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The Crystal Structure of Dichlorodiethyl-3(2-pyridyl)-5,6-diphenyl-1,2,4-triazinetin(IV)*

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$C_{24}H_{24}N_4Cl_2Sn$, monoclinic, Pn, $a = 10.733(3)$, $b = 22.979(5)$, $c = 9.852(1)$ Å, $\beta = 93.82(1)°$, $Z = 4$, $D_{calc} = 1.50$ Mg·m^{-3}. The structure was refined by block diagonal least squares to a residual of $R_F = 0.054$ for 3336 observed reflections ($I > 3\sigma(I)$). Both the crystallographically unique molecules exhibit an octahedral coordination around the Sn atom with cis *Cl atoms and* trans *ethyl groups. The conformation of the 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine moiety in the two molecules is different.*

Introduction

The octahedral 1:1 complexes between diorganotin dichlorides and bidentate α-diimine ligands appear to occur exclusively in the configuration with *trans* organic groups and *cis* chloro groups. We are not aware of any example so far reported which contains the alternative configuration with *cis* organic groups and *trans* chloro groups.

Measurements of dipole moment values in benzene solution have been used to distinguish between the two stereochemical alternatives for these compounds [1–3]. One such investigation [4] carried out on the title complex, *i.e.*, that between diethyltin dichloride and the bidentate chelating ligand 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine indicates that this complex, with a dipole moment of 7 Debyes in benzene solution, had the unusual configuration with *cis* ethyl groups and *trans* chloro groups. Therefore, a crystal structure analysis of the title complex was undertaken to find out if the structure was the same in the solid state.

Experimental

Diethyltin dichloride was obtained from Alpha Inorganics Inc.; 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine was prepared from the corresponding hydrazine by the method of Case [5], and obtained as a yellow crystalline solid which melted at 190 °C. Buff crystals of the title complex were obtained in good yield by mixing stoichiometric quantities of hot ethanolic solutions of diethyltin dichloride and the ligand (m.p. 168 °C). Microanalyses were carried out by the Australian Microanalytical Service, CSIRO, Melbourne, Australia. Found (%): C, 51.83; H, 4.33; N, 10.15; Sn, 20.7. Calcd. (%) for $C_{24}H_{24}N_4Cl_2Sn$: C, 51.65; H, 4.33; N, 10.04; Sn, 21.3.

Structure Solution and Refinement:

Single crystals of the title compound were taken from the same sample prepared for dipole moment studies [3, 4]. The crystals were needles of rectangular cross-section, elongated along the c-axis. A single 0.35 × 0.2 × 0.2 mm crystal was mounted on a glass fibre and randomly oriented on an automatic Picker 4-circle diffractometer. The diffraction intensities were measured at −25 °C. Graphite monochromatised MoKα radiation generated at 50 Kv and 16 mA was used in a $\theta/2\theta$ scan with line-profile analysis [6]. A total of 4448 measurements were made up to 50° in 2θ giving 4300 unique reflections, of which 3336 had a net intensity greater than $3\sigma(I)$, based on counting statistics, and were considered to be observed. The intensities were corrected for measured direct beam polarisation [7]. Absorption corrections were not calculated ($\mu = 1.297$ mm^{-1}). The cell parameters were obtained by least squares refinement of the setting angles of 40 reflections with 2θ greater than 35° ($\lambda MoK\alpha_1 = 0.70932$ Å).

From the systematic absences, the space group was found to be either *Pn* or *P2/n*, and then determined as *Pn*, since the Patterson map could be interpreted only in this space group with two molecules in the asymmetric unit. Subsequent solution and refinement of the structure confirmed the correctness of the space group assignment. *Pn* is a non-standard setting of the space group *Pc*, with equivalent positions x, y, z and $1/2 + x, \bar{y}, 1/2 + z$.

One of the Sn atoms (Sn A) was placed at $x = 0$ and $z = 0$ to fix the origin in the *ac*-plane and the

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position of the second Sn atom was found with respect to this origin. All the non-hydrogen atoms were located in successive Fourier maps. The structure was first refined isotropically, followed by several cycles of anisotropic refinement, which lowered the residual to 0.11. The structure was refined by block diagonal least squares, the quantity minimised being

$$D = \Sigma w(|F_o| - |F_c|)^2$$

The conventional residual and the weighted residual are defined as

$$R_F = \frac{\Sigma||F_o| - |F_c||}{\Sigma|F_o|}$$

$$R_{wF} = \left[\frac{\Sigma w||F_o| - |F_c||^2}{\Sigma w|F_o|^2}\right]^{1/2}$$

where $w = \dfrac{1}{\sigma^2|F_o|}$

based on counting statistics. The effects of anomalous scattering by Sn and Cl atoms were included in the structure factor calculations. The scattering curves for neutral atoms and the real and imaginary parts (f' and f'') of the dispersion term in the scattering factors of Sn and Cl were taken from the literature [8].

The positions of the hydrogen atoms of the ring systems were calculated and included in calculating structure factors but were not refined. Further refinement revealed a certain amount of disorder in the structure. The thermal parameters of some of the ring carbon atoms were very large (Table I), and a difference map showed alternative positions for one of the ethyl groups in molecule B

TABLE I. Atomic Positional Parameters and Equivalent Isotropic Debye-Waller Parameters[a].

	X	Y	Z	BEQ
SnA	0	0.96576 (5)	0	2.59 (5)
Cl1A	0.0726 (5)	0.90306 (23)	-0.1798 (5)	4.1 (3)
Cl2A	-0.1344 (5)	1.0390 (3)	-0.1290 (6)	5.6 (3)
N1A	-0.0190 (15)	1.0043 (6)	0.2403 (14)	3.5 (8)
N2A	0.2100 (13)	0.8715 (6)	0.1391 (13)	2.5 (7)
N3A	0.1199 (13)	0.9074 (6)	0.1707 (13)	2.6 (7)
N4A	0.1343 (14)	0.8732 (7)	0.3945 (13)	3.3 (8)
C1A	-0.1632 (16)	0.9181 (8)	0.0397 (18)	3.2 (9)
C2A	-0.2314 (19)	0.8883 (9)	-0.0824 (20)	4.7 (12)
C3A	0.1546 (18)	1.0258 (8)	0.0095 (18)	4.2 (10)
C4A	0.1853 (20)	1.0508 (8)	-0.1294 (20)	4.4 (11)
C5A	0.0326 (16)	0.9660 (8)	0.3435 (16)	3.1 (9)
C6A	0.0174 (23)	0.9833 (9)	0.4814 (18)	5.6 (12)
C7A	-0.0394 (19)	1.0376 (10)	0.5045 (20)	5.2 (12)
C8A	-0.0861 (21)	1.0715 (9)	0.4061 (19)	5.0 (12)
C9A	-0.0766 (17)	1.0500 (8)	0.2714 (19)	3.6 (10)
C10A	0.0963 (16)	0.9139 (7)	0.3044 (17)	2.6 (8)
C11A	0.2679 (17)	0.8374 (7)	0.2312 (17)	2.9 (9)
C12A	0.2114 (18)	0.8328 (8)	0.3591 (18)	3.2 (9)
C13A	0.2380 (22)	0.7813 (9)	0.4571 (20)	4.9 (12)
C14A	0.2645 (24)	0.7275 (9)	0.4154 (22)	5.9 (13)
C15A	0.280 (3)	0.6858 (10)	0.510 (3)	9.2 (19)
C16A	0.283 (3)	0.6968 (13)	0.641 (3)	12.1 (24)
C17A	0.256 (3)	0.7461 (12)	0.9617 (21)	8.3 (17)
C18A	0.2366 (24)	0.7948 (12)	0.6041 (23)	7.4 (16)
C19A	0.3815 (16)	0.8098 (7)	0.1914 (17)	2.5 (8)
C20A	0.3833 (18)	0.7842 (8)	0.0644 (18)	3.6 (10)
C21A	0.4871 (17)	0.7622 (8)	0.0261 (18)	3.5 (10)
C22A	0.5919 (21)	0.7618 (9)	0.1018 (22)	5.3 (12)
C23A	0.5934 (17)	0.7859 (9)	0.2301 (21)	4.6 (11)
C24A	0.4880 (19)	0.8104 (9)	0.2743 (18)	4.1 (11)
SnB	0.45560 (15)	0.52956 (6)	-0.03323 (15)	3.96 (7)
Cl1B	0.3522 (8)	0.4871 (4)	-0.2433 (7)	9.4 (5)
Cl2B	0.5452 (7)	0.6185 (3)	-0.1282 (6)	6.5 (4)
N1B	0.5329 (15)	0.5571 (6)	0.2034 (15)	3.7 (8)
N2B	0.3770 (17)	0.4010 (7)	0.1104 (14)	4.7 (9)

(continued)

TABLE I *(continued)*

	X		Y		Z		BEQ	
N3B	0.4162	(17)	0.4521	(7)	0.1454	(15)	4.9	(9)
N4B	0.4564	(15)	0.4239	(6)	0.3718	(15)	4.0	(9)
C1B	0.5742		0.4621		−0.0762		7.90	
C2B	0.6015		0.3975		−0.0167		7.90	
C1'B	0.6018		0.4824		−0.0452		7.90	
C2'B	0.6579		0.4640		−0.1537		7.90	
C3B	0.2868	(24)	0.5689	(10)	0.0174	(22)	6.47	(9)
C4B	0.274	(3)	0.6283	(10)	0.066	(3)	7.52	(13)
C5B	0.5120	(19)	0.5214	(8)	0.3017	(18)	3.77	(6)
C6B	0.5334	(23)	0.5389	(9)	0.4410	(19)	5.66	(6)
C7B	0.5691	(22)	0.5950	(10)	0.4661	(21)	5.6	(13)
C8B	0.6012	(21)	0.6317	(9)	0.3666	(19)	4.7	(12)
C9B	0.5791	(20)	0.6100	(8)	0.2349	(20)	4.5	(11)
C10B	0.4551	(20)	0.4614	(8)	0.2704	(19)	4.3	(10)
C11B	0.3770	(19)	0.3583	(8)	0.2023	(19)	3.7	(10)
C12B	0.4219	(20)	0.3722	(8)	0.3428	(19)	4.1	(11)
C13B	0.4280	(20)	0.3287	(8)	0.4550	(20)	4.0	(10)
C14B	0.468	(3)	0.2733	(9)	0.4475	(22)	7.3	(15)
C15B	0.4833	(22)	0.2331	(9)	0.5455	(19)	5.2	(12)
C16B	0.456	(3)	0.2565	(10)	0.6699	(24)	7.5	(16)
C17B	0.4202	(23)	0.3124	(9)	0.6945	(20)	5.6	(13)
C18B	0.4061	(22)	0.3489	(8)	0.5813	(20)	5.0	(12)
C19B	0.3362	(18)	0.3002	(8)	0.1552	(18)	3.4	(10)
C20B	0.4038	(21)	0.2649	(9)	0.0729	(19)	4.7	(12)
C21B	0.3632	(22)	0.2104	(9)	0.0402	(21)	5.4	(13)
C22B	0.2619	(22)	0.1884	(9)	0.0726	(20)	5.2	(12)
C23B	0.1915	(21)	0.2205	(9)	0.1513	(23)	5.5	(13)
C24B	0.2237	(20)	0.2772	(9)	0.1959	(22)	5.1	(12)
H6A	0.0478		0.9541		0.5638		7.69	
H7A	−0.0409		1.0516		0.6075		6.33	
H8A	−0.1288		1.1125		0.4290		5.66	
H9A	−0.1213		1.0744		0.1893		2.63	
H14A	0.2717		0.7191		0.3067		8.17	
H15A	0.2835		0.6405		0.4759		18.67	
H16A	0.3251		0.6639		0.7095		14.70	
H17A	0.2490		0.7498		0.7993		12.36	
H18A	0.2195		0.8407		0.6399		8.94	
H20A	0.2982		0.7830		−0.0015		3.30	
H21A	0.4884		0.7435		−0.0754		2.93	
H22A	0.6795		0.7447		0.0658		5.14	
H23A	0.6790		0.7881		0.2944		2.33	
H24A	0.4886		0.8284		0.3760		4.42	
H6B	0.5162		0.5085		0.5237		8.84	
H7B	0.5795		0.6105		0.5714		8.69	
H8B	0.6392		0.6736		0.3873		7.29	
H9B	0.6062		0.6376		0.1528		7.31	
H14B	0.4938		0.2593		0.3454		10.06	
H15B	0.5148		0.1885		0.5291		7.51	
H16B	0.4657		0.2250		0.7578		9.62	
H17B	0.4005		0.3256		0.7959		7.90	
H18B	0.3757		0.3941		0.5908		9.29	
H20B	0.4903		0.2821		0.0332		6.23	
H21B	0.4246		0.1827		−0.0168		7.18	
H22B	0.2320		0.1453		0.0391		7.48	
H23B	0.1042		0.2019		0.1823		5.25	
H24B	0.1661		0.3023		0.2564		5.35	

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[a] Atomic parameters X, Y, Z and BEQ. E.S.DS. refer to the last digit printed. BEQ is the arithmetic mean of the principal axes of the thermal ellipsoid.

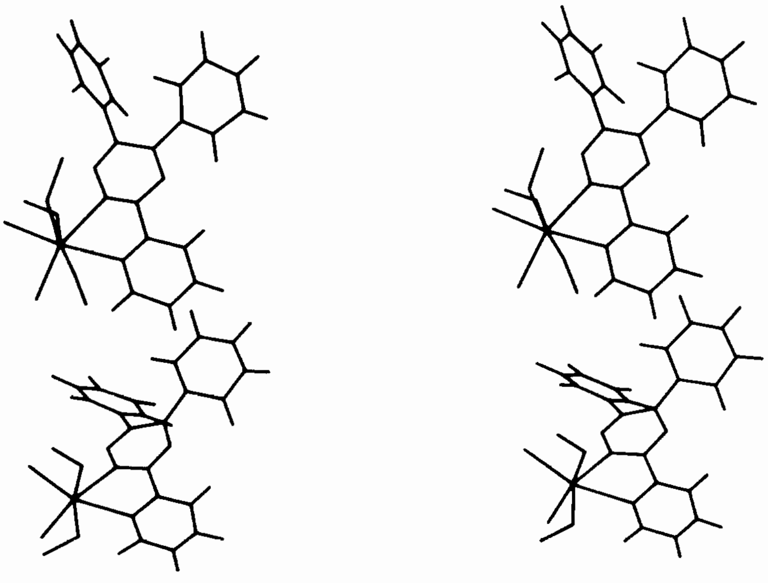


Fig. 1. Stereoscopic pair of the molecules seen approximately along the [100] direction.

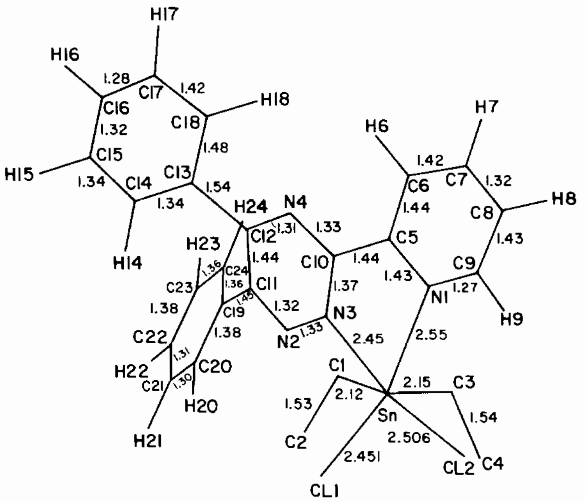
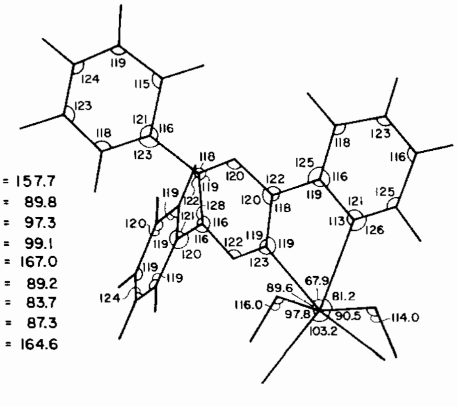


Fig. 2a. Atom names and bond distance (Å) (uncorrected for thermal motion) in molecule A. The esd's on bond distances are Sn–Cl = 0.005 Å, Sn–N = 0.01 Å, Sn–C = 0.02 Å, N–N, C–N and C–C = 0.02 Å.



CL1 - Sn - N1 = 157.7
CL1 - Sn - N3 = 89.8
CL1 - Sn - C3 = 97.3
CL2 - Sn - N1 = 99.1
CL2 - Sn - N3 = 167.0
CL2 - Sn - C1 = 89.2
N1 - Sn - C1 = 83.7
N3 - Sn - C3 = 87.3
C1 - Sn - C3 = 164.6

Fig. 2b. Angles (degrees) in molecule A. The e.s.ds in angles involving Sn are 0.5° and for the others 1.5°.

(Fig. 3, Table I). Both the positions of this ethyl group were included in the calculations, each with an occupancy factor of 0.5 and were not refined any further. Due to the disorder in the structure, no attempts were made to locate the hydrogen atoms in the ethyl groups. An extinction correction was included [9]. The final residuals are $R_F = 0.054$ and $R_{wF} = 0.056$ for 3336 observed reflections. $R_F = 0.074$ and $R_{wF} = 0.056$ for all 4300 reflections. The atomic positional and equivalent isotropic thermal parameters are listed in Table I. All calculations were performed using the NRC PDP8-E system of programs [10]. List of anisotropic thermal parameters and structure factors can be obtained from the authors.

Discussion

A stereo view of the molecules is shown in Fig. 1. The atom names, distances and angles are indicated on Figs. 2 and 3.

The configuration around the Sn atom in both molecules is a distorted octahedron. The Cl atoms are in the *cis* position while the ethyl groups are in the *trans* position. This contradicts the results obtained from dipole moment measurements in solution [4]. Only one other example of a six-coordinate diethyltin species has so far been characterised by X-ray crystallography. The complex formed between diethyltin dichloride and bipyridine, $Et_2SnCl_2 \cdot bipy$ [11]. This too has an octahedral structure with *trans* ethyl groups and *cis* chlorine atoms. The Sn–C(Et) distances reported for this complex are 2.13(1) Å and 2.15(1) Å compared to values in the range 2.07(2)–2.15(2) Å in the present study, which represents good agreement. The Sn–Cl bond lengths

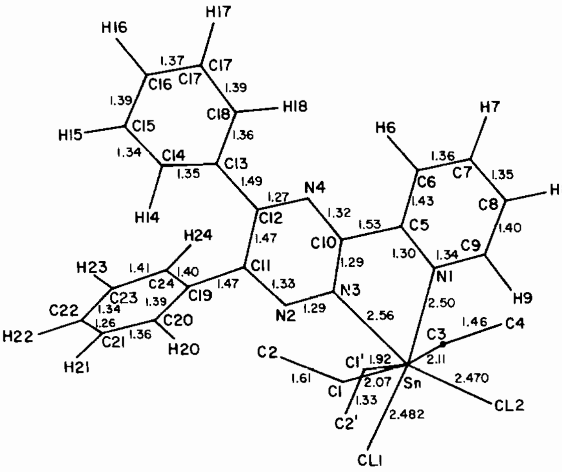


Fig. 3a. Atom names and bond distances (Å) (uncorrected for thermal motion) in molecule B. The e.s.ds are the same as for molecule A.

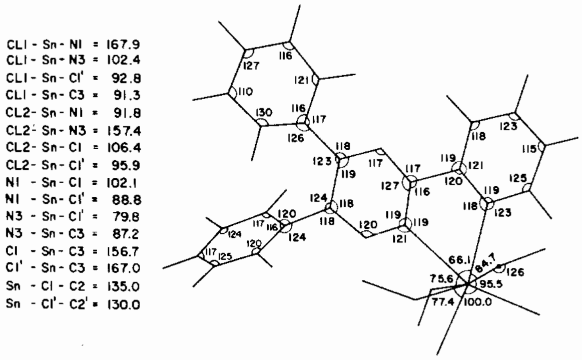


Fig. 3b. Angles (degrees) in molecule B. The e.s.ds are the same as for molecule A.

reported for the bipyridine complex (2.529(1) Å and 2.545(1) Å) are also comparable to those reported here, which lie in the range 2.451(5)–2.506(5) Å. These values of Sn–C and Sn–Cl bond lengths are well within the ranges previously reported in the literature for complexes with comparable structures (Sn–C bond lengths ranging from 2.07–2.22 Å [12, 13] and Sn–Cl bond lengths ranging from 2.34–2.58 Å [14].

The ligand 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine bears a close structural relationship to 1,10-phenanthroline and 2,2′-bipyridyl and its behaviour as a bidentate chelating agent is reported to be similar to these ligands [15]. This fact is borne out in the present structure, the Sn atom being coordinated to N1 and N3 in both molecules A and B. The angle N1–Sn–N3 is equal to 67.9(5) ° in molecule A and 66.1(5) ° in molecule B, and is similar to the N–Sn–N angle of 69.7(2) ° in 2,2′-bipyridyldiphenyldiisothiocyanatotin(IV) [16] and 2.359(6) Å in 2,2′-bipyridyldiphenyldichlorotin(IV) [14]. This is probably so because the ligand 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine is a very bulky and highly conjugated ligand. Some of the C–C bonds are shorter than normal due to the disorder in the structure and the consequent high thermal motion of the carbon atoms.

The conformation of the ligand 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine is not the same in both molecules A and B. In molecule A, the dihedral angle between the planes made up of (N1, C5, C6, C7, C8, C9) and the triazine ring (N2, N3, N4, C10, C11, C12) is 158.7(1.5) ° and the corresponding dihedral angle in molecule B is 165.9(1.5) °. In molecule A, the dihedral angles between the triazine ring and the phenyl rings (C13, C14, C15, C16, C17, C18) and (C19, C20, C21, C22, C23, C24) are 32.9(1.5)° and 131.7(1.5)° respectively. The corresponding dihedral angles in molecule B are 142.3(1.5)° and 109.7(1.5)°.

There are no close contacts between molecules A and B and the molecules are held together in the crystal by weak van der Waals' forces only.

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References

1 M. A. Mullins and C. A. Curran, *Inorg. Chem., 6*, 2017 (1967).
2 M. A. Mullins and C. A. Curran, *Inorg. Chem., 7*, 2584 (1968).
3 F. E. Smith, D. H. Grant and S. Gray, *J. Inorg. Nucl. Chem., 41* , 629 (1979).
4 S. Gray, Hons. Thesis, Mt. Allison University, Sackville, NB, Canada (1977).
5 F. H. Case, *J. Org. Chem., 30*, 931 (1965).
6 D. F. Grant and E. J. Gabe, *J. Appl. Cryst., 11*, 114 (1978).
7 Y. Le Page, E. J. Gabe and L. D. Calvert, *J. Appl. Cryst. 12*, 25 (1979).
8 International Tables of X-Ray Crystallography, Vol. IV, Kynoch Press, Birmingham (1974).
9 A. C. Larson, Crystallographic Computing (Ed. F. R. Ahmed), p. 291, Munksgaard, Copenhagen (1970).
10 A. C. Larson and E. J. Gabe, Computing in Crystallography (Eds. H. Schenk, R. Olthof Hazekamp, H. van Koningsveld and G. C. Bassi), p. 81, Delft Univ. Press (1978).
11 S. L. Chadha, P. G. Harrison and K. C. Molloy, *J. Organometal. Chem., 202*, 247 (1980).
12 T. K. Sham and G. M. Bancroft, *Inorg. Chem., 14*, 2281 (1975).
13 N. W. Alcock and J. F. Sawyer, *J. Chem. Soc. Dalton*, 1090 (1977).
14 P. G. Harrison, T. J. King and J. A. Richards, *J. Chem. Soc. Dalton*, 1723 (1974).
15 H. A. Goodwin and F. E. Smith, *Inorg. Chim. Acta, 7*, 541 (1973).
16 E. J. Gabe, L. Prasad, Y. Le Page and F. E. Smith, *Acta Cryst., B38*, 256 (1982).