Le mode opératoire mis au point par Bonati & Minghetti (1970) permettant la synthèse de composés mercurés de la 2,4-pentanedione a été répété. L'ajout lent (goutte à goutte) de 2,4-pentanedione (1 ml) à une solution aqueuse saturée de chlorure de mercure (20 ml, Hg^{2+} = 0,25 mol l^{-1}) conduit à un précipité blanc qui est par la suite filtré et lavé avec de l'eau glacée. Les données spectroscopiques (IR) du précipité ainsi obtenu ne correspondent pas à celles publiées par Bonati & Minghetti mais se rapprochent de celles obtenues par d'autres auteurs (Allmann, Flatau & Musso, 1972) lors d'une synthèse analogue. Par analyse chimique élémentaire, ces derniers proposent pour le précipité décrit ci-dessus la formule suivante $Hg(C_5H_7O_2)Cl$. Nos propres résultats, obtenus par analyse chimique élémentaire, concordent avec cette formule. Cependant, aucune structure cristallographique n'a été proposée.

Le précipité décrit ci-dessus est moyennement soluble dans l'acétonitrile. Dans une solution à saturation, il se forme à température ambiante des cristaux faisant l'objet de notre étude structurale. Les diffractogrammes de poudre du précipité et des cristaux n'étant pas équivalents, on peut supposer qu'ils correspondent à des structures cristallographiques différentes, bien que les formules chimiques des deux composés soient analogues.

Les atomes Hg et Cl ont été localisés par la méthode de Patterson en utilisant le programme SHELXS86 (Sheldrick, 1986). La structure a été résolue par des synthèses de Fourier différence successives et affinements par moindres carrés en matrice totale en utilisant le programme CRYSTALS (Watkin, Carruthers & Betteridge, 1988), adapté sur un micro-ordinateur Dell 333D (processeur 80386, 33 MHz). Une correction d'absorption a été appliquée en utilisant le programme DIFABS (Walker & Stuart, 1983) après l'affinement isotrope de tous les atomes. En ce qui concerne les atomes H [H(1) à H(7)], leurs coordonnées ont été calculées (avec C—H = 1,08 Å) et leurs positions ont été introduites dans l'affinement et un facteur d'agitation thermique commun a été affiné.

La Fig. 1 a été tracée à l'aide du programme ORTEP (Johnson, 1965).

Les listes des facteurs de structure, des facteurs d'agitation thermique anisotrope, des coordonnées des atomes d'hydrogène et des distances et angles des atomes d'hydrogène ont été déposées au dépôt d'archives de la British Library Document Supply Centre (Supplementary Publication No. SUP 71317: 12 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: DU1042]

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Aqua[1,8-di(2-pyridyl)-3,6-dithiaoctane-N,N',S,S'](nitrato-O)nickel(II) Nitrate

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Abstract

The Ni^{2+} ion is octahedrally coordinated by the 1,8-di(2-pyridyl)-3,6-dithiaoctane (bpdto) ligand, one O atom of a nitrate group and one O atom of the water molecule; the two N atoms of bpdto are mutually trans and the two S atoms are cis. The Ni—S distances are 2.453 (1) and 2.411 (1) Å, and the Ni—N distances are 2.139 (4) and 2.119 (4) Å. The Ni—O distances involving the coordinated nitrate ion and the water molecule are 2.099 (4) and 2.035 (3) Å, respectively. The water ligand is connected to both nitrate ions by interionic hydrogen bonds.

Comment

A view of the title compound with atom labelling is shown in Fig. 1. The Ni centre has an $N_2S_2O_2$ distorted octahedral environment. Similar coordination

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has been demonstrated for other complexes derived from transition-metal nitrates and linear tetradentate chelating ligands with *NSSN* donor systems; for example, complexes of cobalt(II) (Castiñeiras, Carballo, Hiller & Strähle, 1990) and copper(II) (Bermejo, Carballo, Castiñeiras, Lombao, Hiller & Strähle, 1991).
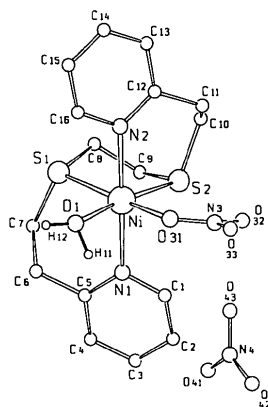

Fig. 1. View of the molecule showing the labelling of the non-H atoms.

The crystal packing is shown in Fig. 2. The interionic hydrogen bonds based on OH···O are as follows: $O(1)$—$H(11)$···$O(41^i)$ = 163.3 (3)°, $O(41^i)$···$H(11)$ = 1.742 (5), $O(1)$—$H(11)$ = 0.969 (4) and $O(1)$···$O(41^i)$ = 2.684 (6) Å; $O(1)$—$H(12)$···$O(32^{ii})$ = 160.0 (3)°, $O(32^{ii})$···$H(12)$ = 2.030 (4), $O(1)$—$H(12)$ = 0.849 (3) and $O(1)$···$O(32^{ii})$ = 2.842 (5) Å [symmetry code: (i) $1 - x$, $y - 0.5$, $-z$; (ii) $1 + x$, y, z].
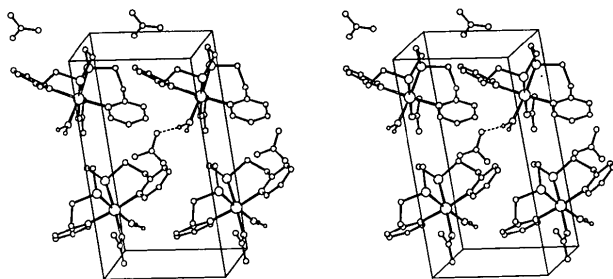

Fig. 2. Stereoscopic illustration of the molecular packing. The origin is at the lower-left-front corner, a is inside of the plane of the paper, b is vertical and c is horizontal.

Experimental

Crystal data

[Ni(NO₃)(C₁₆H₂₀N₂S₂)-
(H₂O)](NO₃)
$M_r = 505.21$

Monoclinic
$P2_1$
$a = 7.4764$ (5) Å
$b = 14.9380$ (7) Å
$c = 9.7315$ (3) Å
$\beta = 110.022$ (4)°
$V = 1021.2$ (2) Å³
$Z = 2$

$D_x = 1.643$ Mg m⁻³
Mo $K\alpha$ radiation
$\lambda = 0.70930$ Å
Cell parameters from 25 reflections
$\theta = 13$–20°
$\mu = 1.195$ mm⁻¹
$T = 293$ K
Prism
$0.30 \times 0.30 \times 0.20$ mm
Green

Data collection

Enraf-Nonius CAD-4 diffractometer
ω–2θ scan
Absorption correction: empirical (Walker & Stuart, 1983)
$T_{min} = 0.87$, $T_{max} = 1.13$
2731 measured reflections
2548 independent reflections

2428 observed reflections
$[I > 3\sigma(I)]$
$R_{int} = 0.010$
$\theta_{max} = 28°$
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 19$
$l = -12 \rightarrow 12$
3 standard reflections
frequency: 60 min
intensity variation: none

Refinement

Refinement on F
Final $R = 0.031$
$wR = 0.034$
$S = 0.74$
2428 reflections
270 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F)]$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.60$ e Å⁻³
$\Delta\rho_{min} = -0.58$ e Å⁻³
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å²)

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

	x	y	z	U_{eq}
Ni	0.46021 (6)	0.2565	0.08168 (5)	0.0245 (2)
S(1)	0.6494 (1)	0.36579 (8)	0.0021 (1)	0.0334 (4)
S(2)	0.2051 (1)	0.36452 (8)	0.0134 (1)	0.0321 (4)
N(1)	0.5360 (4)	0.3173 (3)	0.2930 (4)	0.030 (1)
N(2)	0.3851 (5)	0.2066 (3)	−0.1346 (4)	0.033 (2)
C(1)	0.4031 (6)	0.3169 (3)	0.3567 (5)	0.035 (2)
C(2)	0.4192 (6)	0.3610 (4)	0.4838 (4)	0.041 (2)
C(3)	0.5820 (7)	0.4099 (4)	0.5519 (5)	0.045 (2)
C(4)	0.7235 (7)	0.4097 (4)	0.4912 (5)	0.038 (2)
C(5)	0.6990 (5)	0.3636 (3)	0.3629 (4)	0.030 (2)
C(6)	0.8531 (6)	0.3676 (4)	0.2969 (5)	0.036 (2)
C(7)	0.8021 (6)	0.4267 (3)	0.1609 (5)	0.041 (2)
C(8)	0.4683 (7)	0.4475 (4)	−0.0897 (6)	0.049 (2)
C(9)	0.3288 (7)	0.4643 (3)	−0.0108 (7)	0.047 (2)
C(10)	0.0506 (6)	0.3421 (4)	−0.1719 (5)	0.040 (2)
C(11)	0.0434 (6)	0.2425 (4)	−0.2074 (5)	0.041 (2)
C(12)	0.2121 (6)	0.2083 (3)	−0.2414 (5)	0.036 (2)
C(13)	0.1897 (8)	0.1792 (4)	−0.3825 (5)	0.049 (3)
C(14)	0.3406 (9)	0.1451 (4)	−0.4152 (5)	0.057 (3)
C(15)	0.5169 (8)	0.1422 (4)	−0.3073 (5)	0.051 (2)
C(16)	0.5328 (7)	0.1747 (3)	−0.1712 (5)	0.042 (2)
O(1)	0.6758 (4)	0.1665 (2)	0.1586 (3)	0.032 (1)
N(3)	0.1539 (5)	0.1328 (3)	0.1428 (4)	0.036 (2)
O(31)	0.3156 (4)	0.1493 (2)	0.1362 (4)	0.040 (1)
O(32)	0.0381 (4)	0.1948 (3)	0.1313 (4)	0.053 (2)
O(33)	0.1132 (6)	0.0562 (3)	0.1623 (6)	0.042 (3)
N(4)	0.1973 (5)	0.5540 (3)	0.5186 (4)	0.040 (2)
O(41)	0.2877 (6)	0.6245 (3)	0.5650 (4)	0.066 (2)
O(42)	0.1581 (6)	0.5039 (3)	0.6054 (4)	0.059 (2)
O(43)	0.1448 (6)	0.5365 (3)	0.3871 (4)	0.056 (2)

Table 2. Geometric parameters (Å, °)

Ni—S(1)	2.453 (1)	Ni—S(2)	2.411 (1)
Ni—O(1)	2.035 (3)	Ni—O(31)	2.099 (4)
Ni—N(1)	2.139 (4)	Ni—N(2)	2.119 (4)
S(1)—C(7)	1.820 (6)	S(1)—C(8)	1.816 (6)
S(2)—C(9)	1.812 (6)	S(2)—C(10)	1.809 (6)
N(1)—C(1)	1.339 (6)	N(1)—C(5)	1.363 (6)
N(2)—C(12)	1.354 (7)	N(2)—C(16)	1.357 (7)
C(1)—C(2)	1.371 (7)	C(13)—C(14)	1.37 (2)
C(14)—C(15)	1.38 (1)	C(15)—C(16)	1.377 (8)
C(2)—C(3)	1.379 (8)	C(3)—C(4)	1.376 (9)
C(4)—C(5)	1.383 (7)	C(5)—C(6)	1.500 (7)
C(6)—C(7)	1.526 (8)	C(8)—C(9)	1.513 (9)
C(10)—C(11)	1.52 (1)	C(11)—C(12)	1.499 (8)
C(12)—C(13)	1.394 (8)		
S(1)—Ni—S(2)	87.41 (5)	S(1)—Ni—O(1)	94.9 (2)
S(1)—Ni—O(31)	171.9 (1)	S(1)—Ni—N(1)	91.7 (1)
S(1)—Ni—N(2)	84.6 (1)	S(2)—Ni—O(1)	174.7 (2)
S(2)—Ni—O(31)	98.8 (1)	S(2)—Ni—N(1)	84.6 (1)
S(2)—Ni—N(2)	92.7 (1)	O(1)—Ni—O(31)	79.3 (1)
O(1)—Ni—N(1)	90.6 (2)	O(1)—Ni—N(2)	92.3 (2)
O(31)—Ni—N(1)	94.0 (2)	O(31)—Ni—N(2)	89.9 (2)
N(1)—Ni—N(2)	175.5 (2)	C(7)—S(1)—C(8)	103.2 (3)
C(9)—S(2)—C(10)	101.7 (3)	C(1)—N(1)—C(5)	116.7 (4)
C(12)—N(2)—C(16)	117.0 (5)	S(1)—C(8)—C(9)	112.9 (4)
S(2)—C(9)—C(8)	113.7 (4)	S(2)—C(10)—C(11)	111.6 (5)
N(1)—C(1)—C(2)	124.5 (5)	C(1)—C(2)—C(3)	118.6 (5)
C(2)—C(3)—C(4)	118.4 (5)	C(3)—C(4)—C(5)	120.3 (5)
N(1)—C(5)—C(4)	121.5 (5)	N(1)—C(5)—C(6)	119.5 (4)
C(4)—C(5)—C(6)	118.9 (5)	C(5)—C(6)—C(7)	113.2 (4)
S(1)—C(7)—C(6)	110.2 (4)	C(10)—C(11)—C(12)	114.6 (6)
N(2)—C(12)—C(11)	119.5 (5)	N(2)—C(12)—C(13)	120.7 (6)
C(11)—C(12)—C(13)	119.8 (5)	C(12)—C(13)—C(14)	120.9 (6)
C(13)—C(14)—C(15)	118.9 (6)	C(14)—C(15)—C(16)	117.9 (6)
N(2)—C(16)—C(15)	124.5 (6)		

Data collection: Enraf-Nonius CAD-4 software. Data reduction: *SDP* (Frenz, 1978). Program used to solve structure: *SHELXS*86 (Sheldrick, 1986). Programs used to refine structure: *SDP*. Molecular graphics: *SCHAKAL*88 (Keller, 1988). The structure was solved by direct methods and subsequent difference Fourier methods. Anisotropic thermal parameters were refined for all non-H atoms. H atoms were included in the structure-factor calculations with B_{iso} fixed at 4.00 Å^2.

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Structure of Diaquatetrakis(μ-2,6-difluoro-benzoato-κO:κO′)dicopper(II)

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Abstract

The structure consists of centrosymmetric dimeric units, [Cu(C₆H₃F₂COO)₂(H₂O)]₂, formed from the bridging of pairs of copper(II) ions by carboxylate groups from four different 2,6-difluorobenzoate anions. The distorted octahedral coordination about each Cu^{II} ion consists of four carboxylate O atoms, a water molecule and a centrosymmetrically related copper ion. The Cu⋯Cu distance is 2.613 (1) Å. The most significant feature of the crystalline structure is the water-mediated coordination of one of the carbon-bound F atoms to the copper ion through a strong C—F⋯H—O hydrogen bond [F⋯O 2.962 (4) Å, F⋯H—O 163°]. Each 2,6-difluorobenzoate aryl group is twisted considerably from its corresponding carboxyl group plane [48.9, 104.2°].

Comment

The structure determination of the title compound was carried out as part of a program to investigate the structural environments of carbon-bound F atoms in metal salts of fluorocarboxylic acids. Substitution of F atoms for hydrogen can often lead to structural motifs that are not possible with the corresponding hydrogen homolog. Thus, in fluorocarboxylate salts, carbon-bound F atoms have been found to participate in direct metal-ion binding (C—F⋯M) as well as indirect metal-ion binding through a water-mediated hydrogen bond (C—F⋯H₂O—M) (Murray-Rust, Stallings, Monti, Preston & Glusker, 1983; Karipides & Miller, 1984; Kulawiec & Crabtree, 1990).

The crystal structure consists of centrosymmetric dimeric units similar to those found in copper carboxylate structures (Brown & Chidambaram, 1973). The asymmetric unit includes two independent 2,6-difluorobenzoate groups designated (a) and (b),