

the most acceptable explanation for the line-broadening in the Mössbauer quadrupole doublet already mentioned, the measurements are clearly in favour of possibility (ii).

To verify this, we also performed Mössbauer measurements on [Zn(trz)<sub>2</sub>(NCS)<sub>2</sub>] doped with approximately 0.1% <sup>57</sup>Fe. The Zn compound does not show disorder and although it crystallizes in a different space group (*Pbcn*), the site symmetries of the metal ions are the same in both compounds. Despite the poor statistics of the spectrum, no significant line-broadening was observed. The above results justify the conclusion that the trz rings are orientated in a random way.

No evidence for disorder, such as streaks or diffuse reflections, could be observed in X-ray photographs. This may be due to the high background level, caused by the Cu *K* $\alpha$  radiation used.

Finally we mention that, because the degree of disorder in [Fe(trz)<sub>2</sub>(NCS)<sub>2</sub>] differs significantly from 50%, we have re-examined our results on the corresponding Co compound. In a previous paper (Engel-

friet *et al.*, 1979) we assumed the degree of disorder in the Co compound to be 50%. The occupation rate of one of the enantiomorphs was found to be 42 (1)%. However, refinement of all parameters together with the occupation rate did not produce significant changes in the *R* factors and the positional parameters.

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### Structure of *trans*-Difluoro{[7*R*(*S*),14*S*(*R*)]-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane}nickel(II) Pentahydrate

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**Abstract.** [Ni(C<sub>16</sub>H<sub>36</sub>N<sub>4</sub>)F<sub>2</sub>].5H<sub>2</sub>O, triclinic, *P* $\bar{1}$ , *a* = 11.185 (2), *b* = 13.364 (3), *c* = 8.890 (1) Å,  $\alpha$  = 83.17 (2),  $\beta$  = 104.94 (1),  $\gamma$  = 113.00 (1)°, *U* = 1181.6 (4) Å<sup>3</sup>, *Z* = 2, *D<sub>m</sub>* = 1.32<sub>9</sub>, *D<sub>x</sub>* = 1.32<sub>5</sub> Mg m<sup>-3</sup>,  $\mu$ (Mo *K* $\alpha$ ) = 0.870 mm<sup>-1</sup>; *R* = 0.031 and *R<sub>w</sub>* = 0.039 for 5958 independent reflexions. The Ni<sup>II</sup> ion is surrounded pseudo-octahedrally by four N atoms of the macrocyclic ligand in a single plane and by two F<sup>-</sup> ions occupying the axial positions. The dispositions of water molecules around the Ni<sup>II</sup> ion are discussed.

**Introduction.** This is part of a series of structural investigations on the Ni<sup>II</sup> halide complexes containing the title macrocyclic ligand, hereafter abbreviated as *meso*-Me<sub>6</sub>[14]aneN<sub>4</sub>. A main feature of interest in these studies is a clarification of the dispositions of water molecules around a Ni<sup>II</sup> ion and thereby to explain the role played by water in the spin-state variations among the Ni<sup>II</sup> complexes. The crystal structures of the two

complexes formed with NiCl<sub>2</sub> and the title ligand, which are the low-spin four-coordinate complex [Ni(*meso*-Me<sub>6</sub>[14]aneN<sub>4</sub>)]Cl<sub>2</sub>.2H<sub>2</sub>O and the high-spin six-coordinate complex [NiCl<sub>2</sub>(*meso*-Me<sub>6</sub>[14]aneN<sub>4</sub>)]·2CHCl<sub>3</sub>, have been reported (Ito & Toriumi, 1981). In this paper the structure of the title complex [NiF<sub>2</sub>(*meso*-Me<sub>6</sub>[14]aneN<sub>4</sub>)]·5H<sub>2</sub>O is described. The compound was prepared from the corresponding perchlorate salt [Ni(*meso*-Me<sub>6</sub>[14]aneN<sub>4</sub>)](ClO<sub>4</sub>)<sub>2</sub> (Warner & Busch, 1969) by ion exchange (Dowex 1X8). Slow evaporation of the eluate from the column yielded triclinic single crystals. A pale-violet plate was shaped into an approximate sphere with a diameter of 0.40 mm. X-ray diffraction data were measured on a Rigaku AFC-5 four-circle diffractometer with graphite-monochromatized Mo *K* $\alpha$  radiation. Within the range  $2\theta \leq 60^\circ$ , 5958 independent reflexions with  $|F_o| \geq 3\sigma(|F_o|)$  were obtained. The intensities were corrected for Lorentz and polarization factors, but no absorption correction was applied.

Table 1. Fractional positional parameters ( $\times 10^4$ ) and equivalent isotropic temperature factors for non-hydrogen atoms, with e.s.d.'s in parentheses

	x	y	z	$B_{eq}$ (Å <sup>2</sup> )*
Ni(1)	0	0	0	2.0
Ni(2)	0	5000	5000	2.1
F(1)	259 (1)	1513 (1)	715 (1)	3.2
F(2)	170 (1)	3582 (1)	6142 (1)	3.1
N(1)	1493 (1)	18 (1)	1997 (1)	2.4
N(2)	1328 (1)	765 (1)	-1437 (1)	2.4
N(3)	928 (1)	5701 (1)	7191 (1)	2.5
N(4)	1780 (1)	5330 (1)	4356 (1)	2.6
C(1)	-498 (2)	-531 (1)	3045 (2)	3.1
C(2)	795 (2)	-693 (1)	3163 (2)	3.1
C(3)	2758 (1)	-75 (1)	1894 (2)	3.0
C(4)	3284 (1)	703 (1)	580 (2)	3.1
C(5)	2511 (1)	453 (1)	-1104 (2)	2.9
C(6)	3814 (2)	304 (2)	3435 (2)	4.6
C(7)	2525 (2)	-1248 (1)	1578 (2)	4.0
C(8)	3436 (2)	1014 (2)	-2212 (2)	4.7
C(9)	-1399 (2)	4789 (1)	7358 (2)	3.4
C(10)	-135 (2)	5804 (1)	7785 (2)	3.5
C(11)	2245 (2)	6644 (1)	7464 (2)	3.0
C(12)	3178 (2)	6402 (1)	6683 (2)	3.4
C(13)	2884 (2)	6368 (1)	4909 (2)	3.3
C(14)	2883 (2)	6758 (2)	9219 (2)	4.4
C(15)	2040 (2)	7692 (1)	6797 (2)	4.1
C(16)	4158 (2)	6529 (2)	4413 (3)	6.3
O(1)	2198 (1)	3173 (1)	5785 (2)	5.2
O(2)	2273 (1)	2373 (1)	3116 (2)	4.9
O(3)	967 (2)	3407 (1)	-816 (1)	5.1
O(4)	4355 (2)	3969 (2)	-1649 (2)	6.9
O(5)	3505 (2)	4016 (2)	1096 (2)	7.6

\* The equivalent isotropic temperature factor is calculated from  $B_{eq} = \frac{1}{3} \sum_i \sum_j a_i \cdot a_j \beta_{ij}$ , where the  $a_i$ 's are the unit-cell edges in direct space.

The structure was solved by the heavy-atom method and refined by a block-diagonal least-squares method. The weighting scheme  $w = [\sigma_{count}^2 + (0.015|F_o|^2)]^{-1}$  was employed. All H atoms were located by a difference Fourier synthesis, and included in the refinement with isotropic temperature factors. The final  $R$  values were  $R = 0.031$  and  $R_w = 0.039$ . Atomic parameters are given in Table 1.\*

**Discussion.** The crystal consists of a discrete complex molecule of [NiF<sub>2</sub>(*meso*-Me<sub>6</sub>[14]aneN<sub>4</sub>)] and water of crystallization. There are two crystallographically independent Ni<sup>II</sup> complexes in the unit cell. Both Ni<sup>II</sup> ions are required to lie at centers of symmetry. Since the bond lengths and angles in these two complexes are not significantly different, the average molecular

\* Lists of structure factors, anisotropic thermal parameters for non-hydrogen atoms, and positional and thermal parameters for hydrogen atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35603 (32 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

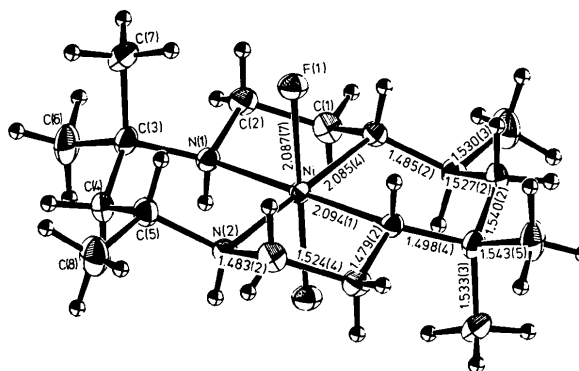


Fig. 1. Perspective view of [NiF<sub>2</sub>(*meso*-Me<sub>6</sub>[14]aneN<sub>4</sub>)]. Mean bond lengths (Å) are shown, though the atom numbering scheme for the Ni(1) complex is depicted.

Table 2. Averaged bond angles (°) within the complex cation, with their e.s.d.'s

Mean bond angles of the Ni(1) and Ni(2) complexes are given, though the atom numbering for the Ni(1) complex is used.

N(1)—Ni(1)—N(2)	94.69 (5)	N(2)—C(1)—C(2)	109.04 (14)
F(1)—Ni(1)—N(1)	84.96 (28)	N(1)—C(2)—C(1)	109.07 (35)
F(1)—Ni(1)—N(2)	89.29 (50)	N(1)—C(3)—C(4)	108.03 (13)
		N(2)—C(5)—C(4)	109.89 (19)
Ni(1)—N(1)—C(2)	105.98 (8)		
Ni(1)—N(2)—C(1)	104.98 (10)	N(1)—C(3)—C(6)	109.56 (26)
Ni(1)—N(1)—C(3)	121.48 (12)	N(1)—C(3)—C(7)	110.49 (14)
Ni(1)—N(2)—C(5)	115.37 (28)	N(2)—C(5)—C(8)	112.53 (17)
C(2)—N(1)—C(3)	116.56 (19)	C(3)—C(4)—C(5)	119.58 (36)
C(1)—N(2)—C(5)	114.17 (22)	C(4)—C(3)—C(6)	107.78 (15)
		C(4)—C(3)—C(7)	111.04 (23)
		C(4)—C(5)—C(8)	109.74 (38)
		C(6)—C(3)—C(7)	109.88 (15)

structure is described. Fig. 1 shows a perspective view of the complex together with the bond lengths.\* Bond angles are given in Table 2. The Ni<sup>II</sup> ion is surrounded pseudo-octahedrally by four N atoms in a single plane and by two F<sup>-</sup> ions occupying the axial positions. The average Ni—N distance is 2.090 (6) Å and is in the normal range for a high-spin Ni<sup>II</sup> complex with four planar N donors (Madaule-Aubry & Brown, 1968; Ito & Toriumi, 1981). The macrocyclic skeleton adopts the most stable conformation: the six-membered chelate rings take the chair form with the single methyl groups in equatorial positions; the five-membered rings are in the *gauche* conformation. The average Ni—F bond distance is 2.087 (7) Å.

Fig. 2 shows the dispositions of water molecules in the vicinities of Ni(1) and Ni(2) as viewed along the normal to each NiN<sub>4</sub> plane. The structures around

\* Throughout this paper, the e.s.d. of a mean value for two chemically equivalent bond lengths or angles is taken to be the largest of three values: the e.s.d. for one parameter ( $q_1$ ), the e.s.d. for the other ( $q_2$ ), or  $|q_1 - q_2|/2$ .

the two independent Ni<sup>II</sup> complexes are very similar, as depicted in Fig. 2. In general, the coordinating ability of water for a Ni<sup>II</sup> ion is greater than that of the F<sup>-</sup> ion (Busch, 1967). In spite of this, the water molecules in [NiF<sub>2</sub>(*meso*-Me<sub>6</sub>[14]aneN<sub>4</sub>)]·5H<sub>2</sub>O do not occupy the coordination sites but are located above the H atoms of the four N–H bonds. The structural feature of the hydrogen-bond acceptor atoms with high coordinating ability being located above the H atoms of N–H bonds but not occupying the coordination sites has also been found in the structure of [Ni(*meso*-Me<sub>6</sub>[14]aneN<sub>4</sub>)]Cl<sub>2</sub>·2H<sub>2</sub>O (Ito & Toriumi, 1981). Of the eight water molecules shown in Fig. 3, three, H<sub>2</sub>O(1), H<sub>2</sub>O(2), and H<sub>2</sub>O(3), are crystallographically independent. These three water molecules participate in four independent N–H···O interactions. Of these, the N–H···O interactions involving O(1) present in the vicinity of Ni(2) and O(2) in the vicinity of Ni(1) are similarly short and strong with the distances N(4)–H···O(1) = 3.166 (2) and N(1)–H···O(2) = 3.131 (2) Å. On the other hand, the H<sub>2</sub>O(3) molecule interacts weakly with both N(2) in the Ni(1) complex and N(3) in the Ni(2) complex [N(3)–H···O(3') = 3.363 (2), N(2)–H···O(3) = 3.825 (2) Å].\* The latter distance might be too long for a normal hydrogen-bond distance. This situation may be caused by the coordination of the F<sup>-</sup> ions. In the structure of [Ni(*meso*-Me<sub>6</sub>[14]aneN<sub>4</sub>)]Cl<sub>2</sub>·2H<sub>2</sub>O, where the axial sites are vacant, both of the N(1)–H and N(2)–H groups are involved in the normal hydrogen bond with the atoms lying above the N–H groups. It should be noted that although the N(1)–H···O(2) and N(4)–H···O(1) bonds are very similar to each other in their features and lengths, the N atoms involved in these interactions are chemically different, N(1) being adjacent to the single methyl C whereas N(4) is adjacent to the geminal dimethyl C. All the H<sub>2</sub>O(1), H<sub>2</sub>O(2), and H<sub>2</sub>O(3) molecules are

\* Hereafter, primes designate atoms transformed by the symmetry operations (')  $x, y, 1 + z$  and (")  $1 - x, 1 - y, -z$ , respectively.

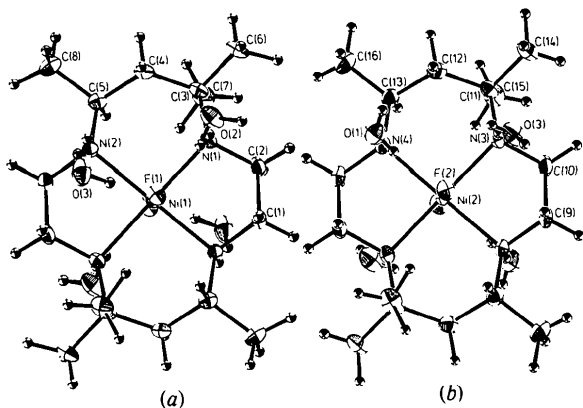


Fig. 2. The dispositions of water molecules in the vicinities of (a) Ni(1) and (b) Ni(2) as viewed along the normals of each NiN<sub>4</sub> plane.

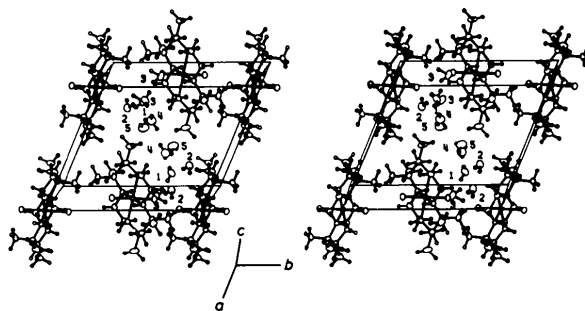


Fig. 3. Stereoscopic drawing of the crystal structure of [NiF<sub>2</sub>(*meso*-Me<sub>6</sub>[14]aneN<sub>4</sub>)]·5H<sub>2</sub>O. The atom numbering for water molecules corresponds to the crystallographic numbering scheme as follows: 1 = H<sub>2</sub>O(1), 2 = H<sub>2</sub>O(2), 3 = H<sub>2</sub>O(3), 4 = H<sub>2</sub>O(4), and 5 = H<sub>2</sub>O(5).

hydrogen-bonded to F<sup>-</sup> ions. All the F···H–O distances are normal: F(1)···H–O(2) = 2.652 (2); F(1)···H–O(3) = 2.657 (2); F(2)···H–O(1) = 2.632 (2); F(2)···H–O(3') = 2.633 (2) Å. A stereoscopic drawing of the crystal structure is shown in Fig. 3. The O–H···O bonds found in the structure are: O(1)···H–O(2) = 2.748 (2); O(1)–H···O(4') = 2.809 (2); O(2)···H–O(5) = 2.814 (2); O(3)···H–O(5) = 2.765 (2); O(4)–H···O(5) = 2.853 (3); O(4)–H···O(5'') = 2.810 (2) Å.

The differences in the environments of the waters of crystallization are well reflected in the results of thermogravimetry (TG) and differential scanning calorimetry (DSC) for a dehydration reaction of [NiF<sub>2</sub>(*meso*-Me<sub>6</sub>[14]aneN<sub>4</sub>)]·5H<sub>2</sub>O. When the pentahydrate was heated at 3 K min<sup>-1</sup>, the weight loss due to the dehydration occurred in two steps. The first began at 328 and ended at 374 K and the second at 393 and at 425 K, respectively. The weight losses of 11.4% for the first step and 7.6% for the second step are in accord with the calculated values for the loss of three moles of water (11.47%) and for the subsequent loss of two moles of water (7.65%), respectively. Corresponding to the weight losses, two clearly separated endothermic peaks appeared in the DSC curve. The heats of dehydration were estimated to be  $\Delta H = 134 \pm 1$  kJ mol<sup>-1</sup> for the first step and  $\Delta H = 109 \pm 1$  kJ mol<sup>-1</sup> for the second step by comparing the peak areas with that for the melting of naphthalene crystals,  $\Delta H = 18.98$  kJ mol<sup>-1</sup> (McCullough, Finke, Messerly, Todd, Kincheloe & Waddington, 1957). The average  $\Delta H$  values for the loss of one mole of water are  $\Delta H = 44.8$  kJ mol<sup>-1</sup> for the first step and  $\Delta H = 54.6$  kJ mol<sup>-1</sup> for the second. In view of the positions of the five water molecules in the crystal of [NiF<sub>2</sub>(*meso*-Me<sub>6</sub>[14]aneN<sub>4</sub>)]·5H<sub>2</sub>O, the three water molecules responsible for the first step of the dehydration are H<sub>2</sub>O(3), H<sub>2</sub>O(4), and H<sub>2</sub>O(5), while those for the second step are the strongly hydrogen-bonded H<sub>2</sub>O(1) and H<sub>2</sub>O(2).

As shown in Fig. 2, the Ni(1)–F(1) and Ni(2)–F(2) bonds are tilted 4.8 and 5.6° from the normal to each NiN<sub>4</sub> plane so as to minimize the steric interaction with the axial methyl groups of C(7) and C(15), respectively.

The calculations were carried out on the HITAC M-180 computer at the Computer Center of the Institute for Molecular Science with the *Universal Crystallographic Computation Program System UNICS III* (Sakurai & Kobayashi, 1979). The TG and DSC curves were measured on a Rigaku DSC-8001, SL/C.

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### *trans*-Dichlorobis(cycloheptylamine)platinum(II)

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**Abstract.** [Pt(C<sub>7</sub>H<sub>13</sub>NH<sub>2</sub>)<sub>2</sub>Cl<sub>2</sub>], triclinic,  $P\bar{1}$ ,  $Z = 2$ ,  $a = 11.445$  (3),  $b = 13.651$  (3),  $c = 5.828$  (1) Å,  $\alpha = 93.93$  (2),  $\beta = 102.55$  (2),  $\gamma = 96.78$  (2)°,  $V = 878.5$  (6) Å<sup>3</sup>,  $D_c = 1.75$ ,  $D_o = 1.73$  (2) Mg m<sup>-3</sup>. The structure was determined by heavy-atom methods and refined to  $R = 0.033$ ,  $R_w = 0.054$  based on 1838 independent reflections. The complex is *trans* even though it was prepared by the method described for the *cis* complex and bond lengths and bond angles are normal. The crystal is held together by hydrogen bonds and van der Waals forces.

**Introduction.** The crystal was prepared by the method supposed to give *cis*-dichlorobis(cycloheptylamine)-platinum(II) (Braddock, Connors, Jones, Khokhar, Melzack & Tobe, 1975; Connors, Jones, Ross, Braddock, Khokhar & Tobe, 1972). The compound was crystallized from acetone. The pale-yellow crystals were thick plates. A crystal, which was homogeneous under the polarizing microscope, was cut to a rough needle and ground into a cylinder of dimensions  $r = 0.075$ ,  $l = 0.25$  mm. Photographs suggested the crystal was triclinic and a Delaunay reduction showed no hidden symmetry. Since  $Z = 2$  the space group  $P\bar{1}$  was assumed and confirmed by the successful solution of the structure. The cell was determined by a least-squares fit of 15 well centred reflections ( $20^\circ < 2\theta < 34^\circ$ ) on a Syntex P2<sub>1</sub> diffractometer, and the density

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was determined by flotation in an iodoethane–diiodo-methane mixture. The intensities of 1838 independent reflections up to  $2\theta = 45^\circ$  were measured with Mo  $K\alpha$  radiation. The computer-controlled Syntex P2<sub>1</sub> diffractometer was operated in a  $2\theta(\text{counter})-\theta(\text{crystal})$  scan mode with a graphite monochromator. Reflections for which  $I \leq 0$  were not considered in data treatment. This left 1487 observed [ $I > 3\sigma(I)$ ] reflections which were used for the structure determination; 340 were considered unobserved [ $3\sigma(I) > I > 0$ ] and were given no weight in the refinement unless  $|F_o| > |F_c|$ . The method of data treatment has been described previously (Hughes, Krishnamachari, Lock, Powell & Turner, 1977; Lippert, Lock, Rosenberg & Zvagulis, 1977). Correction was made for absorption ( $\mu = 8.322$  mm<sup>-1</sup>,  $A^*$  limits 2.92 to 2.43) and extinction (Larson, 1967;  $g = 1.94 \times 10^{-7}$ ). The stability of the experimental system was monitored by a standard reflection (231) after every 49 reflections; it showed an e.s.d. of 1.24% with no time variation.

Initially the Patterson map was solved incorrectly, because of the preconceived idea that we were dealing with the *cis* complex. The Pt atom was placed at  $\frac{1}{4}, 0, 0$  and electron density difference maps revealed other atoms in some peculiar geometric arrangements, including six atoms sufficiently close to Pt to be considered coordinated. The discovery that the reported structure of supposedly *cis*-dichlorobis(cyclohexyl-