

## CRYSTAL AND MOLECULAR STRUCTURE OF THE *meso*-DIASTEREOISOMER OF 1,12-DIMETHYL-2,11-DITHIA-5,8-DIOXA[12](1,1')FERROCENOPHANE

PIER L. BELLON, FRANCESCO DEMARTIN, VLADIMIRO SCATTURIN,  
*Laboratorio di Strutturistica dell'Università, via G. Venezian 21, 20133 Milano (Italy)*

and BRONISLAW CZECH

*Department of Chemistry, Texas Tech University, Lubbock, Texas 79409 (U.S.A.)*

(Received November 8th, 1983)

### Summary

The *meso*-diastereoisomer of 1,12-dimethyl-2,11-dithia-5,8-dioxa[12](1,1')ferrocenophane crystallizes in space group  $P\bar{1}$  with  $a$  8.879(2),  $b$  10.135(2),  $c$  12.030(2) Å,  $\alpha$  100.14(1),  $\beta$  99.02(1),  $\gamma$  103.93(1)°; the ferrocenyl moiety has an eclipsed conformation and the bridging chain a steric arrangement of the type  $aag^+ aag^- g^+ aag^- a$ .

A number of bridged ferrocenophanes have been prepared and characterized. These species have single or multiple bridges, usually consisting of trimethylene [1–4] or heteroatomic chains [5–6]. Crown-like ferrocenophanes have also been studied, with the object of investigating the effects of the presence of an iron atom on the complexing ability of the macrocycle, [7–16] but only one has been structurally characterized [17]. Diastereomeric oxathiaferrocenophanes were synthesized by reaction of 1,1'-bis( $\alpha$ -hydroxyalkyl)ferrocenes with  $\alpha,\omega$ -dithiols in the presence of a catalytic amount of trifluoroacetic acid at high dilution [18,19]. Specifically, the mixture of diastereomeric 1,1'-bis( $\alpha$ -hydroxyethyl)ferrocenes (*meso* + *rac.*) was treated with 1,2-bis(2-mercaptoethoxy)ethane to give the diastereomeric 1,12-dimethyl-2,11-dithia-5,8-dioxa[12](1,1')ferrocenophanes. The *meso* and the racemic forms were separated by preparative thin layer chromatography. This paper reports the results of the structural characterization of the slower migrating isomer, which was previously assumed to be a *meso* form [18].

### Experimental

#### *Synthesis of diastereomeric 1,12-dimethyl-2,11-dithia-5,8-dioxa[12](1,1')ferrocenophanes*

Equimolar amounts of mixed diastereomeric 1,1'-bis( $\alpha$ -hydroxyethyl)ferrocenes and 1,2-bis(2-mercaptoethoxy)ethane dissolved in equal volumes of dichloromethane

were simultaneously added dropwise to vigorously stirred and refluxed dichloromethane containing a catalytic amount of trifluoroacetic acid. After 24 h of refluxing, the diastereomeric products were separated by preparative thin layer chromatography (alumina, benzene/diethyl ether 10/1). Two crystalline diastereoisomeric species with m.p. 96–98°C, and m.p. 88–90°C (faster and slower migrating compounds, respectively) were characterized by spectroscopic methods and elemental analysis. Crystals of the slower migrating diastereoisomer suitable for X-ray structure analysis were obtained from an ethanol/pentane/water mixture.

*Crystal data.*  $C_{20}H_{28}FeO_2S_2$ ,  $M = 420.4$ , orange triclinic crystals,  $a$  8.879(2),  $b$  10.135(2),  $c$  12.030(2) Å,  $\alpha$  100.14(1),  $\beta$  99.02(1),  $\gamma$  103.93(1)°,  $U$  1011.6 Å<sup>3</sup>,  $D_c$  1.380 gm<sup>-3</sup>,  $Z = 2$ , space group  $P\bar{1}$  (No. 2),  $F(000)$  444 electrons,  $\mu(Mo-K_\alpha)$  9.73 cm<sup>-1</sup>. Intensity data were collected on a Nonius CAD-4 automatic diffractometer, by the  $\omega$ -scan technique with graphite-monochromated Mo- $K_\alpha$  radiation ( $\lambda$  0.71073 Å). The standard CAD-4 centering, indexing and data collection programs were used. The lattice parameters and the orientation matrix were obtained from least-squares fitting of 25 reflections having  $7.6^\circ < \theta < 12.4^\circ$ . The scan width for each reflection was taken as  $\Delta\omega = 1.2 + 0.35\tan\theta$ . 3524 independent reflections were obtained at constant rate of 5° min<sup>-1</sup> by exploring the  $\pm h$ ,  $\pm k$ ,  $+l$  region of the reciprocal space in the  $2\theta$  range 6–50°.

Periodical remeasurements of three standard reflections during the data collection did not reveal any deterioration of the crystal. Three orientation standards were checked after every 128 reflections; if the standard deviation of the  $h$ ,  $k$ ,  $l$  values for any orientation reflection exceeded 0.08, a new orientation matrix was calculated by recentering 22 reference reflections. Lorentz, polarization and absorption corrections were applied. Data were corrected for absorption effects by an empirical method based on a set of  $\psi$  scans of reflections having  $\chi$  values near 90° [20]. Minimal transmission factor 0.87.

### Structure solution and refinement

Solution of a tridimensional Patterson map provided the positions of iron and sulphur atoms; subsequent Fourier syntheses revealed all the remaining atoms. The structure was refined by full-matrix least-squares, the minimized function being  $\Sigma w(F_o - k|F_c|)^2$ . The contributions of the scattering amplitudes of all the hydrogen atoms in their expected positions (C–H 0.95 Å), with isotropic temperature factors, were included in the last cycles but no refinement of their coordinates was attempted. The refinement, carried out using 2978 independent reflections having  $I \geq 3\sigma(I)$ , with all the non-hydrogen atoms treated anisotropically led to conventional  $R$  and  $R_w$  values of 0.030 and 0.039 respectively. Weights assigned to individual observations were:  $w_{hkl} = \sigma^{-2}(F_o)$ , where  $\sigma(F_o) = \sigma(F_o^2)/2F_o$ ,  $\sigma(F_o^2) = (\sigma^2(I) + (iI)^2)^{1/2}/Lp$  and  $i$ , an “ignorance factor”, equal to 0.04. Scattering factors and anomalous dispersion factors were taken from ref. 21. The final difference Fourier map had residual peaks of maximum height 0.3 e/Å<sup>3</sup>. All the computations were performed on a PDP 11/34 computer, using the Enraf–Nonius Structure Determination Package (SDP). Table 1 lists the final positional parameters of all non-hydrogen atoms\*.

\* A list of computed and observed structure factors is available from the authors on request.

TABLE 1

FINAL POSITIONAL PARAMETERS WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atom	x	y	z
Fe	0.19774(3)	0.20775(3)	0.19086(3)
S(1)	0.61513(7)	0.41361(6)	0.31099(6)
S(2)	0.26093(7)	0.67692(6)	0.16864(6)
O(1)	0.8475(2)	0.6990(2)	0.3695(1)
O(2)	0.7176(2)	0.8975(2)	0.2455(2)
C(1)	0.4059(2)	0.1576(2)	0.2373(2)
C(2)	0.2731(3)	0.0522(2)	0.2483(2)
C(3)	0.1702(3)	-0.0012(2)	0.1393(2)
C(4)	0.2370(3)	0.0693(3)	0.0601(2)
C(5)	0.3821(3)	0.1672(2)	0.1197(2)
C(6)	0.1834(2)	0.4036(2)	0.1766(2)
C(7)	0.2164(2)	0.3954(2)	0.2948(2)
C(8)	0.0911(3)	0.2894(2)	0.3131(2)
C(9)	-0.0199(3)	0.2329(2)	0.2072(2)
C(10)	0.0355(3)	0.3025(2)	0.1236(2)
C(11)	0.5511(3)	0.2352(2)	0.3295(2)
C(12)	0.8163(3)	0.4678(2)	0.3921(2)
C(13)	0.9125(3)	0.5844(3)	0.3509(2)
C(14)	0.9340(3)	0.8154(3)	0.3351(3)
C(15)	0.8481(4)	0.9248(3)	0.3402(3)
C(16)	0.5727(3)	0.8139(3)	0.2621(2)
C(17)	0.4490(3)	0.7851(2)	0.1553(2)
C(18)	0.2869(3)	0.5019(3)	0.1223(2)
CM(1)	0.5292(4)	0.2291(3)	0.4498(2)
CM(2)	0.2535(4)	0.4578(3)	-0.0090(2)

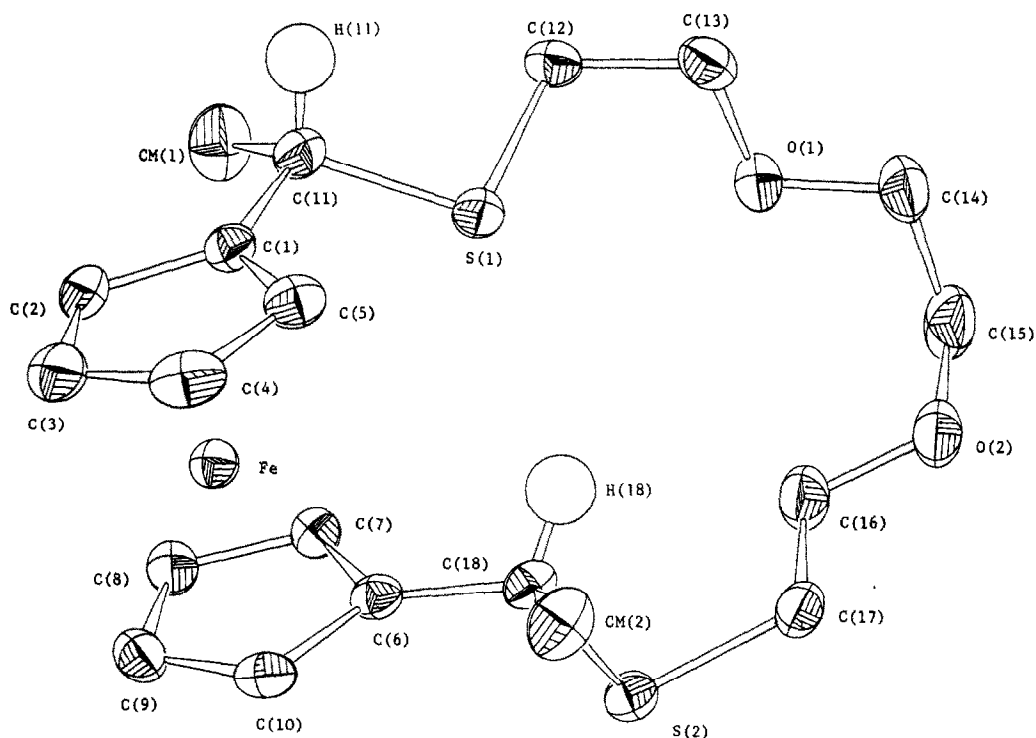


Fig. 1. Perspective view of the *meso*-diastereoisomer of 1,12-dimethyl-2,11-dithia-5,8-dioxo[12](1,1')ferrocenophane. Hydrogen atoms have been omitted with the exception of H(11) and H(18) shown in order to illustrate the enantiomeric configurations of C(11) and C(18). Thermal ellipsoids drawn at 30% probab-

## Results and discussion

Crystals of the diastereoisomer of 1,12-dimethyl-2,11-dithia-5,8-dioxa[12](1,1')ferrocenophane described in this paper consist of discrete molecular units packed in space group  $P\bar{1}$ , the asymmetric unit being a single molecule. This molecule contains two carbon atoms, namely C(11) and C(18), which are asymmetric centers. In space group  $P\bar{1}$ , with two molecules per unit cell, potentially asymmetric molecules can pack in two ways: as a racemic compound containing *R* and *S* molecules or as a packing of identical *meso* molecules. As can be appreciated in Fig. 1, the C(11) and

TABLE 2

SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

<i>(a) within the Fe(C<sub>5</sub>)<sub>2</sub> moiety</i>			
Fe-C(1)	2.053(2)	Fe-C(6)	2.054(2)
Fe-C(2)	2.039(2)	Fe-C(7)	2.038(2)
Fe-C(3)	2.042(2)	Fe-C(8)	2.032(2)
Fe-C(4)	2.048(2)	Fe-C(9)	2.044(2)
Fe-C(5)	2.055(2)	Fe-C(10)	2.056(2)
<i>(b) within the C<sub>5</sub> rings</i>			
C(1)-C(2)	1.429(3)	C(1)-C(2)-C(3)	108.36(19)
C(1)-C(5)	1.422(3)	C(2)-C(3)-C(4)	108.09(19)
C(2)-C(3)	1.409(3)	C(3)-C(4)-C(5)	108.43(19)
C(3)-C(4)	1.407(3)	C(4)-C(5)-C(1)	108.08(19)
C(4)-C(5)	1.415(3)	C(5)-C(1)-C(2)	107.05(18)
C(6)-C(7)	1.427(3)	C(11)-C(1)-C(5)	125.93(18)
C(6)-C(10)	1.428(3)	C(11)-C(1)-C(2)	126.81(18)
C(7)-C(8)	1.422(3)	C(6)-C(7)-C(8)	108.36(17)
C(8)-C(9)	1.415(3)	C(7)-C(8)-C(9)	107.82(18)
C(9)-C(10)	1.411(3)	C(8)-C(9)-C(10)	108.32(18)
C( <i>i</i> )-C( <i>j</i> ) <sub>av.</sub>	1.418	C(9)-C(10)-C(6)	108.60(17)
		C(10)-C(6)-C(7)	106.89(17)
		C(18)-C(6)-C(7)	125.06(17)
		C(18)-C(6)-C(10)	128.04(17)
<i>(c) within the bridging chain</i>			
C(1)-C(11)	1.505(3)	C(1)-C(11)-S(1)	108.32(13)
S(1)-C(11)	1.824(2)	C(11)-S(1)-C(12)	101.00(9)
S(1)-C(12)	1.799(2)	S(1)-C(12)-C(13)	110.11(14)
C(12)-C(13)	1.492(3)	C(12)-C(13)-O(1)	108.60(17)
O(1)-C(13)	1.416(3)	C(13)-O(1)-C(14)	112.30(19)
O(1)-C(14)	1.410(3)	O(1)-C(14)-C(15)	110.05(22)
C(14)-C(15)	1.488(4)	C(14)-C(15)-O(2)	114.07(24)
O(2)-C(15)	1.427(3)	C(15)-O(2)-C(16)	113.85(18)
O(2)-C(16)	1.424(3)	O(2)-C(16)-C(17)	108.83(18)
C(16)-C(17)	1.488(3)	C(16)-C(17)-S(2)	111.61(15)
S(2)-C(17)	1.811(2)	C(17)-S(2)-C(18)	100.51(9)
S(2)-C(18)	1.844(2)	S(2)-C(18)-C(6)	108.09(13)
C(18)-C(6)	1.497(3)	C(1)-C(11)-CM(1)	113.91(19)
C(11)-CM(1)	1.500(3)	CM(1)-C(11)-S(1)	112.57(17)
C(18)-CM(2)	1.525(3)	C(6)-C(18)-CM(2)	113.42(18)
		CM(2)-C(18)-S(2)	110.76(14)

C(18) carbon atoms possess enantiomeric configurations: in the particular molecule shown there C(11) is a *S* center and C(18) a *R* center; the unit cell obviously contains another molecule, related to the one shown by an inversion center, in which C(11) and C(18) are in *R* and *S* configurations, respectively. This confirms the validity of the assumption that the present species is the *meso*-form [18].

A list of selected bond distances and angles is given in Table 2. Figure 1 shows an overall view of the molecule; Fig. 2 gives a perspective view of the ferrocenyl moiety. The latter exhibits an almost exact eclipsed conformation, as is usually found in substituted ferrocenyl compounds, in contrast with ferrocene itself which is staggered [22]. When a constraint is imposed either by the presence of a short bridging chain or of multiple bridges, a situation which is intermediate between eclipsing and staggering can be observed, and in which the two rings are no longer parallel; this is the case, for instance, of 3-(1,1')[4](3,2')ferrocenophane-6-one [4]. In the present compound no significant deviations are observed from the ideal geometry of the two cyclopentadienyl rings from the point of view of their parallelism (the angle between the least-squares planes defined by the two rings being  $2.3^\circ$ ) and of the planarity within each ring, as can be seen from Table 3. These features seem to indicate that the bridging chain is sufficiently strainfree that no distortion of the ferrocenyl moiety is necessary. The distances of the iron atom from the planes of the two rings (1.655(1) and 1.649(1) Å from planes C(1)...C(5) and C(6)...C(10), respectively) compare well with the value of 1.66 Å reported for ferrocene (A) [22], and bis-ferrocenyl (B) [23], and so do the distances Fe-C(*i*) {*i* = 1, 10}, whose mean

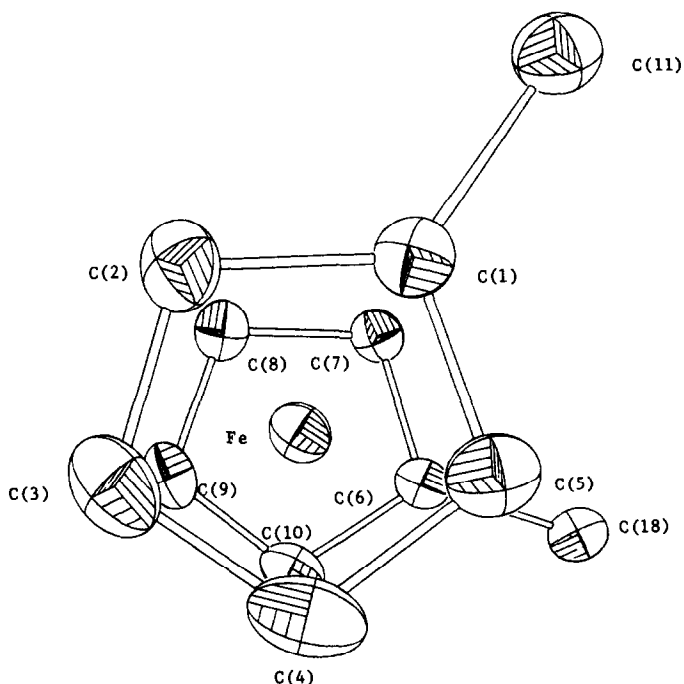


Fig. 2. Projection of the ferrocenyl moiety approximately normal to the cyclopentadienyl rings.

TABLE 3  
WEIGHTED LEAST-SQUARES PLANES IN THE FORM  $Ax + By + Cz + D = 0$

Plane	<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>	Atom	Distance (Å)
1	0.7204	−0.6626	−0.2050	0.8231	C(1)	−0.001(2)
					C(2)	0.001(2)
					C(3)	0.000(3)
					C(4)	0.000(3)
					C(5)	0.001(2)
2	0.7273	−0.6434	−0.2387	−2.5201	C(6)	0.004(2)
					C(7)	−0.004(2)
					C(8)	0.002(2)
					C(9)	0.000(2)
					C(10)	−0.003(2)

value is 2.046 Å here, with a very small spread, and 2.045 Å and 2.035 Å, in A and B, respectively. The mean carbon–carbon bond length within the rings is 1.418 Å which, again, is comparable with the mean value of 1.40 Å found in compounds A and B. As far as the bridging chain is concerned, all the covalent bonding parameters appear comparable to the values usually found; the C–S distances, ranging from 1.799(2) to 1.844(2) Å, agree with the value of 1.81 Å found in dimethyl and diethyl sulphide [24]. The narrow range of C–O distances observed here (1.410(3)–1.427(3) Å) can be compared with the range found in the crown-ether  $C_{56}H_{68}O_{10}$  (1.374(8)–1.456(8) Å) [25].

The values of the torsion angles reported in Table 4 can be used to define the C(1)–C(6) chain conformation. According to the current conventions and starting from the ring carbon atom C(1), the steric arrangement is  $aag^+ aag^- g^+ aag^- a$ . In crown-ether compounds the conformations which are energetically preferred about C–C and C–O bonds are *gauche* (*g*) and *anti* (*a*), respectively (see discussion in ref. 25 and references therein). If the *a* conformation is also preferred about a C–S bond, the energy minimum for the present chain would be associated with an overall arrangement of the type  $aagaagaaga$ , which is not that actually observed. This

TABLE 4  
TORSIONAL ANGLES WITHIN THE BRIDGING CHAIN

Atom 1	Atom 2	Atom 3	Atom 4	angle (°)
C(1)	C(11)	S(1)	C(12)	−161.7
C(11)	S(1)	C(12)	C(13)	156.4
S(1)	C(12)	C(13)	O(1)	61.8
C(12)	C(13)	O(1)	C(14)	178.7
C(13)	O(1)	C(14)	C(15)	171.7
O(1)	C(14)	C(15)	O(2)	−77.7
C(14)	C(15)	O(2)	C(16)	86.8
C(15)	O(2)	C(16)	C(17)	−176.4
O(2)	C(16)	C(17)	S(2)	179.2
C(16)	C(17)	S(2)	C(18)	−86.9
C(17)	S(2)	C(18)	C(6)	154.3

deviation from the minimum of the conformational energy is probably due to the presence of the ferrocenyl moiety.

The present structure determination allows some speculation about the crown nature of the molecule. From a scale model it can be seen that, although there is no strain exerted on the ferrocenyl moiety, the bridging chain has a quite rigid conformation in the sense that the mutual orientations of the cyclopentadienyl rings are affected whenever a torsion angle is modified. Moreover there is no cavity big enough to accommodate a cation nor do the sulphur and oxygen atoms have their lone pairs directed toward the inside of the overall cylinder defined by the chain. Molecular models of the optically active forms exhibit the same lack of a central cavity and the same spread in the directions in which the donor atoms point. These results seem to indicate that very poor, if any, host ability will be observed for these species; and this is in agreement with some preliminary experimental results.

### Acknowledgement

The authors thank the Italian CNR for the use of the diffractometer and of the computer.

### References

- 1 M. Hillman and E. Fujita, *J. Organomet. Chem.*, 155 (1978) 99.
- 2 M. Hillman and E. Fujita, *J. Organomet. Chem.*, 155 (1978) 87.
- 3 L.D. Spaulding, M. Hillman and G.J.B. Williams, *J. Organomet. Chem.*, 155 (1978) 109.
- 4 Y.T. Struchkov, G.G. Aleksandrov and A.Z. Kreindlin, *J. Organomet. Chem.*, 210 (1981) 237.
- 5 A.G. Osborne, R.E. Hollands, J.A.K. Howard and R.F. Bryan, *J. Organomet. Chem.*, 205 (1981) 395.
- 6 A.G. Osborne, R.E. Hollands, R.F. Bryan and S. Lockhart, *J. Organomet. Chem.*, 224 (1982) 129.
- 7 G. Oepen and F. Vögtle, *Liebigs Ann. Chem.*, (1979) 1094.
- 8 B. Czech and A. Ratajczak, *Polish J. Chem.*, 54 (1980) 767.
- 9 A.P. Bell and C.D. Hall, *J. Chem. Soc. Chem. Commun.*, (1980) 163.
- 10 M. Sato, M. Kubo, S. Ebine and S. Akabori, *Tetrahedron Lett.*, (1982) 185.
- 11 S. Akabori, H. Fukuda, Y. Habata, M. Sato and S. Ebine, *Chem. Lett.*, (1982) 1393.
- 12 M. Sato, H. Watanabe, S. Ebine and S. Akabori, *Chem. Lett.*, (1982) 1753.
- 13 P.J. Hammond, A.P. Bell and C.D. Hall, *J. Chem. Soc., Perkin Trans. I*, (1983) 707.
- 14 S. Akabori, Y. Habata, Y. Sakamoto, M. Sato and S. Ebine, *Bull. Chem. Soc. Jpn.*, 56 (1983) 537.
- 15 S. Akabori, M. Ohtomi, M. Sato and S. Ebine, *Bull. Chem. Soc. Jpn.*, 56 (1983) 1455.
- 16 S. Akabori, Y. Habata, M. Sato and S. Ebine, *Bull. Chem. Soc. Jpn.*, 56 (1983) 1459.
- 17 J. Drzymala, Z. Kaluski, A. Ratajczak and B. Czech, *Bull. Ac. Pol. Chem.*, 28 (1980) 621.
- 18 B. Czech and A. Ratajczak, *Chem. Scripta*, 18 (1981) 195.
- 19 B. Czech and A. Ratajczak, *Monatsh. Chemie*, 113 (1982) 965.
- 20 A.C.T. North, D.C. Phillips and F.S. Mathews, *Acta Crystallogr. A*, 24 (1968) 351
- 21 D.T. Cromer and J.T. Waber, *International Tables for X-ray Crystallography*, vol. IV, The Kynoch Press, Birmingham, England, 1974, Tables 2.2.B and 2.3.1.
- 22 J.D. Dunitz, L.E. Orgel and A. Rich, *Acta Crystallogr.*, 9 (1956) 373.
- 23 A.C. MacDonald and J. Trotter, *Acta Crystallogr.*, 17 (1964) 872.
- 24 *Tables of interatomic distances*, The Chemical Society, London, 1958.
- 25 I. Goldberg, *Acta Crystallogr. B*, 36 (1980) 2104.