Inorganica Chimica Acta, *89* (1984) 47–52

Studies on Macrocyclic Complexes Derived from *vic*-Dioximes. XI[†]. The Crystal Structure of the π-Sandwich Compound Formed Between Phenazine and Bis(difluoroborondimethylglyoximato)nickel(II)

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Received February 6, 1984

The 1:1 adduct of phenazine with bis(difluoroborondimethylglyoximato)nickel(II) is monoclinic, space group $P2_1/c$, $a = 9.130(9)$, $b = 8.031(7)$, $c = 15.492(13)$ Å, $\beta = 91.20(5)°$, $Z = 2$. *The structure was refined to* $R = 0.095$ *for 1571 photographic reflexions by full-matrix least-squares methods. The planar macrocycle [average Ni–N 1.850(7) Å, N–Ni–N 82.3(4)°] and phenazine molecules each have a space group imposed centre of symmetry, with the closest non-bonded contacts to the nickel atom being the phenazine N atoms at 3.38 Å. Close intermolecular distances indicate* π–π *interactions which give rise to two sets of alternatively stacked chains directed along b. This stacking arrangement is such that the molecules lie on the* $(11\bar{2})$ *and* $(\bar{1}22)$ *series of planes, which intersect at 67.7° and have 3.32 Å separations. The intermolecular relationship and stacking pattern each closely resemble that of the anthracene adduct previously described.*

Introduction

In this series it has become obvious that in bis(difluoroborondimethylglyoximato)nickel(II), Ni(dmgBF$_2$)$_2$, the nickel atom serves to maintain planarity in the macrocycle so as to allow the formation of π-bonded adducts with planar cyclic organic molecules [1, 2]. The one-dimensional stacking of alternate molecules in the crystals of these adducts suggest that they may possess some of the physical properties of molecular metals.

The formation of such compounds clearly depends on the nature of the adducted organic molecule, and Ni(dmgBF$_2$)$_2$ would appear to favour adduct formation with tricyclic molecules [3]. We report here the crystal structure analysis of the 1:1 adduct which forms with phenazine.

Experimental

The compound was obtained as pale amber crystals from the reaction of bis(difluoroborondimethylglyoximato)nickel(II) with excess phenazine in warm acetone solution. Crystal data: $C_{20}H_{20}B_2F_4N_6O_4Ni$, Mv = 564.7, monoclinic, $a = 9.130(9)$, $b = 8.031(7)$, $c = 15.492(13)$ Å, $\beta = 91.20(5)°$, $U = 1135.7$ Å^3, $Z = 2$, $Dc = 1.651$ Mg m^{-3}, $F(000) = 576$, μ(Cu-K$_\alpha$) = 1.85 mm^{-1}. Systematic absences: $h0l$ if $l \neq 2n$ and $0k0$ if $k \neq 2n$, space group $P2_1/c$ (No. 14).

The adduct crystallises as elongated plates lying on the (001) face and with [010] elongation. Precession, oscillation and Weissenberg photographs were used to determine cell parameters. 2187 reflexions were recorded for the layers 0–$3kl$, $h0$–$3l$ and $hk0$–3 on equi-inclination Weissenberg photographs using Cu-K$_\alpha$ radiation. The intensities were estimated visually and were corrected for Lorentz and polarisation effects but not for absorption or extinction. The observed structure factors were placed on a common scale by internal correlation to yield a data set of 1571 non-zero unique reflexions which were used in subsequent calculations.

The structure was solved by the heavy-atom method and refined by full-matrix least-squares methods in which the function minimised was $\Sigma w\Delta^2$. The weight given to each reflexion initially was $w = (1.0 + 0.1\ |F_0|)^{-1}$ and in the final stages $w = (1.0 + 0.1\ |F_o| + 0.002\ |F_o|^2)^{-1}$. Hydrogen atom positions were calculated for the phenazine molecule with C–H = 1.0 Å and those of the methyl groups were located from a difference map. These hydrogen atoms were held in these positions with B = 6.0 Å^2 during the refinement process. Refinement was terminated when the maximum shift in any parameter

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[†] Part X: F. S. Stephens and R. S. Vagg, *Inorg. Chim. Acta*, *69*, 103 (1983).

0020-1693/84/$3.00

was $<0.04\sigma$. The final value for R was 0.095 and for $R'[= (\Sigma w\Delta^2/\Sigma w|F_o|^2)^{1/2}]$ was 0.125. A final difference map showed no unusual features and a maximum positive electron density of 0.9 e Å^{-3} which is associated with the nickel atom.

Neutral-atom scattering factors were taken from 'International Tables for X-ray Crystallography' [4]. All calculations were carried out on a UNIVAC 1106 computer using programmes written by F.S.S. The final atomic parameters are given in Tables I–III. A list of observed and calculated structure factors has been deposited with the Editor.

TABLE I. Final Atomic Coordinates (fractional, ×10^4) for Non-Hydrogen Atoms with Estimated Standard Deviations in Parentheses.

	x	y	z
Ni	0	0	0
N(1)	−1905(6)	664(8)	−210(3)
N(2)	−266(6)	−907(8)	−1098(3)
O(1)	−2724(5)	1618(7)	344(3)
O(2)	−777(5)	1855(7)	1488(3)
C(1)	−2498(7)	269(9)	−944(4)
C(2)	−1488(7)	−682(9)	−1472(4)
C(M1)	−4024(8)	729(12)	−1237(5)
C(M2)	−1881(8)	−1308(12)	−2355(4)
B	−2312(9)	1387(13)	1273(5)
F(1)	−3190(5)	2469(6)	1713(3)
F(2)	−2536(4)	−220(6)	1507(3)
N(3)	304(7)	3962(8)	−710(3)
C(4)	−982(9)	4730(10)	−646(5)
C(5)	−2081(10)	4472(13)	−1285(5)
C(6)	−3395(10)	5180(12)	−1220(6)
C(7)	−3739(9)	6186(12)	−506(6)
C(8)	−2712(9)	6470(11)	126(5)
C(9)	−1319(8)	5751(9)	94(4)

Discussion

The similarities in the crystal data of the anthracene [1] and of the phenazine 1:1 adducts suggest that the two structures may be closely comparable. This is borne out by an analysis of both the molecular and crystal structures of the complex here reported.

The bond lengths and angles within the macrocycle and phenazine molecules are given in Table IV.

TABLE III. Hydrogen Atomic Coordinates (fractional, ×10^3)*.

	x	y	z
H(5)	−188	370	−180
H(6)	−412	503	−171
H(7)	−477	671	−45
H(8)	−296	720	62
H(11)	−425	−7	−117
H(12)	−390	127	−164
H(13)	−409	150	−68
H(21)	−130	−214	−244
H(22)	−183	−63	−256
H(23)	−265	−197	−230

*For all hydrogen atoms $B = 6.0$ Å^2.

TABLE II. Final Anisotropic Thermal Parameters (×10^4) in the Form $\exp -(h^2b_{11} + k^2b_{22} + l^2b_{33} + 2hkb_{12} + 2hlb_{13} + 2klb_{23})$, with Estimated Standard Deviations in Parentheses.

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Ni	131(2)	228(3)	49(1)	1(2)	−4(1)	−4(1)
N(1)	99(6)	189(10)	39(2)	−13(8)	2(3)	2(4)
N(2)	110(7)	218(12)	33(2)	−2(9)	−2(9)	−9(4)
O(1)	119(6)	224(10)	39(2)	38(8)	4(3)	−3(4)
O(2)	116(6)	220(10)	42(2)	10(8)	−2(3)	−26(4)
C(1)	87(7)	190(13)	38(3)	−11(10)	−5(4)	7(5)
C(2)	113(8)	176(12)	36(2)	−27(11)	−1(4)	2(5)
C(M1)	124(9)	271(18)	49(3)	−6(13)	−18(4)	5(7)
C(M2)	143(10)	269(19)	40(3)	−37(14)	−4(4)	−13(6)
B	113(10)	225(17)	46(4)	15(14)	12(5)	−12(7)
F(1)	147(6)	248(10)	52(2)	47(7)	8(3)	−26(4)
F(2)	121(5)	236(9)	44(2)	−18(7)	−4(2)	10(3)
N(3)	168(9)	180(11)	40(2)	2(11)	9(4)	−5(4)
C(4)	146(10)	188(13)	42(3)	0(12)	6(4)	9(5)
C(5)	177(12)	269(18)	46(3)	−28(15)	−9(5)	3(7)
C(6)	159(12)	275(20)	56(4)	−18(15)	−16(6)	29(7)
C(7)	147(11)	231(17)	73(5)	0(14)	3(6)	37(8)
C(8)	139(10)	209(15)	61(4)	−3(13)	18(5)	5(7)
C(9)	155(10)	169(12)	40(3)	7(12)	6(4)	8(5)

TABLE IV. Bond Lengths and Angles with Estimated Standard Deviations in Parentheses.

(a) Distances (Å)*			
Ni–N(1)	1.842(5)	Ni–N(2)	1.858(5)
N(1)–O(1)	1.382(7)	N(2)–O(2^{I})	1.343(7)
O(1)–B	1.491(9)	O(2)–B	1.483(9)
B–F(1)	1.373(9)	B–F(2)	1.358(11)
N(1)–C(1)	1.289(8)	N(2)–C(2)	1.291(8)
C(1)–C(M1)	1.503(9)	C(2)–C(M2)	1.494(9)
C(1)–C(2)	1.460(10)		
N(3)–C(4)	1.332(9)	N(3)–C(9^{II})	1.335(9)
C(4)–C(5)	1.411(11)	C(7)–C(8)	1.361(11)
C(5)–C(6)	1.333(12)	C(8)–C(9)	1.399(11)
C(6)–C(7)	1.410(14)	C(9)–C(4)	1.448(10)
(b) Angles (°)*			
N(1)–Ni–N(2)	82.3(2)	N(1)–Ni–N(2^{I})	97.7(2)
Ni–N(1)–O(1)	124.9(4)	Ni–N(2)–O(2^{I})	124.8(4)
Ni–N(1)–C(1)	117.6(5)	Ni–N(2)–C(2)	115.8(5)
O(1)–N(1)–C(1)	117.5(5)	O(2^{I})–N(2)–C(2)	119.2(5)
N(1)–C(1)–C(2)	111.3(6)	N(2)–C(2)–C(1)	113.0(6)
N(1)–C(1)–C(M1)	125.2(6)	N(2)–C(2)–C(M2)	123.9(7)
C(2)–C(1)–C(M1)	123.5(6)	C(1)–C(2)–C(M2)	123.1(6)
N(1)–O(1)–B	113.7(5)	N(2^{I})–O(2)–B	113.9(3)
O(1)–B–O(2)	113.8(3)	F(1)–B–F(2)	112.1(6)
O(1)–B–F(1)	105.3(6)	O(2)–B–F(1)	106.7(5)
O(1)–B–F(2)	109.9(7)	O(2)–B–F(2)	109.1(6)
C(9^{II})–N(3)–C(4)	117.8(4)		
N(3)–C(4)–C(5)	119.7(7)	N(3^{II})–C(9)–C(8)	121.4(7)
N(3)–C(4)–C(9)	121.6(4)	N(3^{II})–C(9)–C(4)	120.5(7)
C(9)–C(4)–C(5)	118.6(8)	C(4)–C(9)–C(8)	118.0(7)
C(4)–C(5)–C(6)	120.8(8)	C(9)–C(8)–C(7)	121.3(8)
C(5)–C(6)–C(7)	121.3(8)	C(8)–C(7)–C(6)	119.9(8)

*Roman numeral superscripts refer to the following equivalent positions relative to atoms at x, y, z: I $-x, -y, -z$; II $-x, 1-y, -z$.

Figure 1 shows the relationship between the two molecules with the atomic labelling scheme [5]. Each planar molecule of the adduct possesses a space group imposed centre of symmetry. The molecular symmetry of the phenazine approximates closely to $mmm(D_{2h})$ and the molecular dimensions are in good agreement with those reported for the free species [6]. The symmetry of the macrocycle approximates $2/m(C_{2h})$ which leads to a *trans* arrangement of the two axial F atoms, similar to the anthracene adduct [1]. The geometry of the macrocycle, and of the nickel atom in particular, with the average Ni–N length of 1.850(7) Å and N–Ni–N angle of 82.3(4)°, is consistent with the bonding dimensions in the anthracene [1] and benzimidazole [2] adducts and in the parent macrocyclic complex [7]. The closest approaches to the nickel atom in what would constitute octahedral bonding sites are two N atoms from symmetry related phenazine molecules at Ni...N of 3.380(6) Å. This relationship between the molecules, which are almost parallel (Table V, planes 1 and 2, intersecting at 5.4°) is shown in Fig. 2. This angle represents a rotation of the phenazine molecule around its long axis with respect to the macrocycle plane.

As in the anthracene structure [1] the contact distances given in Table VI(a) indicate that π-type interactions are apparent between the phenazine molecule and the macrocycle. The orientation of the phenazine molecule relative to the macrocycle (see Fig. 2) is shifted to a small extent, compared with that in the anthracene adduct [1], thus permitting better overlap of the two rings that are mostly involved with the π-interactions to the macrocycle [8]. The orientation is still constrained by the F(2)... C(8) contact and the close approach of the carbon atom C(6^{II}) to the methyl group C(M2^{I}). It is probable that this latter steric interaction causes the tilting of the phenazine ring with respect to the macrocycle plane. The π–π interactions between parallel molecules give rise to two sets of alternately stacked chains directed along b (see Fig. 3). This

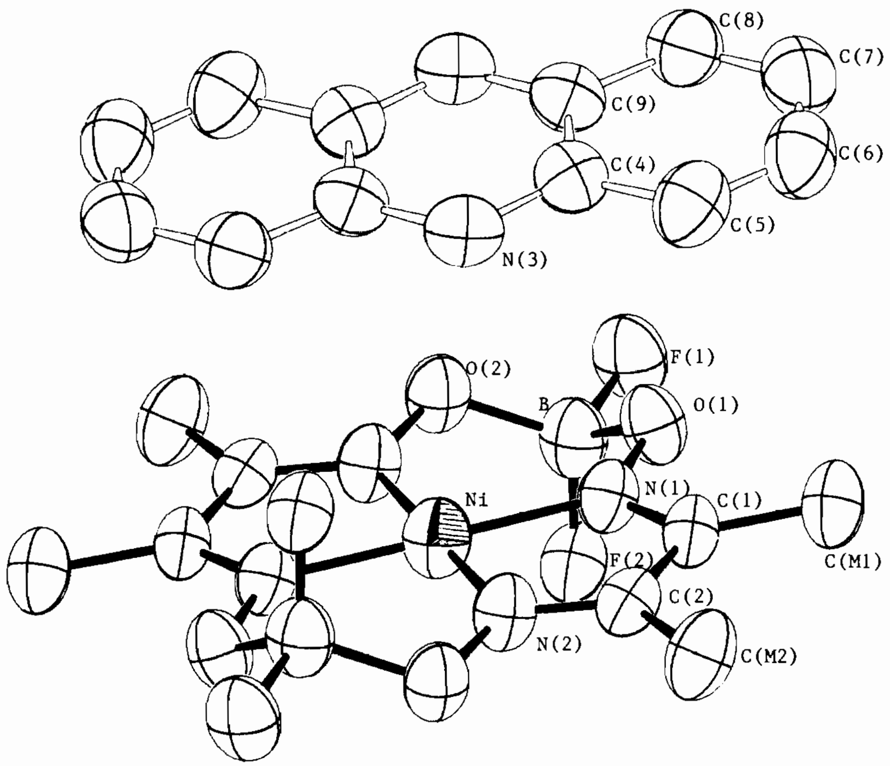

Fig. 1. A perspective drawing of the 1:1 adduct with the labelling of the atoms. Thermal ellipsoids are drawn to include 35% probability.

TABLE V. Least-Squares Planes and their Equations given by $lX' + mY' + nZ' - p = 0$ where X', Y' and Z' are Orthogonal Coordinate (Å) with Respect to the Orthogonal Axes a', b and c. Deviations (Å) of Relevant Atoms from the Planes are given in Square Brackets*.

	l	m	n	p
Plane (1): Ni, N(1), N(2), O(1), O(2), C(1), C(2), C(M1), C(M2), N(1^{I}), N(2^{I}), O(1^{I}), O(2^{I}), C(1^{I}), C(2^{I}), C(M1^{I}), C(M2^{I}) [N(1) −0.027; N(2) 0.021; O(1) −0.002; O(2) 0.048; C(1) −0.013; C(2) 0.008; C(M1) −0.004; C(M2) 0.026; B −0.62; F(1) −0.46; F(2) −1.93]	0.3432	0.8425	−0.4153	0.0000
Plane (2): N(3), C(4), C(5), C(6), C(7), C(8), C(9), N(3^{II}), C(4^{II}), C(5^{II}), C(6^{II}), C(7^{II}), C(8^{II}), C(9^{II}) [N(3) 0.023; C(4) 0.020; C(5) 0.006; C(6), C(8) 0.001; C(7) −0.012; C(9) −0.002]	0.3313	0.8004	−0.4997	3.2139

*For superscript notation see footnote Table IV.

stacking arrangement is such that the molecules lie on the $(12\bar{2})$ and $(\bar{1}22)$ series of planes, which intersect at 67.7° and have a spacing of 3.32 Å. The arrangement is similar to that in the structure of the anthracene adduct [1] except that there the planes are $(22\bar{1})$ and $(\bar{2}21)$, and this change is consistent with the respective cell data.

It is interesting to note that the formation of the phenazine adduct involves no appreciable change of colour from that of the reactants, unlike the anthracene system [1] in which ruby-red crystals are obtained from the yellow reaction solutions. A sim-

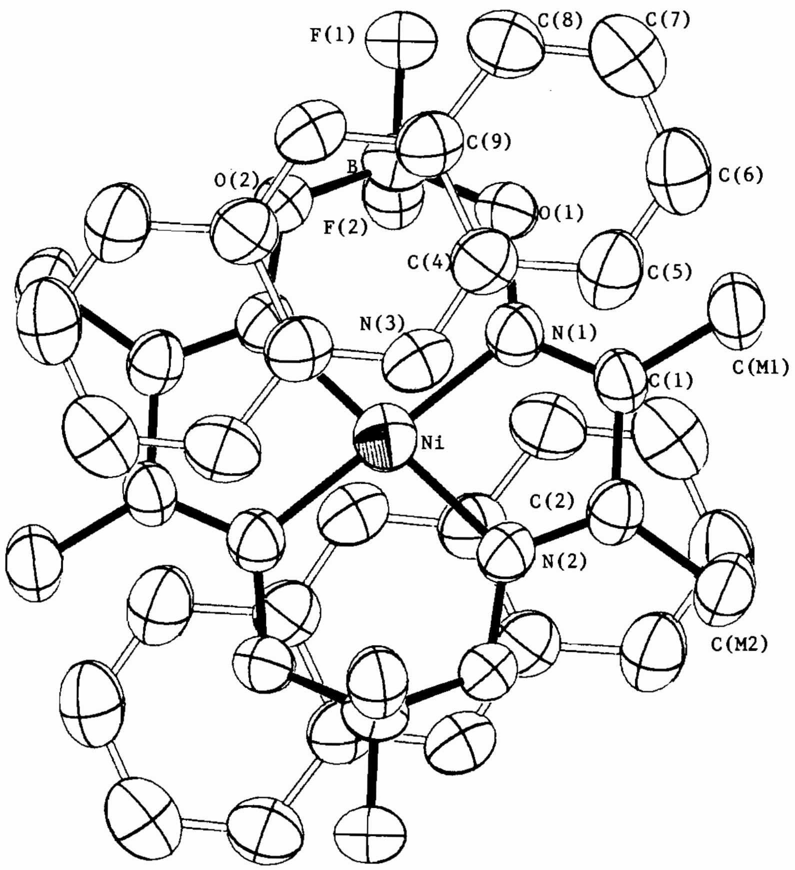

Fig. 2. The orientation of the phenazine molecules with respect to the Ni(dmgBF$_2$)$_2$ molecule.

TABLE VI. Interatomic Contact Distances (Å) with Estimated Standard Deviations in Parentheses*.

	Interatomic distances	Perpendicular distance of relevant atom from	
		Macrocycle plane	Phenazine plane
a) Contacts <3.6 Å suggesting π–π interactions			
O(1)···C(4)	3.351(10)	3.30	3.29
Ni···N(3)	3.380(6)	3.23	3.21
N(2)···C(9^{III})	3.420(9)	3.36	3.41
N(1)···N(3)	3.427(9)	3.23	3.22
C(1)···C(5)	3.439(12)	3.18	3.34
N(1)···C(4)	3.443(10)	3.30	3.22
O(2)···C(4^{II})	3.448(9)	3.45	3.42
O(1)···C(5)	3.468(11)	3.18	3.29
C(1)···C(8^{III})	3.480(11)	3.34	3.34
N(1)···C(5)	3.484(12)	3.18	3.22
N(1)···C(8^{III})	3.490(11)	3.34	3.22
C(1)···C(7^{III})	3.540(11)	3.46	3.34
C(2)···C(8^{III})	3.567(11)	3.34	3.45
O(1)···C(9)	3.582(9)	3.41	3.29
C(2)···C(7^{III})	3.594(11)	3.46	3.45
O(2)···N(3^{II})	3.598(8)	3.53	3.42

TABLE VI *(continued)*

	Interatomic distances
b) Non-bonding contact distances <3.5 Å	
F(2)···C(M1^{IV})	3.186(8)
F(2)···C(M2^{VI})	3.346(8)
F(2)···C(8^{III})	3.415(10)
F(2)···C(5^{V})	3.489(10)
C(M1)···C(5)	3.493(14)
C(M2)···N(3^{VII})	3.360(10)

*For Roman numeral superscripts refer to footnote Table IV and III $x, y-1, z$; IV $-1-x, -y, -z$; V $x, 1/2-y, 1/2+z$; VI $x, -1/2-y, 1/2+z$; VII $-x, y-1/2, -1/2-z$.

ilar coloured adduct has been recently obtained for anthracene and the related monomethylglyoximato complex, Ni(mgBF$_2$)$_2$ [3]. A comparison of the packing in this latter adduct would be of interest since the influence of the methyl groups should be diminished.

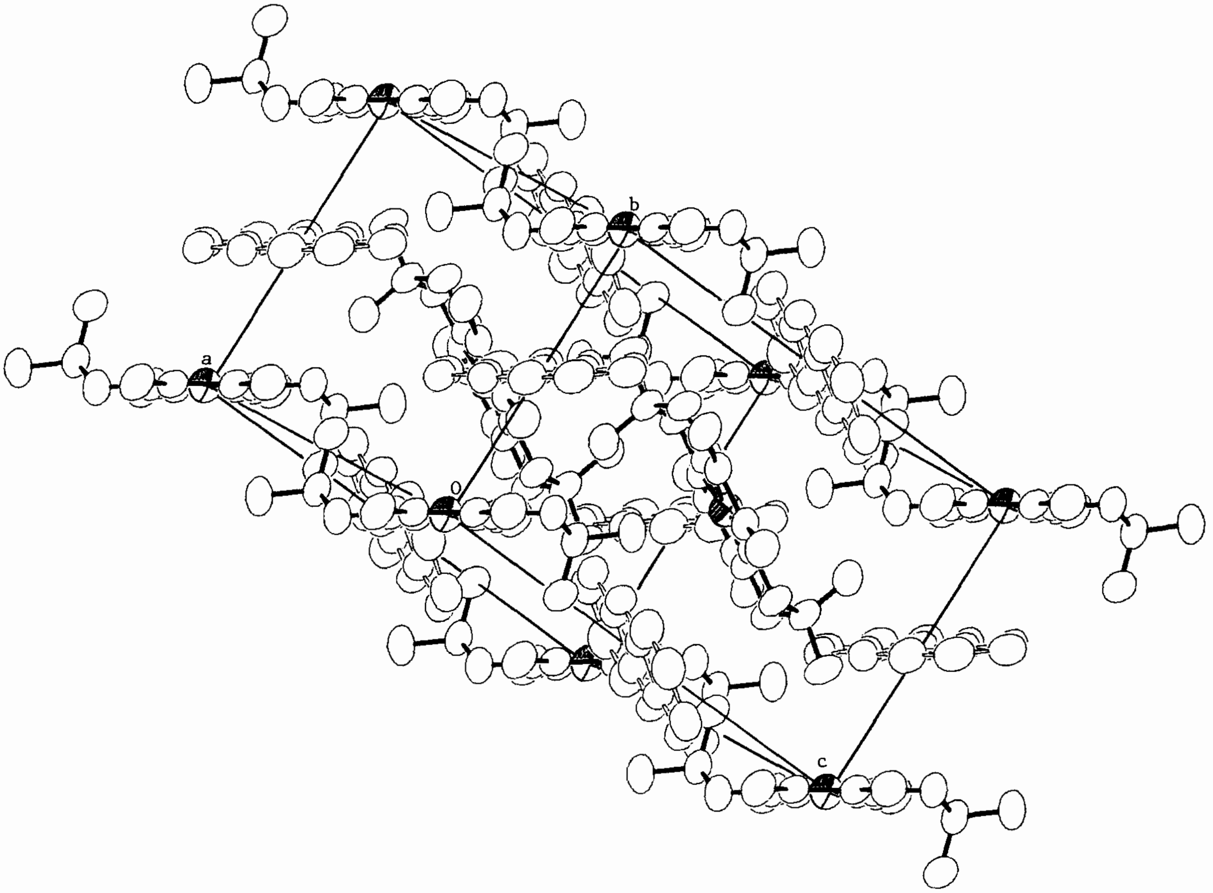

Fig. 3. The packing of the molecules in the crystal.

References

1 F. S. Stephens and R. S. Vagg, *Inorg. Chim. Acta, 51*, 163 (1981).
2 F. S. Stephens and R. S. Vagg, *Inorg. Chim. Acta, 43*, 77 (1980).
3 F. S. Stephens and R. S. Vagg, unpublished results.
4 'International Tables for X-Ray Crystallography', Vol. IV, pp. 72–79, Kynoch Press, Birmingham (1974).
5 C. K. Johnson, ORTEP, Report ORNL-3794 (1965), Revised (1971), Oak Ridge National Laboratory, Tennessee, U.S.A.
6 F. H. Herbstein and G. M. J. Schmidt, *Acta Cryst., 8*, 406 (1955).
7 F. S. Stephens and R. S. Vagg, *Acta Cryst., B33*, 3159 (1977).
8 E. D. McKenzie, *Inorg. Chim. Acta, 29*, 107 (1978); G. J. Palenik, D. A. Sullivan and D. V. Naik, *J. Am. Chem. Soc., 98*, 1177 (1976).