ial F_6acac groups, the latter showing some variation but being well in the range typically observed in *trans* octahedral Ni^{II} complexes containing equatorial F_6acac ligands [Ni—O(1) = 2.041 (3), Ni—O(2) = 2.048 (2) Å] (Porter, Dickman & Doedens, 1988; Cervantes-Lee & Porter, 1991*a*,*b*; Romero, Cervantes-Lee & Porter, 1992). The two F_6acac ligands are essentially coplanar and the Ni atom is displaced by less than 0.20 Å from the least-squares plane defined by the five-atom rings formed by the O—C—C—C—O atoms of these groups. Other structural features of these ligands will not be discussed further, except to note that we found no evidence for significant disorder in the F-atom positions associated with any of the trifluoromethyl groups.

Structural details associated with the triphenylphosphine oxide ligands show many of the structural features typically observed in other transition-metal complexes containing these ligands. The P atoms possess a tetrahedral geometry with interaxial bond angles ranging from 106.7 (1) to 110.8 (2)°. The P—O bond measures 1.486 (3) Å and is longer than the 1.46 Å bond length observed in the crystal structure of free triphenylphosphine oxide (Bandoli, Bortolozzo, Clemente, Croatto & Panattoni, 1970). The triphenylphosphine oxide ligands coordinate in a bent manner with the Ni—O(3)—P(1) atoms defining an angle of 153.9 (1)°. This bond angle is considerably more obtuse than the 140.4 (3)° *M*—O—P angle observed in the structure of *trans* (dinitrato-*O*,*O*′)bis(triphenylphosphine oxide)copper(II), the only other monomeric *trans* triphenylphosphine oxide complex for which structural data are available (Ferrari, Gasparri, Pelizzi & Tarasconi, 1986).

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Structure of μ-Dioxane-bis[(ethanol)bis(hexafluoroacetylacetonato)nickel(II)]

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Abstract. $[Ni_2(C_5HF_6O_2)_4(C_2H_6O)_2(C_4H_8O_2)]$, M_r = 1125.9, triclinic, $P\bar{1}$, a = 9.890 (4), b = 10.942 (4), c = 11.114 (4) Å, α = 100.48 (3), β = 105.45 (3), γ = 108.87 (3)°, V = 1048.5 (7) Å^3, Z = 1, D_x = 1.783 Mg m^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, μ = 1.057 mm^{-1}, $F(000)$ = 560, T = 298 K, R = 0.0747 and wR = 0.0638, for 298 variable parameters (S = 1.40) and 2759 reflections with $F > 0\sigma(F)$. A centrosymmetric complex containing a bridging molecule of dioxane is formed by two $Ni(F_6acac)_2$ complexes, each of which contains a molecule of ethanol coordinating axially [Ni(1)—O(5) = 2.032 (4) Å]. The Ni centers possess an octahedral coordination geometry and each forms bonds to two equatorial F_6acac ligands. The bridging dioxane ligand is located on a crystallographic center of inversion, possesses a chair conformation, and forms bonds to the two Ni atoms that measure 2.136 (4) Å.

Introduction. Examples of transition-metal complexes containing dioxane ligands are rare. In those instances where stable adducts containing a covalently bound dioxane molecule have been prepared, polymeric structures have frequently been obtained

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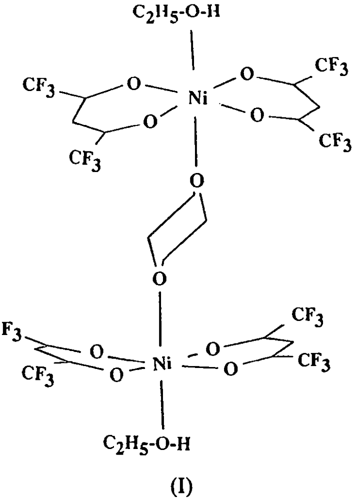
owing to the ability of the dioxane to form bridges between the transition-metal centers. Examples include the reaction of dioxane with the simple halides of both Ni^{II} and Cu^{II}; in both cases an extended network structure consisting of a transition metal alternating with a bridging molecule of dioxane have resulted (Barnes, Sesay & Nicholls, 1977; Barnes & Weakley, 1977). With hydrated transition-metal complexes, different types of network structures are obtained following recrystallization from dioxane. In these systems the dioxane molecules are not coordinated directly to the transition metal, but are instead linked to the coordinated water molecules through a network of hydrogen bonds (Barnes & Weakley, 1976). With Cu^{II} complexes containing (*p*-nitrobenzoyl)trifluoroacetylacetone ligands polymeric structures also result; however, with (*p*-methoxybenzoyl)trifluoroacetylacetone discrete mononuclear bis(dioxane) adducts can be obtained (Evenhuis, Hitchman, McDonald, Goodgame, Kwiatkowski, Dettlaff-Weglikowska, Patkawatchai & White, 1984). Dinuclear complexes containing a bridging molecule of dioxane have been reported on the basis of NMR data following the crystallization of $V(O)(acac)_2$ from a CH_2Cl_2–dioxane solution; however, in a preliminary report of the X-ray crystal structure rather long (2.51 Å) V—O dioxane bond lengths were observed (Dichmann, Hamer, Nyburg & Reynolds, 1970).

In our investigations of the coordination chemistry of bis(F_6acac)Ni^{II}, where F_6acac is the hexafluoro derivative of acetylacetone, we have found that dinuclear Ni^{II} complexes containing a bridging molecule of dioxane can be obtained as condensation products starting from the bis(ethanol) adduct of bis(F_6acac)Ni^{II}. This product (I) constitutes a unique example of a discrete transition-metal complex containing a dioxane ligand; its preparation and its crystal structure are reported herein.



(I)

Experimental. Crystals of the title compound were obtained in good yield by refluxing bis(ethanol)bis(F_6acac)Ni^{II} in toluene containing approximately 5% additional ethanol. Crystallization from hot toluene led to the formation of numerous green crystals. An irregularly shaped crystal of approximate dimensions 0.30 × 0.2 × 0.3 mm was mounted on the end of a glass fiber in a random orientation. Triclinic symmetry was suggested on the basis of interaxial angles and confirmed by a Delaunay reduction. Refined cell parameters were determined from the setting angles of 25 reflections with $15 < 2\theta < 30°$. Data collection was carried out at ambient temperature using a Nicolet *R*3*m* diffractometer utilizing the ω-scan technique in bisecting geometry and graphite-monochromated Mo $K\alpha$ radiation; scan rate variable 3–15° min^{-1}; scan range 1.2° in ω. Three standards ($\bar{3}1\bar{3}$, $\bar{3}0\bar{5}$ and $1\bar{4}0$) measured every 100 data showed no significant variation (< 2%) over the period of data collection. A total of 2954 reflections ($+h$, $\pm k$, $\pm l$; $h_{max} = 10$, $k_{max} = 11$, $l_{max} = 11$) with $3.5 < 2\theta < 45°$ [$(\sin\theta)/\lambda_{max} = 0.538$ Å^{-1}] were obtained and corrected for Lorentz and polarization effects. This led to 2759 unique reflections ($R_{int} = 6.13\%$) that were corrected for absorption effects empirically on the basis of azimuthal scans of six strong reflections spanning a range of 2θ values (minimum and maximum transmission factors 0.669 and 0.796, respectively). Structure solution and refinement was carried out using the *SHELXTL-PC* collection of crystallographic software (Sheldrick, 1990). The Ni-atom position was determined from a sharpened Patterson map; all remaining non-H atoms were located on difference Fourier maps. Ni, O, C 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). Refinement was based on F using weights of the form $w^{-1} = [\sigma^2(F) + 0.0006(F^2)]$. The H atom associated with the OH group of the ethanol ligand was located on a difference Fourier map, but was not refined. All remaining H atoms were included in fixed idealized positions with $U = 0.08$ Å^2. Convergence to conventional R values of $R = 0.0747$ (for all reflections) and $wR = 0.0638$ with a goodness of fit of 1.40 was obtained using 298 variable parameters and 2759 reflections with $F > 0\sigma(F)$. No reflections had intensities beyond the range for valid coincidence correction. For final cycle, maximum shift/σ = 0.000 with minimum and maximum residual electron densities of −0.51 and 0.71 e Å^{-3}.

A view of the structure illustrating the atomic numbering scheme is presented in Fig. 1; in Fig. 2 is shown a stereoview packing diagram of the complex. Atomic positional parameters and equivalent isotropic thermal parameters for all non-H atoms are presented in Table 1.* Pertinent bond distances and angles are given in Table 2.

Discussion. The structure consists of a discrete centrosymmetric dinuclear complex in which two bis(F_6acac)Ni^{II} molecules are linked by a bridging dioxane ligand. Two molecules of ethanol are present and occupy axial positions *trans* to the molecule of dioxane. The complex resides at the cell origin and displays no unusual intermolecular contacts.

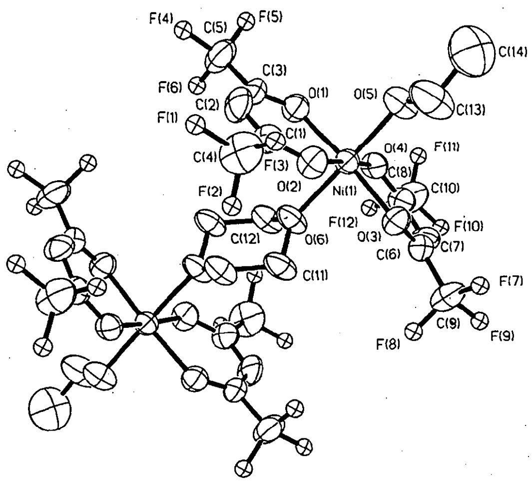


Fig. 1. A perspective view of the structure illustrating the atomic numbering scheme. Thermal ellipsoids have been drawn at the 50% probability level. For clarity, F atoms have been given artificially small isotropic thermal parameters and H atoms have been omitted.

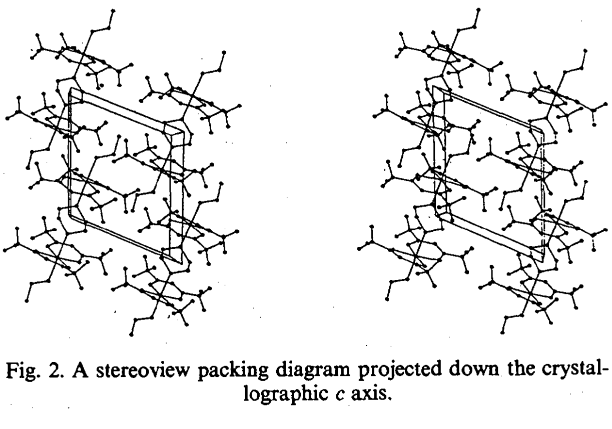


Fig. 2. A stereoview packing diagram projected down the crystallographic *c* axis.

Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic displacement coefficients* ($Å^2 \times 10^3$)

Equivalent isotropic U is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Ni(1)	1285 (1)	3294 (1)	4810 (1)	41 (1)
F(1)	4945 (7)	3458 (9)	9304 (5)	210 (6)
F(2)	4849 (7)	2238 (7)	7588 (6)	171 (4)
F(3)	5949 (6)	4240 (8)	8121 (7)	179 (5)
F(4)	546 (7)	3947 (7)	9382 (4)	153 (4)
F(5)	−746 (6)	4524 (5)	7949 (4)	112 (3)
F(6)	−1258 (8)	2487 (6)	7790 (7)	165 (5)
F(7)	3559 (6)	2804 (6)	1654 (5)	155 (4)
F(8)	2524 (7)	840 (6)	1710 (5)	149 (4)
F(9)	1540 (6)	1459 (5)	163 (4)	118 (3)
F(10)	−2974 (6)	1760 (8)	194 (5)	184 (5)
F(11)	−3092 (6)	3089 (6)	1719 (5)	149 (3)
F(12)	−3605 (6)	1153 (7)	1672 (7)	186 (5)
O(1)	329 (4)	3582 (4)	6176 (3)	52 (2)
O(2)	3182 (4)	3428 (4)	6171 (4)	54 (2)
O(3)	2171 (4)	2846 (4)	3436 (4)	52 (2)
O(4)	−695 (4)	2983 (3)	3445 (3)	48 (2)
O(5)	2123 (5)	5308 (4)	5015 (4)	63 (2)
O(6)	379 (4)	1187 (3)	4632 (4)	58 (2)
C(1)	3297 (7)	3443 (6)	7322 (6)	54 (3)
C(2)	2274 (8)	3541 (6)	7933 (5)	67 (4)
C(3)	900 (7)	3604 (5)	7344 (5)	52 (3)
C(4)	4743 (10)	3334 (10)	8093 (8)	91 (5)
C(5)	−136 (10)	3665 (9)	8132 (7)	78 (5)
C(6)	1378 (7)	2314 (5)	2245 (6)	50 (3)
C(7)	106 (7)	2084 (6)	1621 (5)	61 (3)
C(8)	−1036 (7)	2438 (5)	2242 (5)	52 (3)
C(9)	2286 (10)	1859 (9)	1458 (7)	79 (4)
C(10)	−2660 (10)	2133 (10)	1429 (7)	89 (5)
C(11)	1195 (7)	319 (6)	4490 (6)	60 (3)
C(12)	−1174 (6)	421 (6)	4490 (6)	57 (3)
C(13)	3628 (10)	6058 (8)	5125 (9)	107 (5)
C(14)	4047 (10)	7486 (9)	5249 (9)	129 (6)

Structural features associated with the F_6acac groups are similar to those reported in other octahedral bis(F_6acac)Ni^{II} complexes (Cervantes-Lee & Porter, 1991*a*,*b*). The Ni—O distances range from 2.013 (4) to 2.019 (4) Å and the Ni atom is displaced 0.087 Å from the least-squares plane defined by the four equatorial O atoms. Only minor deviations from ideal octahedral geometry are observed in the interaxial angles associated with these ligands which vary from 88.2 (2) to 91.7 (2)°.

Although not common, the crystal structures of transition-metal complexes containing alcohol ligands have been described. The 2.032 (4) Å Ni(1)—O(5) bond length in this structure is somewhat shorter than the 2.075 (6) Å Ni—O bond length reported in the structure of a mononuclear bis(F_6acac)Ni^{II} complex containing methanol; however, the 123.7 (5)° Ni(1)—O(5)—C(13) bond angle is nearly identical and differs by less than 1° from that reported for the methanol derivative (Cervantes-Lee & Porter, 1991*b*).

Even less common are examples of discrete transition-metal complexes containing dioxane ligands. In the central region of the structure the dioxane ligand forms bonds to the symmetry-related transition-metal centers with Ni—O bonds that measure 2.136 (4) Å. The six-atom heterocyclic framework of the dioxane ligand possesses a chair conformation and displays no unusual features in either the observed bond lengths or angles. Although both boat and chair conformations are possible, to

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* Lists of structure factors, H-atom coordinates, anisotropic thermal parameters, and CF_3 bond angles and distances have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55164 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HH0565]

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

Ni(1)—O(1)	2.019 (5)	Ni(1)—O(2)	2.014 (4)
Ni(1)—O(3)	2.015 (5)	Ni(1)—O(4)	2.013 (4)
Ni(1)—O(5)	2.032 (4)	Ni(1)—O(6)	2.136 (4)
O(1)—C(3)	1.263 (7)	O(2)—C(1)	1.251 (8)
O(3)—C(6)	1.256 (6)	O(4)—C(8)	1.264 (7)
O(5)—C(13)	1.407 (10)	O(6)—C(11)	1.445 (9)
O(6)—C(12)	1.441 (7)	C(1)—C(2)	1.380 (11)
C(1)—C(4)	1.513 (12)	C(2)—C(3)	1.372 (10)
C(3)—C(5)	1.523 (12)	C(6)—C(7)	1.361 (9)
C(6)—C(9)	1.539 (13)	C(7)—C(8)	1.394 (11)
C(8)—C(10)	1.510 (11)	C(11)—C(12*A*)	1.509 (10)
C(12)—C(11*A*)	1.509 (10)	C(13)—C(14)	1.451 (13)
O(1)—Ni(1)—O(2)	91.2 (2)	O(1)—Ni(1)—O(3)	175.4 (2)
O(2)—Ni(1)—O(3)	88.5 (2)	O(1)—Ni(1)—O(4)	88.2 (2)
O(2)—Ni(1)—O(4)	174.8 (2)	O(3)—Ni(1)—O(4)	91.7 (2)
O(1)—Ni(1)—O(5)	90.7 (2)	O(2)—Ni(1)—O(5)	93.0 (2)
O(3)—Ni(1)—O(5)	93.9 (2)	O(4)—Ni(1)—O(5)	92.2 (2)
O(1)—Ni(1)—O(6)	87.8 (2)	O(2)—Ni(1)—O(6)	87.0 (2)
O(3)—Ni(1)—O(6)	87.6 (2)	O(4)—Ni(1)—O(6)	87.8 (1)
O(5)—Ni(1)—O(6)	178.5 (2)	Ni(1)—O(1)—C(3)	123.6 (5)
Ni(1)—O(2)—C(1)	124.1 (4)	Ni(1)—O(3)—C(6)	122.8 (4)
Ni(1)—O(4)—C(8)	123.3 (4)	Ni(1)—O(5)—C(13)	123.7 (5)
Ni(1)—O(6)—C(11)	124.1 (3)	Ni(1)—O(6)—C(12)	124.4 (4)
C(11)—O(6)—C(12)	111.2 (4)	O(2)—C(1)—C(2)	127.6 (6)
O(2)—C(1)—C(4)	113.9 (7)	C(2)—C(1)—C(4)	118.5 (6)
C(1)—C(2)—C(3)	124.8 (6)	O(1)—C(3)—C(2)	127.8 (7)
O(1)—C(3)—C(5)	113.2 (6)	C(2)—C(3)—C(6)	119.0 (6)
O(3)—C(6)—C(7)	129.2 (7)	O(3)—C(6)—C(9)	111.4 (6)
C(7)—C(6)—C(9)	119.4 (5)	C(6)—C(7)—C(8)	124.0 (5)
O(4)—C(8)—C(7)	127.7 (5)	O(4)—C(8)—C(10)	113.8 (6)
C(7)—C(8)—C(10)	118.5 (6)	O(6)—C(11)—C(12*A*)	108.9 (6)
O(6)—C(12)—C(11*A*)	109.8 (5)	O(5)—C(13)—C(14)	117.1 (9)

date, only chair conformations have been observed in complexes containing dioxane.

Unlike other systems containing dioxane ligands, the molecule of dioxane in the structure described here resulted from the condensation of two molecules of ethanol. We do not know if this represents a general class of reactions that can be carried out using bis(acac) adducts of the divalent transition metals, or if it is unique to the system described. As far as we know, it constitutes the first example of this type of reaction and additional experiments are underway in order to address this question as well as others that the isolation of this product raises.

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Structures of *racemic* and *meso* (5,7,7,12,14,14-Hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene)nickel(II) Perchlorate

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Abstract. The crystal structures of *racemic* and *meso* (5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene)nickel(II) perchlorate, [Ni($C_{16}H_{32}N_4$)]$(ClO_4)_2$, $M_r = 538.06$, are reported at 295 K with Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å). The *d* and *l* isomers cocrystallize to form the racemic structure in the orthorhombic space group *Pbca* with $a =$ 19.759 (3), $b = 17.016$ (3), $c = 13.661$ (3) Å, $V =$ 4593 (2) Å^3, $Z = 8$, $D_x = 1.556$ g cm^{-3}, $\mu =$ 11.2 cm^{-1}, $F(000) = 2256$ and refined to $R = 0.051$ for 2245 reflections with $F_o > 3\sigma(F_o)$. The *meso* isomer crystallized in the monoclinic space group $P2_1/c$ with $a = 10.257$ (3), $b = 10.742$ (2), $c =$ 10.885 (2) Å, $\beta = 111.46$ (2)°, $V = 1116.2$ (9) Å^3, $Z =$ 2, $D_x = 1.601$ g cm^{-3}, $\mu = 11.6$ cm^{-1}, $F(000) = 564$ and refined to $R = 0.042$ for 2155 reflections with F_o $> 3\sigma(F_o)$. The values of the Ni—N$_{\rm amine}$ and Ni—

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