

Structure of Aqua{*N,N*-bis[2-(2-pyridyl)ethyl]benzylamine}bis(trifluoromethanesulfonato)nickel(II)

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Abstract. [Ni(bpeb)(CF₃SO₃)₂(H₂O)], C₂₃H₂₃F₆N₃NiO₆S₂, *M_r* = 692.34, orthorhombic, *Pca*2₁, *a* = 19.013 (6), *b* = 8.502 (2), *c* = 17.764 (7) Å, *V* = 2871 (2) Å³, *Z* = 4, *D_x* = 1.60 Mg m⁻³, λ(Mo *Kα*) = 0.71069 Å, μ = 0.91 mm⁻¹, *F*(000) = 1416, *T* = 295 K, *R* = 0.0505 for 1674 unique observed [*F* ≥ 3σ(*F*)] reflections and 265 parameters. [Ni(bpeb)(CF₃SO₃)₂(H₂O)] has a pseudooctahedral coordination geometry with Ni—N bond distances varying from 2.073 (8) Å for one of the pyridine N atoms to a high of 2.134 (7) Å for the amine N atom. The three Ni—O bond distances vary from 2.129 (6) Å for one coordinated CF₃SO₃ to 2.185 (5) Å for the other coordinated CF₃SO₃. The bond angles around the central Ni atom are somewhat distorted from ideal with the smallest O—Ni—O angle being 80.7 (3)°, between the oxygen of the water and one CF₃SO₃, and the largest N—Ni—N angle being 97.0 (3)°, between one pyridine N atom and the coordinated amine.

Experimental. The title complex was prepared by combining equimolar amounts of nickel triflate hexahydrate and bis[2-(2-pyridyl)ethyl]benzylamine in acetonitrile. After removal of the solvent, dark green crystals were obtained by slow diffusion of diethyl ether into a solution in dichloromethane.

An irregularly shaped crystal with dimensions of 0.10 × 0.20 × 0.22 mm was selected for data collection on a Syntex *P2*₁ diffractometer, with graphite monochromator, upgraded to Nicolet *R3* specifications (Campana, Shepard & Litchman, 1981). Lattice constants were calculated from 25 reflections in the range 32 < 2θ < 34°. Data were collected with ω scans (1°); two check reflections (321 and 201) monitored every 96 reflections showed no systematic excursions; 2240 total reflections out to 2θ = 45° were collected, 1674 had *F*_o > 3σ(*F*_o), *hkl* ranges, 0 ≤

h ≤ 20, 0 ≤ *k* ≤ 9, 0 ≤ *l* ≤ 19 (Campana, Shepard & Litchman, 1981).

The structure solution was obtained via the direct-methods routine *SOLV* in the *SHELXTL* crystallographic program package with further refinement also using that set of programs (Sheldrick, 1985). A difference synthesis based on the Ni, S(1), and O(1) positions obtained from *SOLV* yielded all other non-H-atom positions. The final refinement included positional parameters on all non-H atoms. Non-H atoms in the two triflates, the Ni atom and the coordinated water were refined anisotropically. H atoms were constrained to ideal locations (C—H and N—H = 0.96 Å) and assigned isotropic thermal parameters 1.2 times larger than those of the associated atoms.

The final refinement resulted in *R* = 0.0505 (3σ data set) and 0.0628 (all data), and *wR* = 0.0559 [*F* ≥ 3σ(*F*) data set] and 0.0580 (all data), and *w* = 1/[σ²(*F*) + *g*(*F*)²], with *g* = 0.00084. The goodness of fit was 1.165, with parameter changes in the final cycle of least squares being |Δ/σ| (mean) = 0.032 and |Δ/σ| (max.) = 0.169. The largest peak on the final difference map was 0.486 e Å⁻³ near C(14), while the most negative excursion was -0.326 e Å⁻³. Atomic scattering factors as given in *SHELXTL*. Atomic coordinates are listed in Table 1 and bond distances and angles are given in Table 2. A view of the structure is shown in Fig. 1.†

Related literature. Copper complexes containing bis[2-(2-pyridyl)ethyl]benzylamine ligands (Karlin, Gultneh, Hayes & Zubieta, 1984) or related ligands, where the benzylamine is replaced with a hydro-

† Tables of data-collection parameters, anisotropic thermal parameters, H-atom positions and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54348 (18 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. Atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($\text{\AA}^2 \times 10^3$) for [Ni(bpeb)(CF₃SO₃)₂(H₂O)]

	x	y	z	U _{eq}
Ni	-668 (1)	2708 (1)	2500	33 (1)
S(1)	911 (1)	4617 (3)	2524 (2)	50 (1)
O(1)	153 (3)	4507 (6)	2498 (5)	50 (2)
O(2)	1224 (4)	5395 (10)	1906 (4)	71 (3)
O(3)	1235 (3)	3186 (9)	2771 (5)	76 (3)
C(1)	1047 (7)	5953 (16)	3294 (7)	76 (5)
F(1)	701 (5)	7270 (8)	3204 (5)	118 (4)
F(2)	1715 (4)	6345 (12)	3355 (5)	128 (4)
F(3)	852 (4)	5359 (11)	3941 (4)	114 (4)
S(22)	-983 (1)	4423 (3)	4154 (2)	43 (1)
O(23)	-1141 (3)	4030 (7)	3383 (3)	43 (2)
O(24)	-837 (4)	6030 (9)	4288 (5)	78 (3)
O(25)	-520 (4)	3302 (9)	4507 (4)	62 (3)
C(26)	-1836 (6)	4063 (14)	4607 (7)	67 (4)
F(27)	-2062 (4)	2669 (9)	4478 (6)	117 (4)
F(28)	-2294 (3)	5113 (9)	4390 (5)	97 (3)
F(29)	-1752 (5)	4237 (15)	5342 (4)	159 (5)
O(30)	30 (4)	1706 (8)	3323 (4)	46 (2)
N(1)	-140 (4)	1406 (10)	1691 (5)	41 (2)
C(2)	120 (5)	-30 (11)	1874 (6)	51 (3)
C(3)	532 (6)	-900 (13)	1393 (7)	62 (3)
C(4)	687 (6)	-321 (12)	699 (6)	60 (3)
C(5)	423 (5)	1144 (12)	490 (7)	56 (3)
C(6)	11 (5)	1960 (11)	996 (5)	42 (2)
C(7)	-308 (5)	3546 (11)	776 (6)	46 (2)
C(8)	-1087 (4)	3620 (11)	938 (5)	39 (2)
N(9)	-1275 (4)	4075 (8)	1731 (4)	35 (2)
C(10)	-1144 (5)	5818 (9)	1844 (5)	37 (2)
C(11)	-1484 (4)	6916 (10)	1271 (5)	37 (2)
C(12)	-2170 (5)	7412 (11)	1343 (6)	56 (3)
C(13)	-2456 (7)	8441 (14)	832 (7)	76 (3)
C(14)	-2074 (7)	8962 (14)	276 (7)	78 (4)
C(15)	-1380 (7)	8578 (16)	166 (8)	86 (4)
C(16)	-1090 (6)	7494 (13)	697 (6)	63 (3)
C(17)	-2043 (5)	3768 (10)	1848 (6)	42 (2)
C(18)	-2285 (5)	2095 (11)	1827 (6)	50 (3)
C(19)	-2097 (4)	1034 (9)	2445 (6)	38 (2)
N(20)	-1440 (4)	1004 (8)	2732 (4)	40 (2)
C(21)	-1290 (5)	-53 (11)	3271 (5)	48 (3)
C(22)	-1764 (5)	-1108 (12)	3553 (6)	54 (3)
C(23)	-2443 (6)	-1051 (11)	3290 (6)	56 (3)
C(24)	-2608 (6)	-15 (11)	2733 (5)	57 (3)

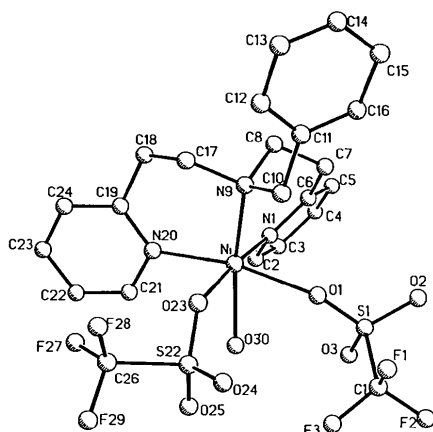


Fig. 1. A view of the title compound.

carbon linked to a second bis[2-(2-pyridyl)ethyl]-benzylamine group (Karlin, Shi, Hayes, McKown, Hutchinson & Zubieta, 1984), have been implicated as model systems for copper metalloenzymes (Karlin, Haka, Cruse, Meyer, Farooq, Gultneh, Hayes &

Table 2. Bond distances (\AA) and angles ($^\circ$) for [Ni(bpeb)(CF₃SO₃)₂(H₂O)]

Ni—O(1)	2.185 (5)	C(3)—C(4)	1.361 (16)
Ni—O(23)	2.129 (6)	C(4)—C(5)	1.393 (15)
Ni—O(30)	2.149 (7)	C(5)—C(6)	1.379 (14)
Ni—N(1)	2.073 (8)	C(6)—C(7)	1.528 (18)
Ni—N(9)	2.134 (7)	C(7)—C(8)	1.511 (12)
Ni—N(20)	2.103 (7)	C(8)—N(9)	1.503 (11)
S(1)—O(1)	1.445 (6)	N(9)—C(10)	1.516 (10)
S(1)—O(2)	1.414 (8)	N(9)—C(17)	1.496 (11)
S(1)—O(3)	1.433 (8)	C(10)—C(11)	1.525 (12)
S(1)—C(1)	1.797 (14)	C(11)—C(12)	1.378 (13)
C(1)—F(1)	1.308 (16)	C(11)—C(16)	1.357 (14)
C(1)—F(2)	1.318 (15)	C(12)—C(13)	1.372 (16)
C(1)—F(3)	1.309 (15)	C(13)—C(14)	1.305 (18)
S(22)—O(23)	1.442 (6)	C(14)—C(15)	1.373 (18)
S(22)—O(24)	1.414 (8)	C(15)—C(16)	1.429 (18)
S(22)—O(25)	1.441 (8)	C(17)—C(18)	1.496 (13)
S(22)—C(26)	1.836 (12)	C(18)—C(19)	1.465 (14)
C(26)—F(27)	1.282 (14)	C(19)—N(20)	1.350 (11)
C(26)—F(28)	1.306 (14)	C(19)—C(24)	1.413 (13)
C(26)—F(29)	1.323 (14)	N(20)—C(21)	1.344 (12)
N(1)—C(2)	1.357 (13)	C(21)—C(22)	1.368 (14)
N(1)—C(6)	1.352 (13)	C(22)—C(23)	1.373 (15)
C(2)—C(3)	1.375 (15)	C(23)—C(24)	1.362 (14)
O(1)—Ni—O(23)	86.2 (3)	F(28)—C(26)—F(29)	107.2 (10)
O(1)—Ni—O(30)	80.7 (3)	Ni—N(1)—C(2)	119.4 (7)
O(23)—Ni—O(30)	88.2 (2)	Ni—N(1)—C(6)	123.4 (6)
O(1)—Ni—N(1)	91.6 (3)	C(2)—N(1)—C(6)	117.1 (8)
O(23)—Ni—N(1)	175.7 (3)	N(1)—C(2)—C(3)	122.9 (10)
O(30)—Ni—N(1)	87.8 (3)	C(2)—C(3)—C(4)	119.5 (10)
O(1)—Ni—N(9)	90.3 (3)	C(3)—C(4)—C(5)	119.1 (10)
O(23)—Ni—N(9)	87.5 (3)	C(4)—C(5)—C(6)	118.8 (10)
O(30)—Ni—N(9)	170.2 (3)	N(1)—C(6)—C(5)	122.7 (9)
N(1)—Ni—N(9)	96.2 (3)	N(1)—C(6)—C(7)	117.2 (8)
O(1)—Ni—N(20)	168.8 (3)	C(5)—C(6)—C(7)	120.2 (9)
O(23)—Ni—N(20)	85.7 (2)	C(6)—C(7)—C(8)	112.1 (8)
O(30)—Ni—N(20)	91.4 (3)	C(7)—C(8)—N(9)	115.1 (7)
N(1)—Ni—N(20)	96.1 (3)	Ni—N(9)—C(8)	109.3 (5)
N(9)—Ni—N(20)	97.0 (3)	Ni—N(9)—C(10)	111.0 (5)
O(1)—S(1)—O(2)	115.3 (5)	C(8)—N(9)—C(10)	109.7 (7)
O(1)—S(1)—O(3)	112.6 (4)	Ni—N(9)—C(17)	110.1 (5)
O(2)—S(1)—O(3)	117.0 (5)	C(8)—N(9)—C(17)	108.5 (7)
O(1)—S(1)—C(1)	102.0 (5)	C(10)—N(9)—C(17)	108.2 (6)
O(2)—S(1)—C(1)	103.6 (5)	N(9)—C(10)—C(11)	116.1 (7)
O(3)—S(1)—C(1)	104.0 (6)	C(10)—C(11)—C(12)	121.8 (8)
Ni—O(1)—S(1)	139.2 (3)	C(10)—C(11)—C(16)	119.4 (8)
S(1)—C(1)—F(1)	112.1 (9)	C(12)—C(11)—C(16)	118.7 (9)
S(1)—C(1)—F(2)	111.2 (9)	C(11)—C(12)—C(13)	120.6 (10)
F(1)—C(1)—F(2)	106.2 (11)	C(12)—C(13)—C(14)	119.8 (12)
S(1)—C(1)—F(3)	112.6 (10)	C(13)—C(14)—C(15)	124.2 (13)
F(1)—C(1)—F(3)	107.1 (11)	C(14)—C(15)—C(16)	115.5 (12)
F(2)—C(1)—F(3)	107.3 (10)	C(11)—C(16)—C(15)	121.1 (12)
O(23)—S(22)—O(24)	115.1 (5)	N(9)—C(17)—C(18)	117.5 (7)
O(23)—S(22)—O(25)	112.8 (4)	C(17)—C(18)—C(19)	119.4 (8)
O(24)—S(22)—O(25)	116.5 (5)	C(18)—C(19)—N(20)	121.3 (8)
O(23)—S(22)—C(26)	101.2 (5)	C(18)—C(19)—C(24)	119.5 (8)
O(24)—S(22)—C(26)	105.1 (5)	N(20)—C(19)—C(24)	119.2 (8)
O(25)—S(22)—C(26)	103.8 (5)	Ni—N(20)—C(19)	124.1 (6)
Ni—O(23)—S(22)	137.3 (4)	Ni—N(20)—C(21)	116.8 (6)
S(22)—C(26)—F(27)	111.8 (8)	C(19)—N(20)—C(21)	118.6 (8)
S(22)—C(26)—F(28)	110.2 (8)	N(20)—C(21)—C(22)	124.0 (9)
F(27)—C(26)—F(28)	110.8 (10)	C(21)—C(22)—C(23)	118.2 (10)
S(22)—C(26)—F(29)	107.9 (8)	C(22)—C(23)—C(24)	119.1 (10)
F(27)—C(26)—F(29)	108.7 (11)	C(19)—C(24)—C(23)	120.9 (10)

Zubieta, 1988). Bis[2-(2-pyridyl)ethyl]benzylamine derivatives have been anchored on various types of polymer matrices and developed as transition-metal-selective chelating resins (Sahni & Reedijk, 1988). The Ni—N bond distances of 2.073–2.134 \AA in the title complex are comparable with those

found in the five-coordinate N,N,N' -tris[2-(2'-pyridyl)ethyl]ethane-1,2-diaminenickel(II) perchlorate of 2·011–2·124 Å (Hoskins & Whillans, 1975).

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Structure of 3,3'-Dimethyl-4,4'-diphenyl-2,2',5,5'-tetrathiafulvalenium Octachlorodirhenate–Dichloromethane (1/2)

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Abstract. $2C_{20}H_{16}S_4^+ \cdot Re_2Cl_8^{2-} \cdot 2CH_2Cl_2$, $M_r = 1595.10$, triclinic, $P\bar{1}$, $a = 9.969$ (9), $b = 10.656$ (8), $c = 13.570$ (8) Å, $\alpha = 105.01$ (6), $\beta = 102.58$ (6), $\gamma = 91.58$ (5)°, $V = 1353.5$ Å³, $Z = 1$, $D_x = 1.957$ g cm⁻³, $\lambda(Mo K\alpha) = 0.71073$ Å, $\mu = 133.61$ cm⁻¹, $F(000) = 770$, $T = 293$ K, $R = 0.036$ for 2801 reflections with $I \geq 6\sigma(I)$. The methyl and phenyl groups are *trans* to each other with respect to the central tetrathiafulvalene part. The structure consists of isolated organic dimers. The eclipsed intradimer overlap of organic molecules implies short S··S contacts ranging from 3.47 to 3.52 Å. The Re—Re bond lengths in the $Re_2Cl_8^{2-}$ dianion are close to those commonly observed for an Re—Re quadruple bond in such a unit.

Experimental. Dimethyldiphenyltetrathiafulvalene (DMDPhTTF) was prepared as described by Takamisawa & Hirai (1969). Its anodic oxidation (10^{-3} M) on a platinum-wire electrode under low constant current ($I = 1.0$ µA) in a dichloromethane solution of the octachlorodirhenate tetrabutylammonium salt (10^{-2} M), which also acted as supporting electrolyte leads, produced blue needle crystals (1–2 mm long) after two weeks. A crystal of dimensions $0.8 \times 0.1 \times 0.25$ mm was selected for the

intensity-data collections which were carried out on an Enraf–Nonius CAD-4 diffractometer equipped with graphite-monochromatized Mo $K\alpha$ radiation. The cell dimensions were obtained and refined by least squares from setting angles of 25 centered reflections ($\theta \leq 15^\circ$). 4759 reflections were recorded by a θ – 2θ scan in the range $2 \leq 2\theta \leq 50^\circ$ and $0 \leq h \leq 11$, $-12 \leq k \leq 12$, $-16 \leq l \leq 16$. Three standard reflections measured every hour: no fluctuations in intensity. The intensities were corrected for Lorentz–polarization and absorption phenomena. The latter correction was performed using the *DIFABS* procedure (Walker & Stuart, 1983) (correction factors 0.783–1.300). The structure was solved by direct methods (*MULTAN84*; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1984) and successive Fourier difference syntheses. 2801 independent reflections with $I \geq 6\sigma(I)$, after averaging the symmetry-related reflections ($R_{int} = 0.036$), were used for the full-matrix least-squares anisotropic (β_{ij}) refinements (on F), secondary extinction refined, $g = 3.75 \times 10^{-10}$, $R = 0.036$, $wR = 0.047$, $w = 4F_o^2/[\sigma(I)^2 + (0.07F_o^2)^2]$, $S = 1.12$, $(\Delta/\sigma)_{max} = 0.01$, $(\Delta\rho)_{max} = 1.28$ e Å⁻³. H atoms were placed at computed positions [$d(C—H) = 1.0$ Å; $B_{eq} = 5.0$ Å²] and not refined. The scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). All the calculations were performed on a

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