

Refinement

Refinement on F	$(\Delta/\sigma)_{\max} = 0.06$
Final $R = 0.034$	$\Delta\rho_{\max} = 0.35 \text{ e } \text{Å}^{-3}$
$wR = 0.045$	$\Delta\rho_{\min} = -0.68 \text{ e } \text{Å}^{-3}$
$S = 0.9$	Extinction correction: $F_c^* =$
525 reflections	$F_c(1-xF_c^2/\sin\theta)$
83 parameters	Extinction coefficient: $x =$
All H-atom parameters re-	3.1×10^{-4}
finéd	Atomic scattering factors
$w = 1/(\sigma_F^2 + 0.0045F^2)$	from <i>SHELX76</i>

Table 1. Fractional atomic coordinates and isotropic or equivalent isotropic thermal parameters (Å^2)

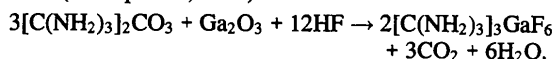
Ga(1) and Ga(2) each have site symmetry $\bar{3}$ and site-occupancy factor $\frac{1}{2}$; the respective values for all the other atoms are 1 and 1. H atoms were treated isotropically; for the other atoms $U_{\text{eq}} = (U_{11} \times U_{22} \times U_{33})^{1/3}$.

	x	y	z	$U_{\text{iso}}/U_{\text{eq}}$
Ga(1)	0	0.5000	0	0.146 (3)
Ga(2)	0	0.5000	0.5000	0.150 (4)
F(1)	0.0269 (1)	0.6302 (1)	0.0237 (1)	0.266 (5)
F(2)	0.0205 (1)	0.6309 (1)	0.4737 (1)	0.279 (5)
C	-0.2337 (2)	0.7514 (1)	0.5261 (3)	0.284 (10)
N(1)	-0.1410 (2)	0.7518 (2)	0.5235 (1)	0.410 (10)
N(2)	-0.2802 (2)	0.8312 (2)	0.5398 (2)	0.426 (10)
N(3)	-0.2794 (2)	0.6699 (2)	0.5166 (2)	0.417 (10)
H(1)	-0.106 (3)	0.803 (2)	0.528 (2)	0.487 (9)
H(2)	-0.104 (3)	0.704 (3)	0.515 (2)	0.541 (10)
H(3)	-0.333 (3)	0.827 (2)	0.537 (2)	0.310 (8)
H(4)	-0.251 (2)	0.880 (2)	0.543 (3)	0.398 (10)
H(5)	-0.333 (3)	0.672 (3)	0.513 (2)	0.497 (11)
H(6)	-0.246 (2)	0.630 (3)	0.503 (2)	0.426 (13)

Table 2. Geometric parameters (Å , $^\circ$)

C—N(1)	1.305 (4)	N(3)—H(6)	0.75 (4)
C—N(2)	1.314 (3)	Ga(1)—F(1)	1.901 (1)
C—N(3)	1.322 (4)	Ga(2)—F(2)	1.901 (1)
N(1)—H(1)	0.87 (4)		
N(1)—H(2)	0.85 (4)	F(1)···F(1)	2.704 (2)
N(2)—H(3)	0.74 (4)	F(1)···F(1)	2.671 (2)
N(2)—H(4)	0.80 (3)	F(2)···F(2)	2.704 (2)
N(3)—H(5)	0.75 (5)	F(2)···F(2)	2.672 (2)
N(1)—C—N(2)	119.9 (2)	H(3)—N(2)—H(4)	126 (3)
N(1)—C—N(3)	119.2 (2)	C—N(3)—H(5)	118 (3)
N(2)—C—N(3)	120.9 (3)	C—N(3)—H(6)	111 (3)
C—N(1)—H(1)	124 (2)	H(5)—N(3)—H(6)	129 (2)
C—N(1)—H(2)	127 (3)	F(1)—Ga(1)—F(1)	90.7 (3)
H(1)—N(1)—H(2)	108 (4)	F(1)—Ga(1)—F(1)	180.0 (3)
C—N(2)—H(3)	115 (2)	F(2)—Ga(2)—F(2)	90.7 (3)
C—N(2)—H(4)	119 (2)	F(2)—Ga(2)—F(2)	180.0 (3)

Guanidinium hexafluorogallate was obtained by the following reaction (Szczepeński, 1990):



The substrates were treated with an excess of hydrofluoric acid (40% aqueous solution) and heated to complete dissolution. Density was measured by flotation in CCl_4 and CH_3I . The background and integrated intensities were obtained by the peak-profile-analysis method of Lehman & Larsen (1974) using *PRARA* (Jaskólski, 1982). Corrections for Lorentz and polarization effects were applied. No absorption correction was made. The H-atom positions were calculated and refined isotropically. Programs used: *SHELX76* (Sheldrick, 1976); *PLUTO* (Motherwell & Clegg, 1978); *PARST* (Nardelli, 1983); *CRYSRULER* (Rizzoli, Sangermano, Calestani & Andreotti, 1986).

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Lists of structure factors, anisotropic thermal parameters and hydrogen-bond geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71010 (5 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: KA1015]

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Structure of Dipotassium *trans*-Diaquabis(oxalato-*O,O'*)nickelate(II)–Water (1/4)

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Abstract

The crystal structure of the title compound was studied by single-crystal X-ray diffraction in order to determine the coordination geometry around the Ni^{II} atom in the anionic complex. The crystal structure comprises centrosymmetric $[\text{Ni}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]^{2-}$

complex anions, K^+ cations and free water molecules linked together through electrostatic interactions, $K-O$ coordination, and an extensive network of hydrogen bonds of types $O_w-H\cdots O$ and $O_w-H\cdots O_w$. The complex anion exhibits octahedral coordination around the Ni atom, with four O atoms belonging to two bidentate oxalate ligands in the equatorial sites and two water molecules occupying the axial positions, in contrast to the Pd and Pt oxalato complexes which, although crystallizing in the same space group, show a square-planar coordination without coordinated water molecules.

Comment

The coordination chemistry of metal complexes with dicarboxylate ligands has been studied for many years because of the analytical, catalytic and biomedical applications of the ligands (Oldham, 1987). One of these ligands is the oxalate dianion whose versatility upon coordination is well known. Crystal structures have been reported in which the oxalate acts as a unidentate, chelating or a bridging ligand. On the other hand, although in the literature there are some works concerning the thermal behaviour of the $K_2[Ni(C_2O_4)_2(H_2O)_x] \cdot (6-x)H_2O$ compound (Broadbent, Dollimore & Dollimore, 1969; Diefallah, Basahl, El-Fass & Al-Sabban, 1991), there are discrepancies about the number of free and coordinated water molecules. The crystal structure study of the title compound was undertaken in order to determine the true coordination geometry around the Ni^{II} atom.

A view of the complex dianion with the atomic numbering scheme is shown in Fig. 1. The asymmetric unit consists of one half of a complex anion, $[Ni(C_2O_4)_2(H_2O)_2]^{2-}$, with the Ni atom lying on a centre of symmetry, one K^+ cation and two free water molecules. The coordination polyhedron of the Ni atom is an octahedron with an equatorial plane formed by four O atoms from two bidentate oxalate ligands and with water molecules in the axial sites. It is interesting to compare this octahedral coordination with that found for the Pd (Krogmann, 1966) and Pt (Mattes & Krogmann, 1964) oxalato complexes which crystallize in the same space group,

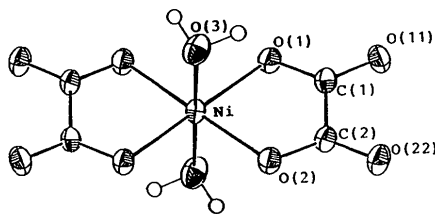


Fig. 1. View of the *trans*-diaquabis(oxalato-*O,O'*)nickelate(II) anion showing the atom-labelling scheme.

$P2_1/n$, but show a very different crystal packing since all water molecules are free and the metal(II) atom is only coordinated to four O atoms belonging to two oxalate ligands in a square-planar configuration.

The equatorial chelate ring is nearly planar, with the O(2) and O(22) atoms displaced from the least-squares plane passing through the rest of the atoms by 0.028 (2) and -0.030 (2) Å, respectively. The Ni—O(3) axial bonds are almost perpendicular [$87.77(8)^\circ$] to the plane of the oxalate ligand. The Ni—O(3) axial bonds [2.086 (2) Å] are longer than the equatorial bonds [2.050 (2) and 2.016 (2) Å]. This axial elongation is similar to that found in other crystals containing the same type of octahedral *trans*-diaquabis(oxalato-*O,O'*)metallate complex anion (Grey, Madsen, Sirat & Smith, 1985; van Nierkerk & Schoening, 1951).

The K atom is surrounded by eight O atoms, two from free water molecules, one from the Ni-coordinated water molecule and five from oxalate groups, at distances ranging from 2.779 (3) to 3.017 (2) Å, and located at the vertices of a strongly distorted square antiprism.

The crystal packing is stabilized by the electrostatic interactions, the $K-O$ coordination described above, and an extensive network of hydrogen-bond contacts involving the water molecules and all of the O atoms from the oxalate ligands. A stereoview of the contents of the unit cell showing these contacts is presented in Fig. 2.

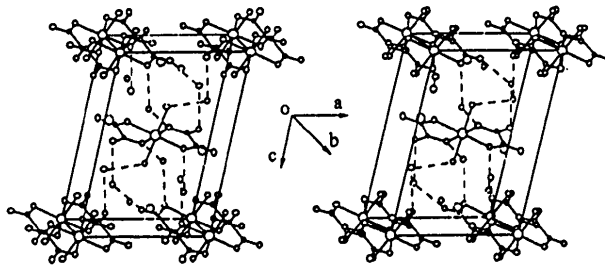


Fig. 2. Stereo packing diagram for $K_2[Ni(C_2O_4)_2(H_2O)_2] \cdot 4H_2O$ (hydrogen bonds are represented by dotted lines).

Experimental

Crystal data

$K_2[Ni(C_2O_4)_2(H_2O)_2] \cdot 4H_2O$

$M_r = 421.028$

Monoclinic

$P2_1/n$

$a = 8.647(6) \text{ \AA}$

$b = 6.627(2) \text{ \AA}$

$c = 12.118(3) \text{ \AA}$

$\beta = 101.58(1)^\circ$

$D_m = 2.04(1) \text{ Mg m}^{-3}$

Density measured by flotation in $CHBr_3/CCl_4$

Mo $K\alpha$ radiation

$\lambda = 0.71069 \text{ \AA}$

Cell parameters from 25 reflections

$\theta = 4-14^\circ$

$\mu = 2.112 \text{ mm}^{-1}$

$V = 680.3 (5) \text{ \AA}^3$
 $Z = 2$
 $D_x = 2.05 \text{ Mg m}^{-3}$

$T = 296 (2) \text{ K}$
 Prism
 $0.35 \times 0.35 \times 0.20 \text{ mm}$
 Green

K $-0.4396 (1)$ $0.6568 (1)$ $-0.1171 (1)$ $0.0385 (2)$
 O(4) $0.6636 (2)$ $0.0102 (3)$ $0.1842 (1)$ $0.0383 (5)$
 O(5) $0.3159 (2)$ $0.0118 (3)$ $0.3090 (1)$ $0.0439 (5)$

† Parameter fixed.

Data collection

CAD-4 diffractometer $R_{\text{int}} = 0.0208$
 $\omega/2\theta$ scans $\theta_{\text{max}} = 35^\circ$
 Absorption correction: $h = 0 \rightarrow 13$
 empirical $k = 0 \rightarrow 10$
 $T_{\text{min}} = 0.818$, $T_{\text{max}} = 1.103$ $l = -19 \rightarrow 19$
 6256 measured reflections 2 standard reflections
 3011 independent reflections frequency: 120 min
 1846 observed reflections intensity variation: <2%
 $[I > 3\sigma(I)]$

Refinement

Refinement on F^2 $\Delta\rho_{\text{max}} = 0.60 \text{ e \AA}^{-3}$
 Final $R = 0.027$ $\Delta\rho_{\text{min}} = -0.68 \text{ e \AA}^{-3}$
 $wR = 0.030$ Atomic scattering factors
 $S = 0.69$ from *International Tables*
 1846 reflections for *X-ray Crystallography*
 121 parameters (1974, Vol. IV)
 $(\Delta/\sigma)_{\text{max}} = 0.43$

Intensity data were corrected for Lorentz and polarization effects. The structure was solved by Patterson methods and subsequent Fourier syntheses maps. An empirical absorption correction following the *DIFABS* procedure (Walker & Stuart, 1983) was applied to data refined with isotropic displacement parameters. A weighting scheme of type $w = w_1 \cdot w_2$ with $w_1 = k_1/(a + b|F_o| + c|F_o|^2)$ and $w_2 = k_2/(d + e \sin\theta/\lambda + f \sin^2\theta/\lambda)$ was used to obtain flat dependence in $\langle w\Delta^2 F \rangle$ versus $\langle F_o \rangle$ and versus $\langle \sin\theta/\lambda \rangle$ (PESOS; Martínez-Ripoll & Cano, 1975); the coefficients used are: $k_1 = 0.543$; $k_2 = 1.043$; $a = 0.603$, $b = 0.145$, $c = 0.000$ for $|F_o| \leq 3.07$; $a = 2.287$, $b = -0.476$, $c = 0.029$ for $3.07 < |F_o| \leq 9.90$; $a = 0.235$, $b = 0.015$, $c = 0.000$ for $9.90 < |F_o| \leq 25.81$; $a = 0.183$, $b = 0.020$, $c = 0.000$ for $|F_o| > 25.81$; $d = 25.410$, $e = -117.502$, $f = 138.898$ for $\sin\theta/\lambda \leq 0.45$; $d = 0.508$, $e = 0.024$, $f = 0.000$ for $0.45 < \sin\theta/\lambda \leq 0.65$; $d = -1.255$, $e = 3.034$, $f = 0.000$ for $\sin\theta/\lambda > 0.65$. Non-H atoms were refined anisotropically. The H atoms were localized from a difference Fourier syntheses and were refined isotropically. Most calculations were carried out using the *XRAY76* system (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) running on a MicroVAX 3800 computer. Geometrical calculations were made with *PARST* (Nardelli, 1983).

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (\AA^2)

$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U_{eq}
Ni	0.0 †	0.0 †	0.0 †	0.0217 (1)
O(1)	-0.2357 (2)	0.0241 (2)	-0.0700 (1)	0.0272 (4)
O(2)	-0.0440 (2)	0.2647 (2)	0.0697 (1)	0.0293 (4)
O(3)	-0.0609 (2)	-0.1448 (3)	0.1381 (1)	0.0378 (5)
C(1)	-0.2967 (2)	0.1834 (3)	-0.0404 (1)	0.0239 (5)
C(2)	-0.1855 (2)	0.3217 (3)	0.0430 (1)	0.0245 (5)
O(11)	-0.4359 (2)	0.2360 (3)	-0.0706 (1)	0.0333 (4)
O(22)	-0.2415 (2)	0.4748 (2)	0.0783 (1)	0.0335 (4)

Table 2. Selected bond lengths (\AA), bond angles ($^\circ$) and hydrogen-bond geometry (\AA , $^\circ$)

Ni—O(1)	2.050 (2)	O(2)—C(2)	1.260 (2)			
Ni—O(2)	2.016 (2)	C(1)—C(2)	1.547 (2)			
Ni—O(3)	2.086 (2)	C(1)—O(11)	1.236 (2)			
O(1)—C(1)	1.264 (2)	C(2)—O(22)	1.237 (2)			
O(1)—Ni—O(2)	81.39 (7)	O(2)—C(2)—C(1)	115.8 (2)			
O(2)—Ni—O(3)	88.00 (7)	O(1)—C(1)—O(11)	126.1 (2)			
O(1)—Ni—O(3)	88.72 (8)	O(2)—C(2)—O(22)	125.7 (2)			
Ni—O(1)—C(1)	112.6 (1)	C(2)—C(1)—O(11)	117.8 (2)			
Ni—O(2)—C(2)	114.1 (1)	C(1)—C(2)—O(22)	118.5 (2)			
O(1)—C(1)—C(2)	116.1 (2)					
K—O(1 ⁱ)	2.992 (2)	K—O(11 ^{iv})	2.796 (2)			
K—O(3 ⁱⁱ)	2.943 (2)	K—O(22 ^{iv})	3.017 (2)			
K—O(4 ⁱⁱⁱ)	2.942 (2)	K—O(11)	2.844 (2)			
K—O(5 ⁱⁱ)	2.779 (3)	K—O(22)	2.892 (2)			
D	H	A	D—H	H...A	D...A	D—H...A
O(3)	H(31)	O(4 ^v)	0.94 (4)	1.83 (4)	2.753 (3)	166 (4)
O(3)	H(32)	O(22 ^{vii})	0.89 (6)	2.20 (6)	2.977 (3)	146 (5)
O(4)	H(41)	O(11 ^{vi})	0.85 (4)	1.86 (4)	2.710 (3)	178 (5)
O(4)	H(42)	O(22 ^{viii})	0.83 (4)	2.01 (4)	2.830 (2)	177 (4)
O(5)	H(51)	O(2 ^{viii})	0.87 (4)	1.89 (4)	2.751 (4)	170 (4)
O(5)	H(52)	O(1 ^{vi})	0.85 (4)	2.00 (4)	2.850 (2)	172 (4)

Symmetry code: (i) $x, 1 + y, z$; (ii) $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$; (iii) $-x, 1 - y, -z$; (iv) $-1 - x, 1 - y, -z$; (v) $x - 1, y, z$; (vi) $-x, -y, -z$; (vii) $x, y - 1, z$; (viii) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$.

The title compound was obtained by slow addition of an aqueous solution of nickel(II) chloride hexahydrate (20 ml, 0.21 M) to an aqueous potassium oxalate monohydrate solution (50 ml, 0.34 M). Single crystals were grown by slow evaporation of the resulting green solution (pH = 7.5) at room temperature.

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71054 (21 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB1046]

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A Highly Solvated Zinc(II) Tetrakis-(pentafluorophenyl)- β -octabromoporphyrin

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Abstract

The title compound, {4,5,9,10,14,15,19,20-octabromo-2,7,12,17-tetrakis(pentafluorophenyl)-21,22,23,24-tetraazapentacyclo[16.2.1.1^{3,6}.1^{8,11}.1^{13,16}]tetracos-1,3(21),4,6,8(22),9,11,13(23),14,16,18(24),19-dodecene}zinc(II) (carbon tetrachloride, *o*-dichlorobenzene, acetone, methanol, water solvate) has a large tetrahedral distortion, with the Br atoms as much as 1.83 Å from the plane of the N atoms. The distortion affects primarily bond angles and bond torsion angles; bond distances in the molecule are normal. Several different solvents are incorporated into the crystal, providing a close (2.16 Å) O atom as an axial neighbor to Zn and a more distant (3.16 Å) Cl atom, in the opposite axial site.

† Contribution No. 8622.

Comment

The Zn complex was synthesized by published procedures (Lyons & Ellis, 1991) and attempts were made to grow crystals by evaporation and/or solvent diffusion from acetone, methanol, dichloromethane and mixtures of these. Solid materials formed, but no good crystals were found, and the solids were dissolved in new solvent without purification. A satisfactory crystal was finally obtained by evaporation over several weeks at 277 K from a solution in *o*-dichlorobenzene and carbon tetrachloride.

The material crystallizes with the porphyrin plane perpendicular to a crystallographic mirror plane that includes N1, Zn and N3. Fig. 1 is a drawing of the molecule showing the numbering system. The Zn atom is displaced from the plane of the four N atoms (which are planar to ± 0.08 Å) by 0.19 Å toward the O atom of an acetone/methanol solvent position. The porphyrin is ruffled in a tetrahedral distortion: the *meso*-C atoms are close to the 4N plane (± 0.02 Å) but the pyrrole C atoms deviate by ± 0.89 Å on average (maximum 0.97 Å) and the Br atoms by ± 1.67 Å (maximum 1.83 Å). The causes of this distortion are severe steric interactions between the Br atoms and the pentafluorophenyl groups. The shortest of these Br...C distances (average 3.13, closest 3.09 Å) are to the apical C atoms; distances to the *ortho*-C atoms of the phenyl groups are also short, averaging 3.37 Å (van der Waals distance is 3.60 Å). The angles C2—C1—Br1, C4—C5—Br2, C7—C6—Br3 and C9—C10—Br4 are also increased

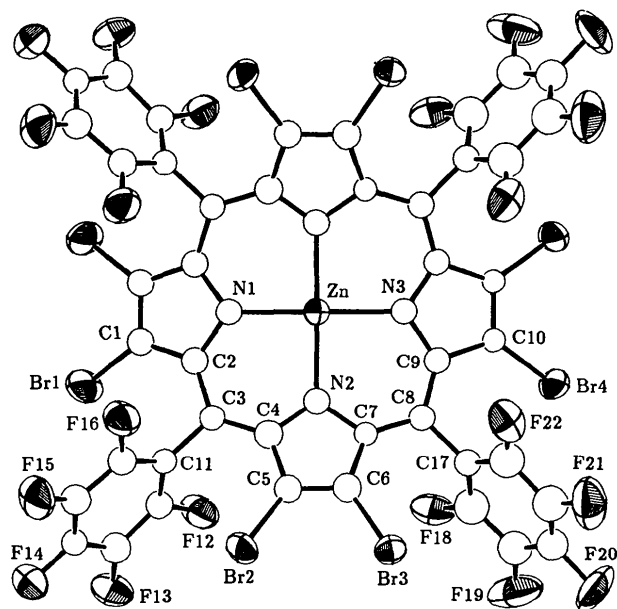


Fig. 1. An ORTEP drawing of the porphyrin molecule with 50% probability ellipsoids showing the numbering system. Unlabelled C atoms on the numbered half of the molecule have the same number as the attached F atom.