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Fig. 9. The hydrogen-bonded surroundings of the phospnate group. Numbers appearing after hyphens are the symmetry numbers of Table 9.

The Refinement of the Crystal Structure of the Perylene–Tetracyanoethylene Complex

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Crystals of the 1:1 complex of perylene and tetracyanoethylene (TCNE) are monoclinic, space group $P2_1/a$ with $a=15\cdot763$, $b=8\cdot234$, $c=7\cdot346$ Å, $\beta=96\cdot4°$, $Z=2$. The structure was refined by the block-diagonal least-squares method, on the basis of three-dimensional photographic data. Perylene and TCNE molecules are stacked alternately along the *b*-axis direction, making their molecular planes almost parallel to each other. The mean separation of the molecular planes is $3\cdot186$ Å.

Introduction

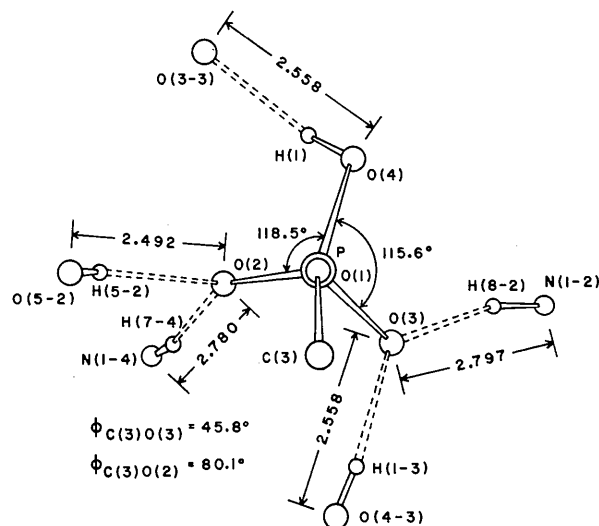There is a common feature in the π-molecular complex; the donor and acceptor molecules are alternately stacked, plane-to-plane, along some crystal axis with relatively small separation between molecular planes. The relative orientations of donor and acceptor molecules in the crystal are various (Prout & Wright, 1968).

In order to understand the nature of the intermolecular interaction, it is particularly interesting to examine the relative orientation of the molecules in a series of π-molecular complexes and to see if it is predictable from the charge-transfer theory.

It is considered that the tetracyanoethylene (TCNE) complexes of naphthalene, pyrene, and perylene are most suitable for this purpose. The crystal structure of the naphthalene–TCNE complex was determined by Williams & Wallwork (1967). The authors determined the crystal structure of the pyrene–TCNE complex (Ikemoto & Kuroda, 1968). In these complexes, the position of the centre of an acceptor molecule relative to that of the neighbouring donor molecule was found to coincide with a potential minimum predicted by theoretical calculations, but the relative orientation of the molecules does not agree with the most favourable orientation predicted from the charge-transfer theory (Kuroda, Amano, Ikemoto & Akamatu, 1967).

We have already reported the results of the preliminary analysis of the crystal structure of the perylene–TCNE complex by using the two-dimensional method (Ikemoto & Kuroda, 1967). The relative position of the molecular centres was also found to agree with the potential minimum in the perylene–TCNE complex. The purpose of the present study is to elucidate the further details of the crystal structure of this molecular complex by the three-dimensional analysis.

Experimental

Lattice constants were redetermined by least-squares calculation based on the results of observation of 8 diffraction lines with a diffractometer, Geigerflex. Quartz powder was used as the internal standard.

Crystal data
Monoclinic
$a = 15\cdot763 \pm 0\cdot012$ Å
$b = 8\cdot234 \pm 0\cdot006$
$c = 7\cdot346 \pm 0\cdot005$
$\beta = 96\cdot4 \pm 0\cdot1°$

Table 1. *Atomic parameters*

(a) Atomic coordinates in fractions of cell edges and their standard deviations (10^{-3} Å)

	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$
Perylene						
C(1)	$-0\cdot1803$	9	$0\cdot2752$	9	$0\cdot0873$	10
C(2)	$-0\cdot1335$	9	$0\cdot2870$	8	$0\cdot2517$	10
C(3)	$-0\cdot0541$	9	$0\cdot2008$	7	$0\cdot2825$	9
C(4)	$-0\cdot0263$	7	$0\cdot0997$	7	$0\cdot1426$	7
C(5)	$-0\cdot0803$	7	$0\cdot0895$	7	$-0\cdot0287$	7
C(6)	$-0\cdot0542$	7	$-0\cdot0120$	7	$-0\cdot1723$	7
C(7)	$-0\cdot1065$	8	$-0\cdot0221$	8	$-0\cdot3381$	8
C(8)	$-0\cdot1843$	8	$0\cdot0690$	10	$-0\cdot3569$	9
C(9)	$-0\cdot2091$	8	$0\cdot1669$	8	$-0\cdot2230$	9
C(10)	$-0\cdot1576$	8	$0\cdot1775$	7	$-0\cdot0570$	8
TCNE						
C(11)	$-0\cdot0358$	7	$0\cdot5466$	7	$-0\cdot0047$	8
C(12)	$-0\cdot0565$	7	$0\cdot6415$	8	$0\cdot1516$	8
C(13)	$-0\cdot0954$	8	$0\cdot5550$	7	$-0\cdot1676$	8
N(1)	$-0\cdot0684$	8	$0\cdot7156$	8	$0\cdot2765$	8
N(2)	$-0\cdot1414$	7	$0\cdot5591$	8	$-0\cdot2925$	8

(b) Thermal parameters. The β's are used in the expression:

$$\exp\{-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+hk\beta_{12}+hl\beta_{13}+kl\beta_{23})\}\,.$$

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Perylene						
C(1)	0·00571	0·01648	0·05207	0·00156	0·01414	0·01644
C(2)	0·00768	0·01537	0·03872	0·00297	0·01695	0·00435
C(3)	0·00873	0·01207	0·02896	$-0\cdot00636$	0·01361	$-0\cdot00288$
C(4)	0·00542	0·01136	0·02417	$-0\cdot00085$	0·00883	$-0\cdot00017$
C(5)	0·00462	0·01371	0·02261	$-0\cdot00285$	0·00497	0·00413
C(6)	0·00455	0·01076	0·02271	$-0\cdot00411$	0·00294	0·00385
C(7)	0·00621	0·01393	0·02709	$-0\cdot00451$	0·00189	0·00466
C(8)	0·00602	0·02545	0·03325	$-0\cdot00959$	$-0\cdot00886$	0·02253
C(9)	0·00515	0·01634	0·03894	$-0\cdot00270$	$-0\cdot00032$	0·01852
C(10)	0·00493	0·01267	0·03273	$-0\cdot00232$	0·00991	0·00600
TCNE						
C(11)	0·00488	0·01310	0·02417	$-0\cdot00213$	0·00521	$-0\cdot00021$
C(12)	0·00434	0·01532	0·03285	$-0\cdot00141$	0·00870	0·00142
C(13)	0·00514	0·01305	0·02742	$-0\cdot00091$	0·00300	0·00098
N(1)	0·00744	0·02231	0·04007	$-0\cdot00512$	0·01495	$-0\cdot01672$
N(2)	0·00623	0·02779	0·03671	$-0\cdot00606$	$-0\cdot00614$	0·00908

$V = 947.4 \text{ Å}^3$

Formula $C_{20}H_{12} . C_6N_4$; F.W. 380·0

D_x (calculated density) = 1·33 g.cm^{-3}

Table 2. *Observed and calculated structure factors* (× 10)

(dense numerical structure-factor data table)

Table 2 (*cont.*)

(dense numerical structure-factor data table continued)

D_m (measured density) = 1·3 g.cm^{-3}

$Z = 2$

$\mu = 5.9$ cm^{-1} (Cu $K\alpha$)

Space group $P2_1/a$ (from Weissenberg photographs)

(Absent spectra $h0l$ when h is odd, $0k0$ when k is odd).

A dark green lath-shaped crystal of about 0·3 mm length was used for data collection on a Weissenberg camera. It gradually decomposed on exposure to the atmosphere. To avoid decomposition, it was sealed into a thin-wall glass capillary. A set of intensity data were obtained up to the 6th layer around the b axis and the 4th layer around the c axis. The intensities were measured visually from multi-film Weissenberg photographs. Ni-filtered Cu $K\alpha$ radiation was used. No correction was made for absorption, while the correction for the Lorentz and polarization factors was made in the usual way.

The data were placed on the same relative scale by the method of Rollett & Sparks (1960). In all, 1425 independent reflexions from 2336 possible reflexions were obtained, but the intensity was not measurable on 291 of them.

Refinement

The structure was refined by the least-squares method. The calculation was carried out by means of the computer program, *HBLS* IV (Okaya & Ashida, 1967). This program uses the block-diagonal approximation with a 9 × 9 matrix for each atom with anisotropic temperature factors and a 4 × 4 matrix for each atom with an isotropic temperature factor. The scale factor was refined by assuming the overall temperature factor. The weighting scheme used was $w = 1.0$ for $F_o > 3.6$ and $w = 0.5$ for $F_o \leq 3.6$.

The parameters previously reported (Ikemoto & Kuroda, 1967) were used as the starting values of the refinements by introducing anisotropic temperature factors in place of the previous isotropic temperature factors. After several cycles of refinement neglecting hydrogen atoms, the R value decreased to 14%. The positions of hydrogen atoms were determined by the usual $(F_o - F_c)$ synthesis. The hydrogen atoms were then included in the subsequent refinements, assuming isotropic temperature factors for them.

Finally R decreased to 10·31%, excluding non-observable reflexions. Final parameters with their standard deviations are given in Table 1. Since the positions of some hydrogen atoms are not certain, hydrogen atoms are omitted from this Table. F_o and F_c are compared in Table 2.

Results and discussion

The atomic numbering of the molecule is shown in Fig. 1 with the thermal ellipsoids of the individual atoms drawn with the use of the *ORTEP* program (Johnson, 1965).

The arrangement of the component molecules in the

crystal is shown in Fig. 2. The donor and acceptor molecules are stacked alternately along the b axis, making their molecular planes almost parallel to each other.

The molecules can be considered planar. The equations of the planes of perylene and TCNE molecules were calculated by the method of least-squares. The equations are

$$0.5227X + 0.7771Y - 0.4070Z = 0$$

for perylene (without the hydrogen atoms) and

$$0.5427X + 0.7738Y - 0.3854Z = 3.186$$

for TCNE, where X, Y and Z are coordinates, in Å, with respect to the crystal axes a, b and c. The devia-

tions of the atoms from the each least-squares plane are listed in Table 3. These two planes make an angle

Table 3. *Atomic deviations* (Å) *from the least-squares planes of the perylene and* TCNE *molecules*

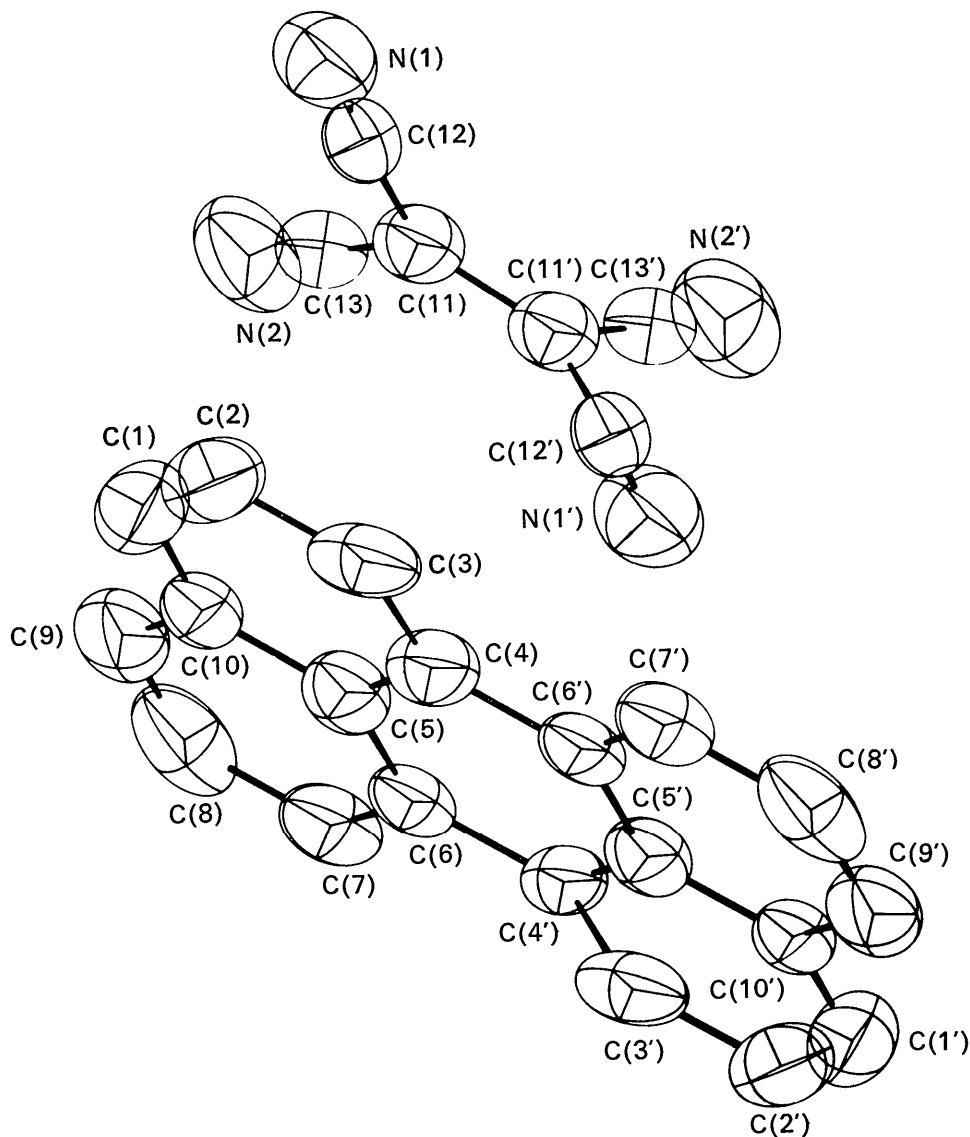| Perylene		TCNE	
C(1)	0.014	C(11)	0.004
C(2)	−0.016	C(12)	−0.011
C(3)	−0.005	C(13)	0.009
C(4)	−0.006	N(1)	0.006
C(5)	−0.003	N(2)	−0.005
C(6)	−0.009		
C(7)	−0.008		
C(8)	−0.010		
C(9)	0.012		
C(10)	0.007		

Fig. 1. The atomic numbering of the molecules. Ellipsoids represent anisotropic thermal parameters.

of about 1·7° with each other. The mean separation between the planes is 3·186 Å, which is smaller than the usual van der Waals separation.

The distances between the atoms of the nearest neighbour perylene and TCNE molecules are listed in Table 4, where the shortest is C(6)–N(1')=3·258 Å. Such close contact between the donor and acceptor molecules suggests the presence of a strong intermolecular interaction.

The molecular structures of the constituent molecules are illustrated in Fig. 3. The bond lengths given in Fig. 3 have not been corrected for thermal motion.

Molecular dimensions of perylene have been determined for perylene itself (Camerman & Trotter, 1964)

Table 4. *Distances less than 3·4 Å between atoms of the nearest-neighbour perylene and* TCNE *molecules and their standard deviations* (Å)

Perylene–TCNE

C(1)—C(13)	3·342 (0·013)
C(1)—C(11)	3·315 (0·013)
C(2)—C(11)	3·337 (0·012)
C(2)—C(12)	3·276 (0·013)
C(3)—C(11')	3·339 (0·012)
C(3)—C(13')	3·279 (0·012)
C(4)—C(11')	3·270 (0·010)
C(4)—C(12')	3·398 (0·011)
C(5)—C(12')	3·287 (0·011)
C(6)—N(1')	3·258 (0·011)
C(10)–C(13)	3·386 (0·011)
C(4')–N(1')	3·399 (0·011)

Table 5. *Bond lengths of perylene and* TCNE (Å)

Perylene	Perylene–TCNE	Perylene–fluoranil	Perylene–PMDA	Perylene
C(1)–C(2)	1·347	1·368	1·364	1·366
C(1)–C(10)	1·408	1·406	1·366	1·402
C(8)–C(9)	1·362	1·364	1·366	1·372
C(9)–C(10)	1·391	1·415	1·445	1·397
C(2)–C(3)	1·435	1·419	1·407	1·416
C(5)–C(10)	1·413	1·434	1·443	1·424
C(7)–C(8)	1·430	1·401	1·383	1·421
C(3)–C(4)	1·429	1·360	1·393	1·404
C(4)–C(5)	1·440	1·431	1·423	1·417
C(5)–C(6)	1·441	1·427	1·407	1·434
C(6)–C(7)	1·395	1·379	1·381	1·390
C(4)–C(6')	1·456	1·473	1·493	1·471
σ	0·01	0·005	0·01	0·005

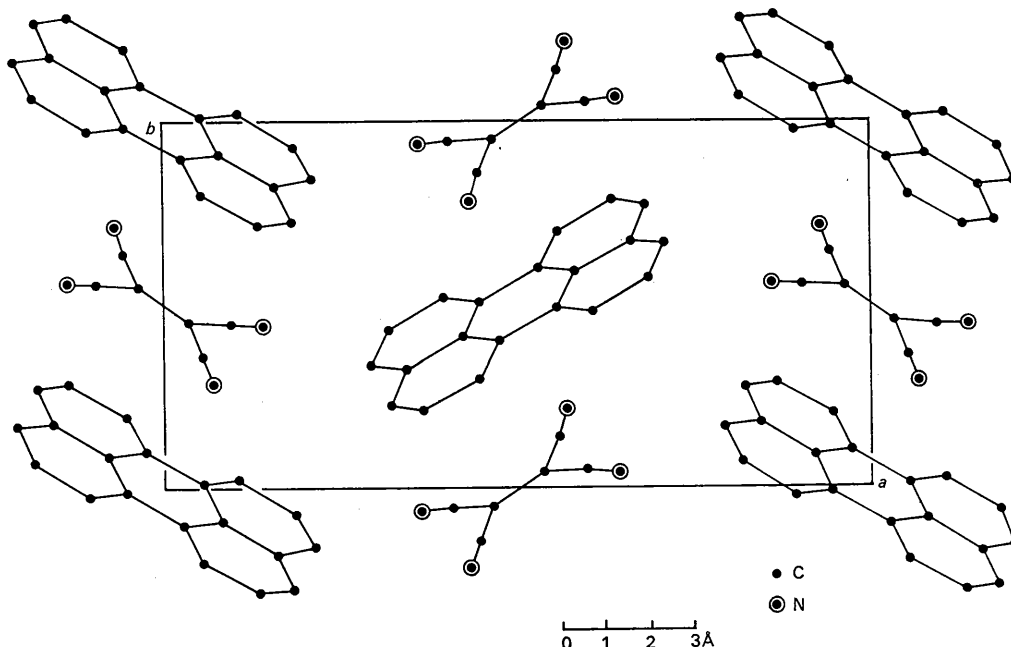| TCNE	Perylene–TCNE	Pyrene–TCNE	Naphthalene–TCNE	TCNE
C(11)–C(11')	1·359	1·309	1·35	1·313
C(11)–C(12)	1·456	1·464	1·426	1·449
C(11)–C(13)	1·438	1·472	1·426	1·439
C(12)–N(1)	1·135	1·124	1·131	1·129
C(13)–N(2)	1·105	1·113	1·131	1·129
σ	0·01	0·01	0·01	0·01

Fig. 2. Projection of the molecular arrangement on to the (001) plane.

(a)

(b)

Fig. 3. Bond lengths and their e.s.d.'s (Å) and bond angles and their e.s.d.'s (°). (*a*) Perylene, (*b*) TCNE.

dimensions and our results are shown in Table 5. The difference between our results and the other three sets is, first, that the C(1)–C(2) and C(4)–C(6') bond lengths are shorter than the corresponding values in the other three sets, and second, that C(5)–C(10) is shorter than C(2)–C(3) and C(7)–C(8).

The bond lengths and angles of TCNE are studied in the complexes naphthalene–TCNE (Williams & Wallwork, 1967) and pyrene–TCNE (Ikemoto & Kuroda, 1968), and in TCNE itself (Bekoe & Trueblood, 1960). These molecular dimensions are shown also in Table 5. They are almost in good agreement with each other if the standard deviations are taken into account. A large discrepancy is found, however, in the C–C≡N angle: in perylene–TCNE and pyrene–TCNE, C–C≡N seems not to be linear but slightly bent. This is seemingly due to the interaction between the molecules which belong to neighbouring columns.

The relative orientation of TCNE with respect to perylene found in the crystal in which we are most interested is shown in Fig. 4. The theoretical calculation of the charge-transfer interaction in the system perylene–TCNE shows that the relative position of the molecular centres of the perylene and TCNE molecules almost agrees with the potential minimum due to charge-transfer interaction. But the relative orientation of the component molecules does not agree with the most favourable orientation predicted from the charge-transfer theory. This was also the case in pyrene–TCNE as well as in naphthalene–TCNE (Kuroda *et al.*, 1967). It might be concluded that in the charge-transfer complexes, the relative position of the molecular centres of the donor and acceptor molecules, which are in face-to-face contact with each other, corresponds to the potential minimum associated with the charge-transfer force, but their relative orientation is not necessarily the most favourable with respect to the charge-transfer interaction. This seems to be reasonable since the variation of the charge-transfer force

and for perylene in the perylene–fluoranil complex (Hanson, 1963) and in perylene–pyromellitic dianhydride (PMDA) (Boeyens & Herbstein, 1965). In these molecular complexes the perylene molecule is centrosymmetric, but in the polymorph of perylene studied by Camerman & Trotter (1964) it is not centrosymmetric, although the deviations from centrosymmetry are not significant. These three sets of molecular
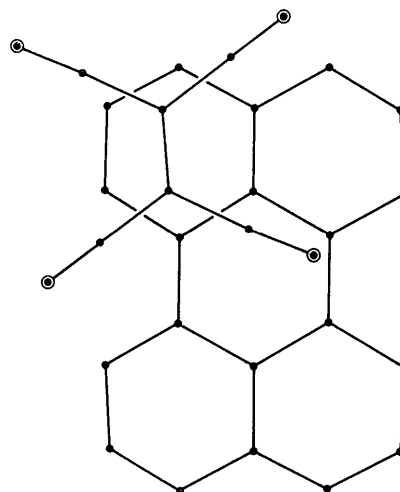

Fig. 4. Relative orientation of TCNE with respect to perylene found in the crystal.

with change of relative orientation is expected to be small, as pointed out in a previous paper. Hence the relative orientation could naturally be affected by various factors such as the molecular packing and the dispersion and repulsion forces.

The computer used in this work was the HITAC 5020E in the Computer Centre, University of Tokyo. The *UNICS* computer programs were used in this work (the Universal Crystallographic Computing System, Japanese Crystallographic Association).

The authors wish to thank Professor Hideo Akamatu for valuable discussions. We are also grateful to C. Itoh Electronic Computing Service for the use of a CDC 3600 computer.

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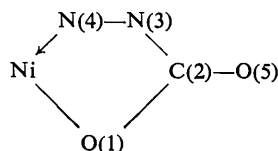WILLIAMS, R. M. & WALLWORK, S. C. (1967). *Acta Cryst.* 22, 899.

The Crystal and Molecular Structure of Bis(hydrazinecarboxylato-N',O)-nickel Dihydrate and Comparisons with other Complexes of the Ligand

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Bis(hydrazinecarboxylato-N',O)-nickel dihydrate is monoclinic, space group $C2/c$, with unit-cell constants: $a=11\cdot78$ (1), $b=6\cdot95$ (1), $c=10\cdot54$ (1) Å, $\beta=111\cdot55$ (10)°. The structure determination shows how the complex around the metal is a *trans*(O),*trans*(N),*trans*(L)-octahedral chelate, with L=OH$_2$. The chelate ring

$$\begin{array}{ccc} & \text{N(4)—N(3)} & \\ \diagup & & \diagdown \\ \text{Ni} & & \text{C(2)—O(5)} \\ \diagdown & & \diagup \\ & \text{O(1)} & \end{array}$$

is not planar. The atoms N(3), C(2), O(5), O(1) however, which probably form a conjugate system, deviate only slightly from a common plane. The statistical significance of the deviations from this plane is discussed in comparison with the deviations and the χ^2 significance tests as calculated for other chelate rings formed by the same ligand. The nickel–oxygen bond in the ring is shorter (2·038 Å) than the nickel–nitrogen bond (2·092 Å) and this is probably related to the negative charge on O(1). Other characteristics of the chelate ring and of the octahedral complex are discussed. The structure is held together by a network of hydrogen bonds. The hydrogen atoms, as determined by difference synthesis, are slightly off the line joining the two atoms involved in each hydrogen bond. The water molecule at O(6) forms two dative hydrogen bonds and behaves as acceptor in a third, the latter bond implying one lone pair of electrons on O(6). The second lone pair on O(6) forms a bond with the nickel atom.

Introduction

As part of a programme of study of the structures and related properties of the complexes of hydrazinecar- boxylic acid, H$_2$N'–NH–COOH (abbreviated to hycH), the structure of bis(hydrazinecarboxylato-N', O)- nickel dihydrate, Ni(hyc)$_2$.2H$_2$O, has been investi- gated. The octahedral complexes which have been