

obtain information about the magnitude of the exchange coupling between the copper(II) ions the magnetic susceptibilities have been recorded in the temperature range 300–6.7 K. A least-squares fit on the Bleaney–Bowers equation (Bleaney & Bowers, 1952) based on the exchange Hamiltonian $\hat{H} = -2J[\hat{S}_1 \cdot \hat{S}_2]$ in which J = exchange coupling constant and \hat{S} = spin operator, yielded $g = 2.02$, $J = -96.5 \text{ cm}^{-1}$ and p (percentage paramagnetic impurities) = 1.95. These parameters are in the same range as has been found for [Cu(C₄H₁₀N₆)Br(H₂O)]₂·Br₂·2H₂O·CH₃OH (Koomen–van Oudenniel, de Graaff, Haasnoot, Prins & Reedijk, 1989). Apparently, the slightly longer Cu–Cu' distance as well as the differences in the axial coordination sphere do not have much influence on the magnitude of the antiferromagnetic interaction between nearest-neighbour copper(II) ions.

The authors would like to thank the Werkgroep Fundamenteel Materialen Onderzoek (WFMO) for

financial support. Mr S. Gorter is thanked for assistance with the data collection.

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Acta Cryst. (1992). **C48**, 1926–1929

Structure of the Hydrogen-Bond-Rich Dinickel(II) Complex of *N,N',N'',N'''*-Tetrakis(2-aminoethyl)-1,1,2,2-ethanetetraamide

BY ZHU SHOURONG, LUO QINHUI* AND SHEN MENGCHANG

Coordination Chemistry Institute, Nanjing University, Nanjing, People's Republic of China

AND HUANG LIANGREN

Fuzhou Research Laboratory of Structural Chemistry, Fuzhou, People's Republic of China

(Received 9 May 1991; accepted 9 March 1992)

Abstract. μ -[*N,N',N'',N'''*-Tetrakis(2-aminoethyl)-1,1,2,2-ethanetetraamido-*N,N':N'',N'''*]-dinickel(II) hexahydrate, [Ni₂(C₁₄H₂₆N₈O₄)₂·6H₂O], $M_r = 595.93$, monoclinic, $P2_1/c$, $a = 7.363$ (3), $b = 8.886$ (2), $c = 18.321$ (4) Å, $\beta = 96.18$ (2)°, $V = 1191.6$ Å³, $Z = 2$, $D_m = 1.65$, $D_x = 1.66 \text{ g cm}^{-3}$, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, graphite monochromator, $\mu = 16.5 \text{ cm}^{-1}$, $F(000) = 628$, $T = 296 \text{ K}$, $R = 0.037$ and $wR = 0.037$ for 2362 unique reflections with $I > 3\sigma(I)$. The structure is composed of two symmetry-related chelating groups linked through a C–C bond. Each Ni^{II} is coordinated by four N atoms (two amino and two amido) and exhibits square-planar geometry. All atoms capable of forming hydrogen bonds do so, resulting in 20 hydrogen bonds in the complex.

Introduction. *N,N',N'',N'''*-Tetrakis(2-aminoethyl)-1,1,2,2-ethanetetraamide is a tetradentate double-chelating ligand in which each cavity consists of four N atoms of two aminoethyl-substituted amide groups, and is similar in structure to the double-ring dioxotetraamine ligand (Buttafava, Fabbri, Perotti, Poggi & Seghi, 1984). It is difficult to obtain single crystals of complexes with either of the above ligands owing to the effect of the amide groups. Until now, the crystal structure of the single-ring platinum(II) complex of dioxotetraamine has been the only one reported with this ligand (Kimura, Korenari, Shonoya & Shiro, 1988) and a complex of the double-chelating ligand has been studied only in solution (Hay, Bembi & McLaren, 1981). Some interest has been shown in the physiological functions of dioxotetraamine complexes (Kimura,

* Author to whom correspondence should be addressed.

Yatsunami, Watanabe, Machida, Koike, Fujioka, Kuramoto, Sumomogi, Kunimitsu & Yamashita, 1983), but their structures are still unknown. We have synthesized the title complex and studied its structure.

Experimental. The title ligand was synthesized by dissolving tetraethyl 1,1,2,2-ethanetetra-carboxylate in a large excess of ethylenediamine at 273 K. The ligand (1 g, 2.7 mmol) was dissolved in approximately 5–10 ml H₂O, then NiSO₄·6H₂O (1.4 g, 5.3 mmol) and NaOH (0.42 g, 10.5 mmol) were added; golden yellow tetragonal crystals of [Ni₂(C₁₄H₂₆N₈O₄)]·6H₂O settled during storage. The density of the crystal was measured by pycnometry with benzene.

A crystal of dimensions 0.2 × 0.3 × 0.4 mm was mounted on a Rigaku four-circle diffractometer. Unit-cell parameters were determined from the positions of 20 carefully centred reflections in the range 19 < 2θ < 24°. Data were collected using ω–2θ scan made with ω-scan width (0.95 + 0.35tanθ)°, a scan speed of 16° min⁻¹ (in ω), and with graphite-monochromated Mo Kα radiation over a range of 3 < 2θ < 58° (0 < h < 10, 0 < k < 12, -24 < l < 24). 3582 unique (3605 total) reflections were measured, of which 2362 reflections with I > 3σ(I) were used for refinement. Three check reflections were monitored for crystal orientation and stability. The total gain in intensity was 2.8%. An anisotropic decay correction was applied. The correction factor on I ranged from 0.924 to 1.109 with an average value of 1.018. Corrections for Lp factors and an empirical absorption correction based on ψ scans of several reflections were applied to the data; transmission factors ranged from 0.563 to 0.996.

The structure was solved by direct methods whereby the Ni and four N atoms were located on an E map; remaining atoms were located on subsequent difference maps. H-atom positions were refined but their isotropic thermal parameters were held fixed. When the isotropic thermal parameters of all the non-H atoms refined to R = 0.072, an empirical absorption correction using the DIFABS program (Walker & Stuart, 1983) was applied to all the data; the correction coefficients ranged from 0.905 to 1.057 with an average value of 0.995. The structure was refined by full-matrix least squares where the function minimized was Σw(|F_o - |F_c||²) and the weight w was defined as [σ²(F_o²) + (0.010F_o)² + 1.0]⁻¹. The final cycle of refinement included 211 variable parameters and converged (maximum Δ/σ = 0.26) with unweighted and weighted agreement factors of R = 0.037 and wR = 0.037; S = 1.00. The highest peak in the final difference Fourier map had a height of 0.43 e Å⁻³; the maximum negative peak had a height of -0.41 e Å⁻³. All calculations were per-

Table 1. Positional parameters and equivalent isotropic temperature factors (Å²) for [Ni₂(C₁₄H₂₆N₈O₄)]·6H₂O

$$B_{eq} = (4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)].$$

	x	y	z	B _{eq}
Ni	0.33129 (5)	0.41649 (4)	0.11954 (2)	1.439 (6)
N(1)	0.3610 (4)	0.4868 (3)	0.2187 (1)	1.97 (5)
N(2)	0.2577 (4)	0.6136 (3)	0.0974 (1)	1.63 (5)
N(3)	0.4097 (4)	0.2137 (3)	0.1394 (1)	2.24 (5)
N(4)	0.3148 (3)	0.3544 (3)	0.0217 (1)	1.61 (4)
C(1)	0.4247 (5)	0.6453 (4)	0.2159 (2)	2.14 (6)
C(2)	0.3005 (5)	0.7232 (4)	0.1562 (2)	2.02 (6)
C(3)	0.5225 (5)	0.1741 (4)	0.0797 (2)	2.88 (7)
C(4)	0.4125 (4)	0.2158 (4)	0.0081 (2)	2.04 (6)
C(5)	0.1591 (4)	0.6596 (3)	0.0377 (2)	1.53 (5)
C(6)	0.0832 (4)	0.5391 (3)	-0.0161 (1)	1.36 (5)
C(7)	0.2167 (4)	0.4173 (3)	-0.0341 (1)	1.46 (5)
O(5)	0.1151 (3)	0.7958 (2)	0.0240 (1)	2.13 (4)
O(7)	0.2149 (3)	0.3763 (2)	-0.1005 (1)	2.09 (4)
OW(1)	0.6946 (4)	0.3921 (3)	0.3219 (1)	3.06 (5)
OW(2)	0.5482 (4)	0.4460 (3)	0.5979 (1)	2.70 (5)
OW(3)	0.5452 (3)	0.0152 (3)	0.2667 (1)	3.13 (5)

formed on a VAX computer using SDP/VAX software (Frenz, 1978). Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (Cromer & Waber, 1974). Table 1 lists the atomic coordinates and equivalent isotropic temperature factors for non-H atoms.*

Discussion. The complex is centrosymmetric, as shown in Fig. 1, with each Ni atom situated at the centre of a planar square consisting of four N atoms. The distance of the Ni atom from the least-squares plane through the four N atoms is 0.0341 (4) Å. Both cavities of the ligand are symmetrically distributed about the centre of symmetry located at the middle of the C(6)—C(6) bond which links the two moieties. Ni—N distances range from 1.867 (2) to 1.915 (3) Å (Table 2), somewhat shorter than the normal value of 1.956 Å (McAuley, Subramanian & Whitcombe, 1987), indicating comparatively strong coordination. The lack of a proton on each of the amido N atoms compared with the amino N atoms results in an increased electron donating ability of the amido N atoms, which is manifested in the shorter Ni—N distances. In a comparable complex, Kimura, Koike, Machida, Nagai & Kodama (1984) have observed similar Ni—N(amido) distances.

The C(6)—C(6) bond linking the two identical parts, has a distance of 1.58 Å and is slightly longer than a normal C—C single bond (1.51 Å) because of steric hindrance. C(6), C(7), N(4) and O(7) form a C(7)-centred plane, showing that the carbonyl C

* Lists of structure factors, anisotropic thermal parameters, complete bond distances and angles, and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55290 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: BR0003]

atom is *sp* hybridized. The two carbonyl planes are not in the same plane but form a 41.77° dihedral angle. The six-membered ring has a boat conformation. The N—Ni—N bond angles in the five-membered and six-membered rings are 84.3 (1) and 94.7 (2)° respectively. The shortest Ni...Ni distance is 5.468 Å. As expected, the square-planar coordination of the Ni^{II} results in a diamagnetic complex, no electron-spin resonance signal is observed.

The complex binds six water molecules by twenty hydrogen bonds. Fig. 2 is the packing diagram of the complex. Table 3 presents the distances and angles of hydrogen bonds in each half of the complex. From Fig. 2 it can be seen that each complex molecule forms four hydrogen-bond chains and the hydrogen-bond chains cover the complex. One complex mol-

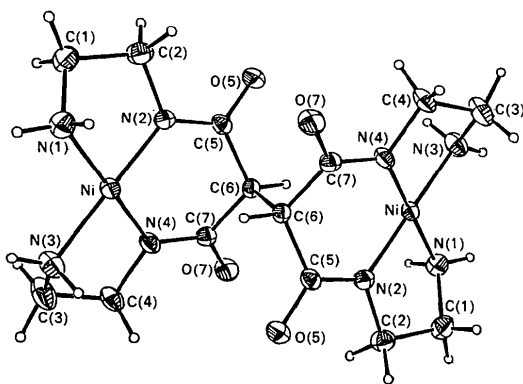


Fig. 1. A perspective view of the complex [Ni₂(C₁₄H₂₆N₈O₄)].

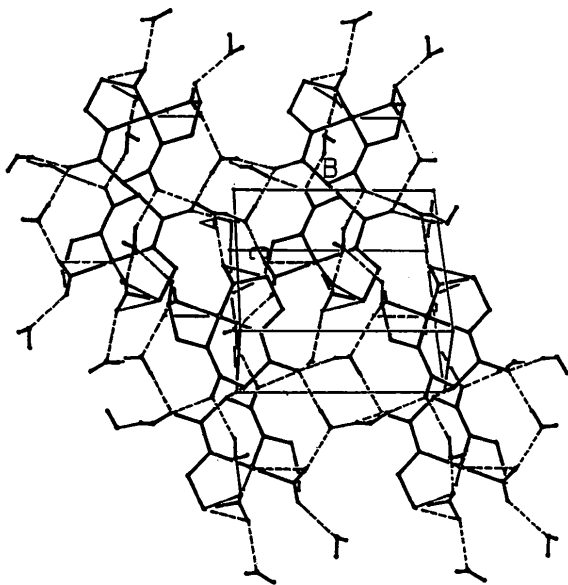


Fig. 2. A packing diagram of the complex [Ni₂(C₁₄H₂₆N₈O₄)]·6H₂O; *x*(0–0.5), *y*(0–1), *z*(0–0.5). The dashed lines denote hydrogen bonds.

Table 2. Important bond distances (Å) and bond angles (°) for [Ni₂(C₁₄H₂₆N₈O₄)]·6H₂O

Ni—N(1)	1.912 (3)	C(1)—C(2)	1.515 (5)
Ni—N(2)	1.865 (2)	C(5)—C(6)	1.522 (4)
Ni—N(3)	1.915 (3)	C(5)—O(5)	1.271 (3)
Ni—N(4)	1.867 (2)	C(6)—C(7)	1.578 (6)
N(1)—C(1)	1.487 (4)	N(2)—C(2)	1.461 (4)
N(3)—C(3)	1.486 (5)	N(4)—C(4)	1.460 (4)
N(2)—C(5)	1.311 (4)	C(6)—C(7)	1.521 (5)
N(4)—C(7)	1.309 (4)	C(7)—O(7)	1.272 (3)
N(1)—Ni—N(2)	84.3 (1)	N(1)—Ni—N(3)	97.2 (1)
N(1)—Ni—N(4)	176.6 (1)	N(2)—Ni—N(3)	178.3 (1)
N(2)—Ni—N(4)	94.7 (2)	N(3)—Ni—N(4)	83.8 (1)
H(1)—N(1)—H(2)	109 (4)	N(1)—C(1)—C(2)	106.8 (3)
N(3)—C(3)—C(4)	107.0 (3)	N(4)—C(4)—C(3)	106.8 (3)
N(2)—C(5)—C(6)	116.9 (3)	N(2)—C(5)—O(5)	124.7 (3)
C(6)—C(5)—O(5)	118.3 (3)	C(5)—C(6)—C(7)	108.3 (3)
C(5)—C(6)—C(7)	116.1 (2)	N(4)—C(7)—C(6)	116.8 (2)
N(4)—C(7)—O(7)	124.9 (3)	C(6)—C(7)—O(7)	118.0 (2)

Table 3. Hydrogen-bond geometry (Å, °) for [Ni₂(C₁₄H₂₆N₈O₄)]·6H₂O

D—H...O	D—H	H...O	D—H...O
OW(1)—H(14)...OW(2)	0.78 (6)	2.07 (5)	165 (5)
OW(1)—H(15)...O(7)	0.85 (5)	1.94 (6)	171 (5)
OW(2)—H(16)...O(5)	0.75 (5)	2.00 (5)	169 (6)
OW(2)—H(17)...O(5)	0.80 (5)	1.97 (5)	171 (5)
OW(3)—H(18)...OW(1)	0.87 (5)	2.02 (5)	164 (5)
OW(3)—H(19)...O(7)	0.87 (5)	1.97 (5)	155 (5)
N(1)—H(1)...OW(3)	0.91 (5)	2.17 (6)	158 (4)
N(1)—H(2)...OW(1)	0.86 (4)	2.24 (5)	158 (5)
N(3)—H(7)...OW(3)	0.87 (4)	2.24 (5)	146 (4)
N(3)—H(8)...OW(2)	0.91 (5)	2.14 (5)	166 (4)

ecule is linked to another by an eight-membered ring [O(5), H(16), OW(2), H(17), O(5), H(16), OW(2), H(17)] consisting of hydrogen bonds. It is interesting that all the H atoms in the amino groups, the O atoms in the carbonyls, and the water molecules are saturated by hydrogen bonds. The large network of hydrogen bonds stabilizes the crystal structure in a way seldom seen in crystals of these complexes.

The project was supported by Fuzhou Research Laboratory of Structural Chemistry Foundation and the National Natural Science Foundation of China.

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Acta Cryst. (1992). **C48**, 1929–1931

Etude Structurale du Dihydrate de l'Hexafluorostannate de Triméthylammonium

PAR A. TAHA, B. LIAUTARD ET W. GRANIER

Laboratoire de physicochimie des matériaux solides, URA 407, Université des Sciences et Techniques du Languedoc, Place E. Bataillon, 34095 Montpellier CEDEX 5, France

(Reçu 15 juillet 1990, accepté le 25 juin 1992)

Abstract. Bis(triméthylammonium) hexafluorostannate dihydrate, $[(\text{CH}_3)_3\text{NH}]_2[\text{SnF}_6] \cdot 2\text{H}_2\text{O}$, $M_r = 388.7$, monoclinic, $C2/m$, $a = 14.763$ (2), $b = 7.316$ (1), $c = 8.177$ (3) Å, $\beta = 119.7$ (3)°, $V = 767.2$ (8) Å³, $Z = 2$, $D_m = 1.72$ (6), $D_x = 1.69$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.70906$ Å, $\mu = 1.726$ mm⁻¹, $F(000) = 388$, $T = 295$ K, final $R = 0.038$ for 1034 reflections. The structure consists of a linear linkage of $(-\text{SnF}_6-\text{H}_2\text{O}-\text{SnF}_6-\text{H}_2\text{O}-)$ rings with branches of organic radicals bonded to the O atoms. The water molecules maintain the stability of the crystal packing by hydrogen bonding. The O atom has a pyramidal environment composed of three H atoms at short distances and N and F heteroatoms as second neighbours.

Introduction. Dans le cadre de l'étude des composés fluorés de l'étain avec des cations organiques asymétriques, nous nous sommes d'abord intéressés à l'hydrazine (Vilminot, Granier & Wahabi, 1987), puis aux mono-, di- et triméthylamines. Si, dans le premier cas, le caractère réducteur de l'hydrazine conduit toujours à des sels de l'étain(II), il n'en est pas de même avec les méthylamines pour lesquelles une oxydation plus ou moins totale de l'étain(II) en étain(IV) est observée. Ceci a été vérifié par des études infra-rouges et Mössbauer. La cristallisation de ces sels est par ailleurs très délicate (grande solubilité, oxydation facile et rapide...) et c'est seulement avec la triméthylamine que nous avons pu isoler un sel de l'étain(IV) dont nous présentons ici la structure.

Partie expérimentale. La synthèse a été réalisée par évaporation lente d'une solution de difluorure d'étain(II) (SnF_2), acidifiée par l'acide fluorhydrique (HF) et additionnée de triéthylamine. La densité a été mesurée par pycnométrie dans le benzène. Les mesures des intensités de diffraction ont été effec-

tuées à l'aide d'un diffractomètre CAD-4 Enraf-Nonius utilisant la radiation $K\alpha$ du molybdène ($\lambda = 0,70906$ Å), sur un cristal de dimensions $0,1 \times 0,2 \times 0,7$ mm. Les paramètres de maille ont été déterminés à partir de 25 réflexions indépendantes ($2 < \theta < 15^\circ$). 1554 réflexions ont été mesurées ($\theta < 30^\circ$) dans l'hémisphère ($h, k, \pm l$) (h : 0 à 20, k : 0 à 6, l : -11 à 11) dont 1034 sont considérées comme observées [$\sigma(I)/I < 0,5$]. Trois réflexions standards (006, 60 $\bar{1}$, 420) ont été utilisées pour contrôler l'intensité toutes les 50 mesures (variation < 6%). Les corrections de Lorentz et de polarisation ont été effectuées mais les effets d'absorption négligés. La structure a été résolue par la méthode des atomes lourds et les affinements effectués sur les F par LINUS (Coppens & Hamilton, 1970). Les atomes d'hydrogène ont été localisés à partir de sections différences. Les calculs ont été effectués sur un micro-ordinateur Olivetti M28. $R = 0,038$, $wR = 0,049$, $S = 14,5$, $w = 1$, $\Delta\rho_{\text{max}} = 0,66$ e Å⁻³, $(\Delta/\sigma)_{\text{max}} = 0,13$. Les facteurs de diffusion utilisés sont ceux donnés par Doyle & Turner (1968) pour Sn, F, O, N, C et par Stewart, Davidson & Simpson (1965) pour l'hydrogène.

Discussion. Le Tableau 1 rassemble les paramètres de position et d'agitation thermique isotrope des atomes.* Une projection de la structure est représentée sur la Fig. 1.

La structure est bâtie avec pour éléments de base, des chaînes $[\text{SnF}_6-(\text{H}_2\text{O})_2-\text{SnF}_6]_n$ qui se développent

* Les listes des facteurs de structure, des facteurs d'agitation thermique anisotrope et des paramètres des atomes d'hydrogène ont été déposées au dépôt d'archives de la British Library Document Supply Centre (Supplementary Publication No. SUP 55247: 20 pp.). On peut en obtenir des copies en s'adressant à: The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, Angleterre. [Référence de CIF: DU0247]