal parameters along with the estimated standard deviations are given in Table 2.\*

## Discussion

Fig. 1 shows the two-dimensional layer structure which lies parallel to the  $ab$  plane while Fig. 2 gives the molecular structure and numbering system used in all tables. Table 3 lists bond distances, bond angles and torsion angles. The configuration at C atom 10' is known to be  $S$  in zearalenone (Kuo *et al.*, 1967; Taub *et al.*, 1968) and this study shows the configuration at 8' in 8'-hydroxyzearalenone to be  $R$ . The torsion angles are consistent with this assignment of absolute configuration.

The molecules composing the two-dimensional sheets are held together by an extensive network of hydrogen bonds and electrostatic interactions involving the water of hydration. Hydroxyl groups O(8) and O(15') interact with the water molecule O(9) at distances of 2.60 and 2.77 Å to form chains parallel to the  $a$  axis. An intramolecular hydrogen bond is formed between hydroxyl O(7) and carbonyl O(13') with H(12)-O(7) = 1.30 Å and H(12)-O(13') = 1.43 Å. These atoms also interact with the water molecule to bind the chains into the two-dimensional sheets parallel to the  $ab$  plane with O(7)-O(9) = 3.14, O(13')-O(9) = 3.28 and H(12)-O(9) = 2.52 Å. The two-dimensional sheets are held together by an interaction between carbonyl oxygen O(16') and the water molecule, O(9)-O(16') = 2.88 Å. There is a 12°C discrepancy in literature reported melting points for 8'-hydroxyzearalenone (Bollinger & Tamm, 1972; Jackson *et al.*, 1974) which may be associated with the degree of hydration.

The phenyl ring and atoms O(7), O(8), C(1'), C(12'), O(13'), C(11'), C(10') and C(9') form a reasonably planar system as indicated by the torsion angles. A sharp step occurs out of the plane to C(2') and C(8') and the molecule is bounded by a plane of atoms C(4'), C(5'), C(6'), C(7'), O(16') essentially perpendicular to the phenyl ring plane. In zearalenone enolization of O(16') occurs in the C(5') direction rather than the C(7') direction (Jensen *et al.*, 1972). If the conformation is similar to that of 8'-hydroxyzearalenone, enolization in the 5' direction requires little change in conformation while enolization in the 7' direction requires almost a 90° rotation about C(6')-C(7').

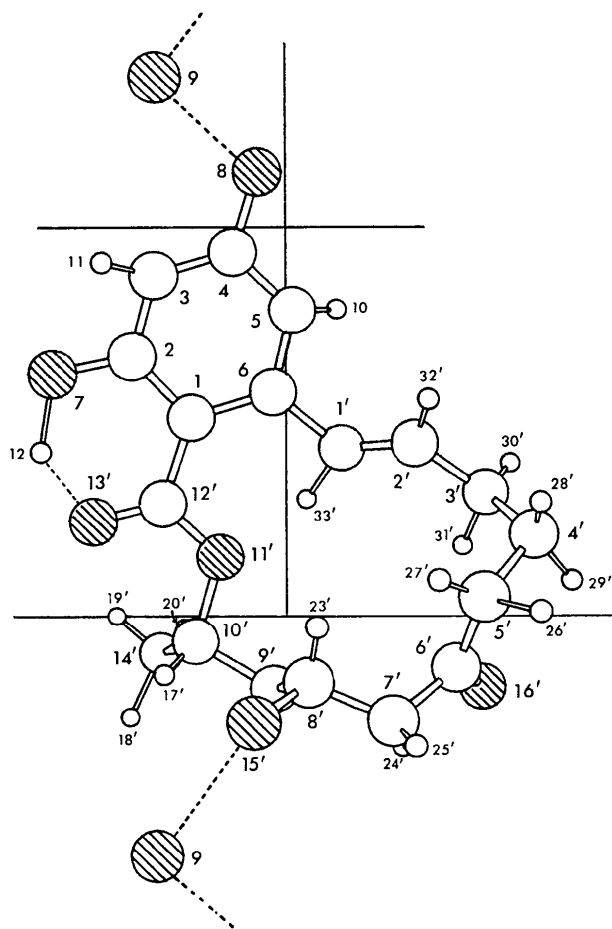


Fig. 2. Molecular structure of 8'-hydroxyzearalenone and the numbering system used in all tables and discussion.

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31256 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

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## Structure Cristalline du Complexe de l'Hexakis(benzotriazolyl)-hexakis(allylamine)-trisnickel(II) avec la Triphénylphosphine Oxyde

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Crystals of the complex  $\text{Ni}_3\text{C}_{90}\text{H}_{96}\text{N}_{24}\text{O}_2\text{P}_2$  are trigonal, space group  $R\bar{3}c$ , with hexagonal cell dimensions  $a = 17.383$  and  $c = 50.461$  Å. The structure was solved by the heavy-atom method from 2480 diffractometer data and refined by full-matrix least-squares calculations. The complex, which belongs to the point group  $\bar{3}$ , can be formulated as:  $\text{Ni}[-(\text{BT})_3-\text{Ni}-(\text{AA})_3]_2 \cdot 2[\text{Ph}_3\text{PO}]$  with AA = allylamine and BT = benzotriazolyl. There is no direct bonding between the phosphine oxide molecules and the metal atoms.

### Introduction

Dans le cadre d'une étude sur les transporteurs d'oxygène, Drapier & Hubert (1973) ont préparé des complexes du nickel et du cobalt susceptibles d'agir comme catalyseurs sélectifs d'oxydation. Nous décrivons ici la structure du complexe  $\text{Ni}_3\text{C}_{90}\text{H}_{96}\text{N}_{24}\text{O}_2\text{P}_2$ ; son analogue  $\text{Co}_3\text{C}_{90}\text{H}_{96}\text{N}_{24}\text{O}_2\text{P}_2$  lui est parfaitement isostructural, comme nous l'ont montré les spectres de diffraction. Il serait intéressant d'établir la structure du complexe dans lequel l'oxydation de la molécule de triphénylphosphine n'a pas encore eu lieu, toutefois la mauvaise qualité des cristaux ne l'a pas permis jusqu'à présent.

### Partie expérimentale

Les cristaux sont violets, parfaitement limpides, de forme rhomboédrique. Le cristal choisi mesure 0,25

mm d'arête, il a été monté suivant un de ses axes binaires. Les paramètres cristallins pré-évalués sur chambre de Weissberg ont été affinés à partir de mesures effectuées sur un diffractomètre à quatre cercles Picker. Quelques 2480 réflexions indépendantes ont été mesurées au moyen du diffractomètre (radiation  $\text{Cu K}\alpha$ ) dans un sixième de la sphère de diffraction (angle  $2\theta$  max =  $129^\circ$ ), parmi celles-ci 1432 sont significatives [ $I_o > 2,5\sigma(I_o)$ ]. Les intensités ont été corrigées par les facteurs de Lorentz et de polarisation, mais il n'a pas été tenu compte de l'absorption.

### Données cristallines

Stoichiométrie  $\text{Ni}_3\text{C}_{90}\text{H}_{96}\text{N}_{24}\text{O}_2\text{P}_2$ . Groupe spatial  $R\bar{3}c$ ;  $a = b = 17,383$  (4);  $c = 50,461$  (7) Å;  $V = 13205,0$  Å<sup>3</sup>;  $Z = 6$ ;  $M = 1784,03$ ;  $D_c = 1,346$ ,  $D_o = 1,38$  g cm<sup>-3</sup>;  $\lambda(\text{Cu K}\alpha) = 1,5418$  Å;  $F(000) = 5604$ .