

1990); however, the Zn—O (perchlorate) distance of 2.380 (2) Å is considerably shorter than we observe.

The mean Ag—N bond distance of 2.195 (3) Å in [Ag(tmc)]²⁺ is slightly longer than the corresponding distances in Ag(tet a)²⁺ [2.160 (3) Å] and Ag-(cyclam)²⁺ [2.158 (2) Å]. This is presumably a result of cavity enlargement in tmc arising from ring strain caused by the methyl substituents.

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Acta Cryst. (1991). **C47**, 2312–2315

Structure of (4-Amino-2,2,6,6-tetramethylpiperidinyl-1-oxy)-bis(hexafluoroacetylacetonato)(methanol)nickel(II) Methanol Solvate

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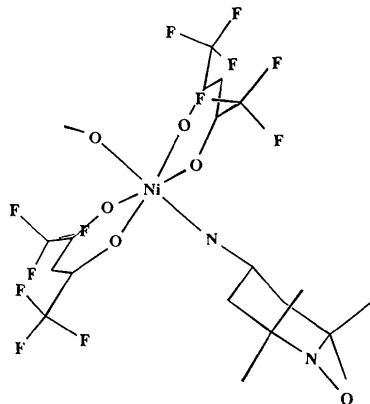
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Abstract. [Ni(C₅H₂F₆O₂)₂(C₉H₁₇N₂O)(CH₃OH)]·CH₃OH, *M_r* = 707.2, monoclinic, *P*2₁/*n*, *a* = 12.125 (3), *b* = 12.379 (3), *c* = 20.438 (5) Å, β = 92.07 (2)°, *V* = 3066 (1) Å³, *D_x* = 1.532 Mg m⁻³, *Z* = 4, μ = 0.743 mm⁻¹, λ(Mo *K*α) = 0.71073 Å, *F*(000) = 1440, *T* = 298 K, *R* = 0.0678 and *wR* = 0.0912 for 2365 averaged reflections with *I* > 3σ(*I*). The Ni atom in this structure possesses an octahedral geometry and forms bonds to two equatorial F₆AcAc ligands, one molecule of methanol and the nitroxyl radical. Coordination of the nitroxyl is through the N atom of the amine group at a distance of 2.075 (6) Å. There are no unusual intermolecular contacts and the asymmetric unit contains a molecule of methanol.

Introduction. Nitroxyl radicals have been used extensively as spin labels in biological systems and, more recently, as ligands in the preparation of coordination compounds. The coordination behavior of these compounds is varied and diverse, examples of which include direct coordination through the O atom of the N—O group (Dickman & Doedens, 1981; Porter, Dickman & Doedens, 1983, 1985, 1988), and an η² type of coordination involving both the N and O atoms in reduced nitroxyls (Dickman & Doedens, 1982; Porter & Doedens, 1985). In instances where

substituted nitroxyl radicals such as 3-cyano-2,2,5,5-pyrrolidino-1-oxyl (TMPCN) have been used, coordination *via* the CN group has also been observed (Dickman & Doedens, 1983) including formation of a cocrystallized solid with no specific interactions involving the nitroxyl group (Porter & Doedens, 1984). In this paper we report the X-ray crystal structure of an Ni^{II} complex obtained from the reaction of Ni(F₆AcAc)₂ with 4-amino-2,2,6,6-tetramethylpiperidinyl-1-oxy, or simply 4-amino-TEMPO.



Experimental. The title compound was prepared by refluxing one equivalent of 4-amino-TEMPO with

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anhydrous bis(hexafluoroacetylacetonato)nickel(II) in pentane. Several regularly shaped dark green crystals were obtained by crystallization from methanol. A small crystal of approximate dimensions $0.1 \times 0.1 \times 0.15$ mm was selected and mounted on the end of a glass fiber in a random orientation. Monoclinic symmetry suggested on the basis of the interaxial angles and confirmed by axial rotation photographs. Refined cell parameters obtained from the setting angles of 25 reflections with $15 < 2\theta < 30^\circ$. Data collection was carried out using a Nicolet *R3m/V* diffractometer and graphite-monochromated Mo $K\alpha$ radiation using the ω -scanning technique in bisecting geometry. Scan rate variable, $3\text{--}20^\circ \text{min}^{-1}$; scan range 1.5° in ω . Intensities were measured for a total of 4402 reflections ($-3 < h < 13$, $0 < k < 13$, $-21 < l < 21$) with $3.5 < 2\theta < 45^\circ$ and averaged to give 4004 unique reflections ($R_{\text{int}} = 0.0116$) with $(\sin\theta/\lambda_{\text{max}}) = 0.582 \text{ \AA}^{-1}$. Three standards (202, $0\bar{2}0$, $\bar{1}\bar{1}\bar{1}$) measured every 100 data showed a decline in intensity of approximately 10% over a period of data collection. The data were corrected for standard decay, Lorentz and polarization effects, but not absorption. Structure solution and refinement carried out using the *SHELXTL-Plus* collection of crystallographic software (Sheldrick, 1986). Coordinates of most of the atoms were obtained using direct methods; remaining non-H atoms located on difference Fourier maps. It was not possible to locate all the H atoms in this structure; however, when possible, these atoms were placed in idealized positions with fixed isotropic $U = 0.080 \text{ \AA}^2$. Ni, O and F atoms were refined anisotropically using scattering factors, including terms for anomalous dispersion, taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). An alternate refinement of the structure in which all non-H atoms were refined anisotropically yielded no improvement in the model and resulted in a much poorer data-to-parameter ratio.

Refinement based on F using weights of the form $w^{-1} = \sigma^2(F) + 0.0012(F^2)$. Convergence to conventional R values of $R = 0.0678$ and $wR = 0.0912$ with a goodness-of-fit equal to 1.92 was obtained using 327 variable parameters and 2365 observed reflections with $I > 3\sigma(I)$. No reflections had intensities beyond the range for valid coincidence correction. For final cycle, max. $\Delta/\sigma = 0.068$ with min. and max. residual electron densities of -0.39 and 0.82 e \AA^{-3} , respectively. Table 1 gives the atomic coordinates and thermal parameters and Table 2 lists bond lengths and angles.*

* Lists of structure factors, H-atom coordinates, C—F bond lengths and angles, and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54053 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Ni	1091 (1)	1207 (1)	836 (1)	44 (1)
O(1)	-585 (4)	1292 (4)	705 (3)	50 (1)
O(2)	1192 (4)	2831 (4)	825 (3)	60 (1)
O(3)	2722 (4)	1147 (4)	1088 (3)	58 (1)
O(4)	1001 (4)	-434 (4)	907 (3)	51 (1)
O(5)	4250 (6)	3283 (7)	-1717 (4)	142 (1)
O(6)	798 (5)	1283 (5)	1838 (3)	74 (1)
O(7)	5223 (7)	4897 (7)	2361 (4)	139 (1)
N(1)	1313 (5)	1066 (5)	-163 (3)	51 (1)
N(3)	3571 (6)	2786 (6)	-1349 (4)	85 (1)
C(1)	-2369 (7)	1928 (7)	819 (5)	68 (1)
C(2)	-1127 (6)	2121 (6)	802 (4)	48 (1)
C(3)	-756 (6)	3167 (6)	899 (4)	59 (1)
C(4)	365 (7)	3422 (6)	898 (4)	61 (1)
C(5)	711 (8)	4637 (8)	1011 (5)	91 (1)
C(6)	4473 (8)	532 (8)	1455 (5)	95 (1)
C(7)	3242 (6)	309 (6)	1266 (4)	54 (1)
C(8)	2872 (6)	-731 (6)	1300 (4)	57 (1)
C(9)	1799 (6)	-1010 (6)	1116 (4)	51 (1)
C(10)	1505 (7)	-2207 (7)	1163 (4)	63 (1)
C(11)	1902 (6)	1901 (6)	-568 (4)	56 (1)
C(12)	3028 (6)	2128 (6)	-285 (4)	66 (1)
C(13)	3655 (7)	2988 (7)	-650 (4)	73 (1)
C(14)	2596 (7)	2328 (7)	-1708 (5)	77 (1)
C(15)	2005 (6)	1522 (6)	-1263 (4)	65 (1)
C(16)	4865 (8)	2940 (8)	-445 (6)	121 (1)
C(17)	3191 (8)	4101 (8)	-513 (6)	116 (1)
C(18)	1795 (8)	3242 (7)	-1919 (5)	108 (1)
C(19)	2965 (7)	1730 (8)	2317 (5)	100 (1)
C(20)	1417 (8)	1935 (8)	2301 (5)	108 (1)
C(21)	4395 (10)	4190 (10)	1865 (8)	223 (1)
F(1)	-2970 (4)	2806 (5)	840 (4)	136 (1)
F(2)	-2603 (4)	1374 (6)	1349 (3)	117 (1)
F(3)	-2726 (4)	1332 (5)	335 (3)	112 (1)
F(4)	1216 (10)	4688 (8)	1538 (7)	144 (1)
F(5)	1283 (9)	4950 (8)	523 (6)	111 (1)
F(6)	-149 (8)	5276 (7)	925 (8)	157 (1)
F(7)	5061 (8)	-285 (8)	1482 (7)	136 (1)
F(8)	4475 (9)	1081 (9)	2014 (7)	145 (1)
F(9)	4844 (8)	1181 (10)	1041 (8)	183 (1)
F(10)	1103 (6)	2439 (5)	1731 (3)	145 (1)
F(11)	2343 (5)	-2853 (4)	1122 (4)	141 (1)
F(12)	762 (5)	-2516 (4)	734 (3)	123 (1)
F(4A)*	1668 (8)	4856 (8)	910 (9)	173 (1)
F(5A)*	-49 (11)	5304 (10)	699 (9)	239 (1)
F(6A)*	495 (10)	4967 (9)	1605 (7)	184 (1)
F(7A)*	4765 (8)	16 (10)	1998 (7)	174 (1)
F(8A)*	4705 (8)	1498 (8)	1521 (8)	177 (1)
F(9A)*	5042 (8)	225 (10)	952 (8)	195 (1)

* Denotes alternate positions for disordered F atoms.

Discussion. Further evidence of the reluctance of nitroxyl radicals to coordinate using the O atom of the nitroxyl group is provided by this structure. Instead of obtaining the anticipated product consisting of $\text{Ni}(\text{F}_6\text{AcAc})_2$ molecules linked together by the nitroxyl radical ligand in a head-to-tail fashion forming a one-dimensional chain, we find that this structure consists of discrete units in which only the amine group is involved in coordination. A view of the molecule illustrating the atomic numbering scheme is given in Fig. 1; Fig. 2 presents a stereo-view packing diagram.

The overall structure of this complex is that of an Ni^{II} center possessing an octahedral coordination geometry with bonds to two equatorial F_6AcAc ligands, a molecule of methanol and the nitroxyl radical. Ni—O bonds to the O atoms of the F_6AcAc ligands

Table 2. Bond lengths (Å) and angles (°)

Ni—O(1)	2.042 (5)	Ni—O(2)	2.014 (5)
Ni—O(3)	2.027 (5)	Ni—O(4)	2.040 (5)
Ni—O(6)	2.094 (6)	Ni—N(1)	2.075 (6)
O(1)—C(2)	1.238 (9)	O(2)—C(4)	1.255 (9)
O(3)—C(7)	1.261 (9)	O(4)—C(9)	1.263 (9)
O(5)—N(3)	1.291 (11)	O(6)—C(20)	1.436 (12)
O(7)—C(21)	1.652 (16)	N(1)—C(11)	1.518 (10)
N(3)—C(13)	1.450 (12)	N(3)—C(14)	1.480 (11)
C(1)—C(2)	1.526 (11)	C(2)—C(3)	1.382 (10)
C(3)—C(4)	1.395 (11)	C(4)—C(5)	1.576 (12)
C(6)—C(7)	1.554 (12)	C(7)—C(8)	1.366 (11)
C(8)—C(9)	1.385 (10)	C(9)—C(10)	1.528 (11)
C(11)—C(12)	1.490 (11)	C(11)—C(15)	1.505 (11)
C(12)—C(13)	1.519 (12)	C(13)—C(16)	1.513 (13)
C(13)—C(17)	1.519 (13)	C(14)—C(15)	1.543 (12)
C(14)—C(18)	1.543 (13)	C(14)—C(19)	1.529 (14)
O(1)—Ni—O(2)	90.5 (2)	O(1)—Ni—O(3)	172.7 (2)
O(2)—Ni—O(3)	88.8 (2)	O(1)—Ni—O(4)	90.3 (2)
O(2)—Ni—O(4)	176.5 (2)	O(3)—Ni—O(4)	90.0 (2)
O(1)—Ni—O(6)	85.5 (2)	O(2)—Ni—O(6)	88.8 (2)
O(3)—Ni—O(6)	87.2 (2)	O(4)—Ni—O(6)	87.9 (2)
O(1)—Ni—N(1)	92.3 (2)	O(2)—Ni—N(1)	93.6 (2)
O(3)—Ni—N(1)	95.0 (2)	O(4)—Ni—N(1)	89.8 (2)
O(6)—Ni—N(1)	176.8 (2)	Ni—O(1)—C(2)	123.6 (5)
Ni—O(2)—C(4)	122.1 (5)	Ni—O(3)—C(7)	125.2 (5)
Ni—O(4)—C(9)	123.0 (5)	Ni—O(6)—C(20)	124.6 (6)
Ni—N(1)—C(11)	124.0 (5)	O(5)—N(3)—C(13)	117.9 (7)
O(5)—N(3)—C(14)	114.1 (8)	C(13)—N(3)—C(14)	125.5 (7)
O(1)—C(2)—C(1)	113.8 (6)	O(1)—C(2)—C(3)	128.9 (7)
C(1)—C(2)—C(3)	117.3 (7)	C(2)—C(3)—C(4)	121.6 (7)
O(2)—C(4)—C(3)	130.6 (7)	O(2)—C(4)—C(5)	111.4 (7)
C(3)—C(4)—C(5)	118.0 (7)	O(3)—C(7)—C(6)	113.0 (7)
O(3)—C(7)—C(8)	129.0 (7)	C(6)—C(7)—C(8)	118.0 (7)
C(7)—C(8)—C(9)	121.9 (7)	O(4)—C(9)—C(8)	130.6 (7)
O(4)—C(9)—C(10)	113.0 (6)	C(8)—C(9)—C(10)	116.4 (7)
N(1)—C(11)—C(12)	111.0 (6)	N(1)—C(11)—C(15)	111.1 (6)
C(12)—C(11)—C(15)	108.6 (6)	C(11)—C(12)—C(13)	114.2 (7)
N(3)—C(13)—C(12)	110.2 (7)	N(3)—C(13)—C(16)	107.4 (8)
C(12)—C(13)—C(16)	109.5 (7)	N(3)—C(13)—C(17)	108.9 (8)
C(12)—C(13)—C(17)	110.5 (7)	C(16)—C(13)—C(17)	110.3 (7)
N(3)—C(14)—C(15)	109.6 (7)	N(3)—C(14)—C(18)	110.0 (7)
C(15)—C(14)—C(18)	109.7 (7)	N(3)—C(14)—C(19)	109.7 (7)
C(15)—C(14)—C(19)	108.8 (7)	C(18)—C(14)—C(19)	109.1 (8)
C(11)—C(15)—C(14)	114.3 (7)		

show some variation, ranging from 2.014 (5) to 2.042 (5) Å. Bonds to the axial ligands are somewhat longer, measuring 2.094 (6) and 2.075 (6) Å for Ni—O(6) and Ni—N(1), respectively. None of the observed interaxial angles show substantial deviations and nearly all are within 3° of that expected for a complex possessing an octahedral geometry.

Structural features of the F_6AcAc ligands are unexceptional. Two of the four CF_3 groups suffered from some degree of static disorder which could be resolved into two alternate sets of coordinates for the F atoms which were refined with fixed occupancies of 0.50. Although small peaks of residual electron density could be seen in the vicinity of the remaining CF_3 groups, the refined positions were the principal (at least 95%) contributors of electron density within these regions. Considerable variation in the derived C—F bond lengths exists with C—F bond lengths ranging from a minimum of 1.22 (2) Å to a maximum of 1.38 (2) Å. In view of the limited precision of these values, however, these variations cannot be regarded as being of any chemical significance.

The nitroxyl radical in this structure possesses many of the same structural features observed in the TEMPO free radical and others (Shibaeva, 1975).

Important structural parameters for the nitroxyl group include the N—O distance [1.29 (1) Å] and the coplanar arrangement of N—O atoms and the two carbons to which it is attached. These values are well within the range typically observed for free nitroxyl radicals and indicate that the nitroxyl group has retained its radical character. The nitroxyl N atom together with the five C atoms comprising the central region of this molecule form a six-membered ring possessing a chair configuration and we find all the C—C bond angles and lengths to be within the range expected for a C—C bonded framework.

The stoichiometry of this structure and structural features of the nitroxyl group provide strong evidence that the nitroxyl group has retained its radical character. Because the nitroxyl group is not coordinated to the Ni center and is in fact quite far

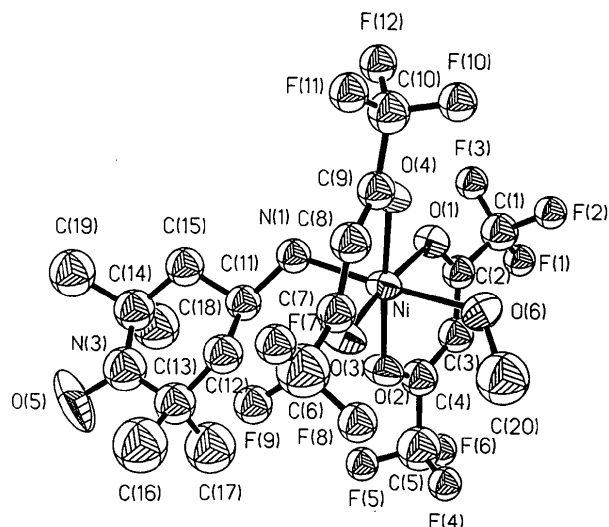


Fig. 1. A perspective view of the complex illustrating the atomic numbering scheme. Thermal ellipsoids have been drawn at the 50% probability level. For clarity, H atoms have been omitted and F atoms have been provided with arbitrary isotropic thermal parameters. Molecule of methanol not shown.

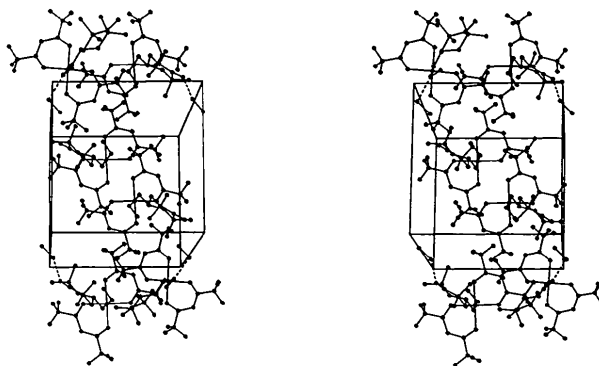


Fig. 2. A stereoview packing diagram projected down the crystallographic c axis.

removed, we expect this complex to be paramagnetic with a value close to the spin-only value of 3.87 Bohr magnetons.

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Structure of Tetrasodium 1,4,5,8-Naphthalenetetracarboxylate Octahydrate

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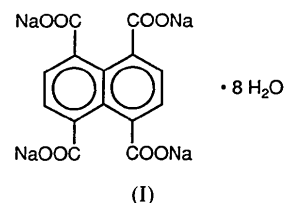
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Abstract. $\text{Na}_4[\text{C}_{14}\text{H}_4\text{O}_8]\cdot 8\text{H}_2\text{O}$, $M_r = 536.3$, monoclinic, $P2_1/n$, $a = 6.142$ (1), $b = 8.144$ (3), $c = 20.527$ (4) Å, $\beta = 93.97$ (1)°, $V = 1024.4$ (5) Å³, $Z = 2$, $D_x = 1.74$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 2.14$ cm⁻¹, $F(000) = 552$, $T = 295$ K, $R = 0.039$ for 1769 unique reflections having $I > \sigma_f$. In this structure, the title compound has an inversion center at the midpoint of the central naphthalene ring bond. The average C—C bond length in the naphthalene core is 1.41 (3) Å; the average interior angle is 119.9 (1.0)°. The exterior angle at the central naphthalene carbon is 122.7 (3)°, significantly smaller than in 1,8-substituted naphthalenes. The two inequivalent carboxyl groups adopt a non-planar arrangement with respect to the naphthalene core, making an average dihedral angle of 53.8 (1)° with it. The two inequivalent sodium ions have quite different environments. Na(1) is coordinated by six O atoms in a highly distorted octahedral arrangement with an average Na—O distance of 2.44 (10) Å. Na(2) is coordinated by five O atoms in a highly distorted trigonal bipyramidal arrangement with an average Na—O distance of 2.36 (3) Å. Each of the eight inequivalent water H atoms is involved in a single hydrogen bond. The average H...O (acceptor) distance is 2.00 (5) Å, the average O...O (acceptor) distance is 2.85 (5) Å and the average O—H...O (acceptor) angle is 165 (8)° for these hydrogen bonds. The average equivalent isotropic displacement parameter for the C and O atoms in the present

structure is less than half the corresponding value for typical organic structures.

Introduction. As part of a series of investigations of hydrogen bonding in organic solids, investigation of the structure of 1,4,5,8-naphthalenetetracarboxylic acid became of interest. We report here an investigation of crystalline tetrasodium 1,4,5,8-naphthalenetetracarboxylate octahydrate (I) whose structure has not previously been described.



Experimental. 1,4,5,8-Naphthalenetetracarboxylic acid obtained from Aldrich Chemical Company was suspended in water and reacted with excess analytical reagent grade NaOH to prepare an aqueous solution of tetrasodium 1,4,5,8-naphthalenetetracarboxylate. The solution was then purified by mixing it with Norit-A decolorizing carbon followed by filtration. The sodium salt thus purified was twice recrystallized from water by slow evaporation at room temperature to provide the experimental sample, a clear rectangular prism with approximate principal dimensions 0.23 × 0.23 × 0.38 mm. This was mounted on a glass rod with epoxy cement and coated with

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