distances cited in this paragraph are of the type $O(x,y,z)\cdots O(1+x,y,z)$.]

Thanks are due to a referee for helpful comments.

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Structure of Binuclear Hexaaqua-μ-[1,2,4,5-benzenetetracarboxylato(4−)]-bis(ethylenediamine)dinickel(II) Tetrahydrate

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(*Received* 1 *July* 1987; *accepted* 1 *October* 1987)

Abstract. $[Ni_2(C_2H_8N_2)_2(C_{10}H_2O_8)(H_2O)_6].4H_2O$, $M_r = 667{\cdot}89$, monoclinic, $P2_1/c$, $a = 9{\cdot}192$ (1), $b = 13{\cdot}919$ (2), $c = 10{\cdot}754$ (1) Å, $\beta = 107{\cdot}70$ (1)°, $V = 1311$ (4) Å^3, $Z = 2$, $D_x = 1{\cdot}69$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 2{\cdot}805$ mm^{-1}, $F(000) = 700$, $T = 293$ K, final $R = 0{\cdot}035$ for 1908 independent reflexions having $I \geq 2{\cdot}5\sigma(I)$. The structure consists of binuclear centrosymmetric $[(en)(H_2O)_3Ni\text{-}(pyr)\text{-}Ni(H_2O)_3(en)]$ units [pyr=tetraanion of pyromellitic acid (1,2,4,5-benzenetetracarboxylic acid); en=ethylenediamine] and water of hydration. The complex molecules are oriented parallel to the [201] direction. The packing is governed by a three-dimensional network of hydrogen bonds. The Ni atom is octahedrally coordinated, and the pyr anion functions as a bis monodentate ligand. Differences between analogous ternary Ni^{II} and Cu^{II} complexes including the aromatic polycarboxylate ions are discussed. They can be attributed to different coordination geometries, and to a higher degree of hydration found in the Ni complexes.

Introduction. Structures of numerous ternary Ni^{II} and Cu^{II} complexes containing various amines and the phthalate (1,2-benzenedicarboxylate) ion are known (Krstanović, Karanović & Stojaković, 1985; Krstanović, Karanović, Stojaković & Golič, 1982; Poleti, Prelesnik, Herak & Stojaković 1986; Biagini Cingi, Manotti Lanfredi, Tiripicchio & Tiripicchio Camellini, 1981). These data as well as structures of binary Cu^{II}–phthalato complexes (Biagini Cingi, Manotti Lanfredi, Tiripicchio & Tiripicchio Camellini, 1978) demonstrate that this anion can coordinate in many different ways, acting as a mono- or polydentate ligand having a chelating, bridging or combined function.

In order to study the factors that determine the coordination mode of the phthalate ion it seemed appropriate to us to broaden the investigations by including other aromatic polycarboxylate ions–*e.g.* the tetraanion of pyromellitic acid. Salts of the latter acid are also of considerable theoretical and practical interest (Ward & Luehrs, 1983).

As far as we know, beside the structure of pyromellitic acid itself (Takusagawa, Hiratsu & Shimada, 1971), the structures of only two compounds containing pyromellitic acid anions and transition-metal ions have been published to date, the compounds being $[Co(H_2O)_6][H_2pyr]$ (Ward & Luehrs, 1983) and $[Cu_2(H_2O)_6(pyr)].4H_2O$ (Usubaliev, Shnulin & Mamedov, 1982). No ternary complexes of this type have been synthesized.

We have prepared two complexes that have empirical formulae $Cu_2(en)_2(pyr)$ and $Ni_2(en)_2(pyr).10H_2O$. The synthetic procedure and properties of these compounds will be published elsewhere. Regrettably, attempts to grow monocrystals of the first compound have been unsuccessful. From the physicochemical properties and the empirical formula of the Cu^{II} compound, its structure (probably a network one) is entirely different from the structure of the Ni^{II} complex described in this work.

Experimental. Complex prepared by precipitation from a dilute aqueous solution containing $[Ni(en)]^{2+}$ and pyr ions. Pale blue crystals grown by recrystallization from water. Preliminary unit cell and space group from oscillation and Weissenberg photographs (Cu $K\alpha$, Ni-filtered radiation). Accurate cell parameters by least-squares refinement of the θ values of 25 general reflexions ($10{\cdot}70 \leq \theta \leq 17{\cdot}56°$). Crystal $0{\cdot}15 \times 0{\cdot}10 \times 0{\cdot}08$ mm; Enraf–Nonius CAD-4 diffractometer; Mo $K\alpha$ (graphite monochromated) radiation, $\omega/2\theta$ scan, $(2\theta)_{\min} = 4°$, $(2\theta)_{\max} = 60°$ ($h \leq 12$, $k \leq 19$, $|l| \leq 14$). Two standard reflexions ($\bar{6}34$; $\bar{6}\bar{5}2$) monitored every 100 reflexions, no variations. 1908 independent reflexions with $I \geq 2{\cdot}5\sigma(I)$ collected (1904 unobserved), corrected for Lp, not for absorption. Structure solved by Patterson method. Full-matrix least-squares refinement on F with anisotropic thermal parameters for all non-H atoms. Most water H atoms from ΔF maps, remaining H atoms placed at calculated positions. All H atoms introduced in the final structure-factor calculation at fixed positions with fixed thermal parameters ($B = 4{\cdot}5$ Å^2 for water H atoms, $B = 4{\cdot}0$ Å^2 for others). Final agreement parameters $R = 0{\cdot}035$, $wR = 0{\cdot}041$, $w = 1/\sigma^2(F_o)$, for 172 independent parameters, $(\Delta/\sigma)_{\max} = 0{\cdot}15$, maximum height in final ΔF synthesis $0{\cdot}57$ e Å^{-3}. Scattering factors for neutral atoms and anomalous dispersion for Ni from *International Tables for X-ray Crystallography* (1974). The main programs used on the CDC 3600 computer were *FORDAP*, Zalkin's (1965) Fourier program, *NUCLS*, a modification by J. A. Ibers and R. J. Doedens of the full-matrix least-squares program *ORFLS* (Busing, Martin & Levy, 1962) and *GEOM*, L. W. Muir & P. Mallinson's program for molecular geometry calculation.

Table 1. *Positional* ($\times 10^4$) *and equivalent isotropic thermal parameters with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{8}{3}\pi^2 \textstyle\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}(Å^2)
Ni	6318 9 (6)	481·5 (4)	2697·8 (5)	2·03 (2)
O(1)	4038 (3)	314 (2)	1629 (3)	2·39 (10)
O(2)	2823 (4)	1118 (3)	2824 (3)	2·58 (11)
O(3)	2558 (4)	−2053 (2)	413 (3)	3·82 (11)
O(4)	2717 (4)	−1510 (2)	2394 (3)	2·99 (10)
O*W*(1)	8691 (4)	670 (3)	3708 (3)	3·43 (12)
O*W*(2)	5810 (3)	1318 (2)	4097 (3)	2·50 (10)
O*W*(3)	6405 (4)	1703 (2)	1633 (3)	3·71 (12)
O*W*(4)	383 (4)	2127 (3)	3226 (4)	5·62 (16)
O*W*(5)	597 (5)	−949 (4)	3577 (4)	7·65 (19)
N(1)	6893 (4)	−480 (3)	1438 (4)	3·40 (13)
N(2)	6158 (5)	−756 (3)	3741 (4)	3·29 (13)
C(1)	6397 (6)	−1448 (4)	1739 (5)	3·95 (19)
C(2)	6817 (6)	−1571 (4)	3208 (6)	4·78 (19)
C(3)	2848 (4)	590 (3)	1886 (4)	1·96 (12)
C(4)	2213 (4)	−1471 (3)	1172 (4)	2·27 (12)
C(5)	1101 (4)	−689 (3)	561 (4)	2·28 (12)
C(6)	1356 (4)	271 (3)	942 (4)	1·79 (12)
C(7)	247 (5)	947 (3)	377 (4)	2·01 (12)

Discussion. Atomic coordinates and equivalent isotropic thermal parameters are given in Table 1,* intramolecular bond lengths and valence angles with the numbering scheme of atoms belonging to the complex molecule are presented in Fig. 1, and packing of the molecules in the unit cell is shown in Fig. 2.

The crystal structure consists of binuclear centrosymmetric $[(en)(H_2O)_3Ni\text{-}(pyr)\text{-}Ni(H_2O)_3(en)]$ units and water of hydration. The molecules of the complex are oriented in the same direction, parallel to [201]. The packing of the molecules in the crystal is controlled mainly by a three-dimensional network of hydrogen bonds. Equatorially coordinated water O atoms [O*W*(2) and O*W*(3)] and O atoms belonging to the water of hydration [O*W*(4) and O*W*(5)] act as

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, hydrogen bonding and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44420 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

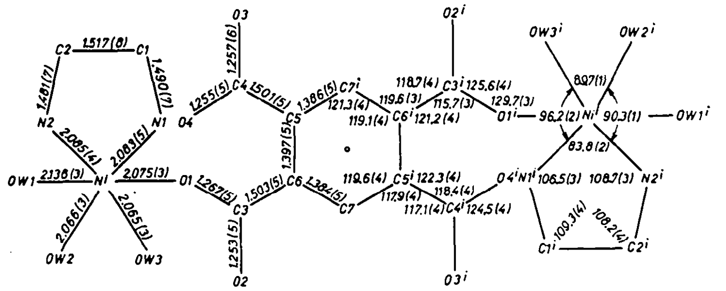

Fig. 1. Numbering of atoms and geometry of the complex molecule. Symmetry code: (i) $-x$, $-y$, $-z$.

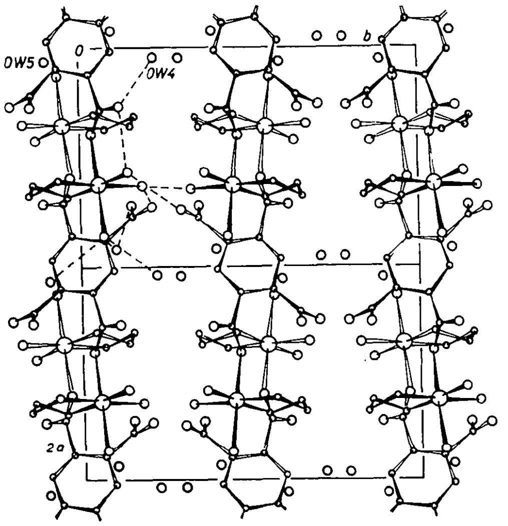

Fig. 2. Projection of the structure on the *ab* plane. Only one section of the hydrogen bonding (dashed lines) is presented, and H atoms are omitted, for clarity.

hydrogen-bond donors to the uncoordinated carboxylate O atoms. Thus, the latter O atoms all participate in two hydrogen bonds. The axially coordinated water O atom, O*W*(1), functions both as a hydrogen-bond donor and as an acceptor. There are no unusual hydrogen bonds in the structure; however, it should be noticed that one of them [O*W*(2)···O(2)] is intramolecular and relatively short [2·684 (4) Å].

Bond lengths and interbond angles in the complex have expected values, and the values relating to the pyromellitate ion are in good agreement with the corresponding ones found in $[Co(H_2O)_6][H_2pyr]$ (Ward & Luehrs, 1983) and $[Cu_2(H_2O)_6(pyr)].4H_2O$ (Usubaliev, Shnulin & Mamedov, 1982).

The coordination polyhedron around the Ni atom is distorted octahedral, the three water molecules being mutually in *cis* positions. The remaining three octahedral sites are occupied by two N atoms of the ethylenediamine ligand and by an O atom of the monodentately coordinated carboxylato group. The axial Ni—O*W*(1) bond length of 2·136 (3) Å is longer than the corresponding equatorial Ni—O*W*(2) and Ni—O*W*(3) bonds [2·066 (3) and 2·065 (3) Å respectively], probably because O*W*(1) forms one more hydrogen bond than do the latter two O*W* atoms. Displacements of atoms forming the basal plane [defined by the NiN(1)N(2)O*W*(2)O*W*(3) atoms] are relatively large (up to 9σ), probably induced by the nonrigidity of the en ligand and by steric requirements of hydrogen bonding.

The benzene ring is perfectly planar – as required by the space group – and is twisted by 76·5 (3)° with respect to the metal-coordination basal plane; this is a logical consequence of axial coordination of the COO^- group. Carboxylate groups are inclined to the benzene ring by 50·8 (2) and 49·2 (3)°. A similar situation has been found in $[Cu_2(H_2O)_6(pyr)].4H_2O$ (Usubaliev, Shnulin & Mamedov, 1982), the corresponding angles being 51·5 and 52·8°.

The coordination mode of the pyr anion is of special interest. The pyr ion in this structure functions as a bridge, and is coordinated in a bis monodentate fashion; the two donor COO^- groups are in *para* positions. Therefore, the pyromellitato ligand practically behaves as a terephthalato (1,4-benzenedicarboxylato) ligand. Indeed, some structural similarities (the binuclear type, the crystallographic inversion centre located at the centre of the benzene ring, the presence of a short intramolecular hydrogen bond) do exist between this complex and (μ-terephthalato)-bis[aqua(*N*,*N*,*N*′,*N*″,-*N*″-pentamethyldiethylenetriamine)copper(II)] perchlorate (Verdaguer, Gouteron, Jeannin, Jeannin & Kahn, 1984).

The fact that of every two *ortho*-carboxylate groups only one is coordinated to the central atom is not surprising since this behaviour is also observed in the Ni^{II} complexes that have the same Ni environment and geometry but have a phthalate instead of a pyr ion as a ligand (Poleti, Prelesnik, Herak & Stojaković, 1986). This function of aromatic polycarboxylate ions is in contrast to their role in analogous Cu^{II} complexes (Krstanović, Karanović & Stojaković, 1985; Krstanović, Karanović, Stojaković & Golič, 1982; Usubaliev, Shnulin & Mamedov, 1982; Biagini Cingi, Manotti Lanfredi, Tiripicchio & Tiripicchio Camellini, 1981), where they are polydentate in nature and, as a consequence, these Cu complexes are polymers of chain or layer type. This can probably be attributed to differences in the coordination polyhedra (the Cu complexes of this type usually have square-pyramidal geometry). An additional factor could be the higher degree of hydration generally found in Ni complexes as compared with their Cu analogues; the presence of H_2O allows the O atoms of the uncoordinated COO groups to satisfy their affinity for bonding by formation of hydrogen bonds.

This work was supported by the Research Fund of SR Serbia.

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Acta Cryst. (1988). C**44**, 245–246

Structure of Bis(ethylenediamine)isothiocyanatocopper(II) Tetrafluoroborate, Violet Isomer

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(*Received* 6 *May* 1987; *accepted* 9 *October* 1987)

Abstract. $[Cu(NCS)(C_2H_8N_2)_2]BF_4$, $M_r = 328{\cdot}67$, orthorhombic, *Pnam*, $a = 15{\cdot}379\,(4)$, $b = 10{\cdot}788\,(2)$, $c = 7{\cdot}610\,(2)$ Å, $V = 1262{\cdot}5\,(1)$ Å^3, $Z = 4$, $D_m = 1{\cdot}73$, $D_x = 1{\cdot}73$ g cm^{-3}, $\lambda(\text{Cu}\,K\alpha) = 1{\cdot}5418$ Å, $\mu = 43{\cdot}7$ cm^{-1}, $F(000) = 668$, $T = 293$ K, $R = 0{\cdot}042$ for 593 observed reflections. The Cu atom is in a tetragonally distorted octahedral environment with the four ethylenediamine N atoms in an approximately square-planar configuration [Cu—N1 2·018 (4) and Cu—N2 2·009 (4) Å] and two N(isothiocyanate) atoms in axial positions [Cu—N 2·720 (2) Å]. The isothiocyanate group thus forms a bridging unit between two $[Cu(en)_2]^{2+}$ cations, giving an infinite chain structure.

Introduction. The complexes of $[Cu(NCS)(en)_2]X$ where $X = Cl^-$, Br^-, NO_3^-, BF_4^- and ClO_4^- were investigated as models for the study of the isomerism of Cu^{II} complexes, as well as for the study of the influence of anion X exchange on the bonding mode of the NCS groups (Macašková, Otrubová, Ondrejovič & Gažo, 1987). For $X = BF_4^-$ two isomers of $[Cu(NCS)(en)_2]$-BF_4 were prepared: blue and violet; these isomers differ in electronic and infrared spectra. The present paper reports the crystal structure of the violet isomer.

Experimental. Dark-violet prismatic crystals, 0·30 × 0·40 × 0·25 mm; D_m measured by flotation; Weissenberg photographs indicated space group *Pnam*, Syntex $P2_1$ computer-controlled four-circle diffractometer with graphite-monochromated Cu $K\alpha$ radiation; cell parameters by least squares from the 15 selected reflections with $3{\cdot}95 \leq 2\theta \leq 23{\cdot}28°$; intensity

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