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**Structure of *cis*-Bis(2,2'-bipyridine)bis(benzenethiolato)nickel(II) Dideuteriohydrate,
[Ni(C₁₀H₈N₂)₂(C₆H₅S)₂].D₂O**

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Abstract. $M_r = 609.44$, monoclinic, $P2_1/n$, $a = 15.999$ (2), $b = 12.421$ (1), $c = 15.343$ (2) Å, $\beta = 106.61$ (1)°, $V = 2921.6$ (6) Å³, $Z = 4$, $D_x = 1.385$, $D_m = 1.361$ g cm⁻³, $\lambda(\text{Cu } K\alpha) = 1.54184$ Å, $\mu(\text{Cu } K\alpha) = 17.7$ cm⁻¹, $F(000) = 816$, room temperature. $R = 0.077$ for 3973 observed reflections. The Ni^{II} coordination is a distorted octahedron with two chelating bipyridine ligands and two thiophenolate anions. The complex has approximate 2 (C_2) symmetry. Hydrogen bonding between an S atom and the D₂O molecule is observed, the S...O distance being 3.220 (8) Å.

Introduction. The title compound was prepared from the reaction of bis(1,5-cyclooctadiene)nickel with diphenyl disulfide, PhSSPh, in the presence of bipyridine. The most plausible structure of the compound deduced from its chemical and spectroscopic analyses is an

octahedral one around a Ni^{II} center with two thiophenolate ligands which are formed by cleavage of the S—S bond in the reactant. However, the structure of complexes of the type NiX₂(bpy)₂ ($X = \text{Cl, Br, etc.}$) has not been confirmed by X-ray study, as the 20-electron configuration is not as common in nickel complexes. An alternative configuration around a nickel(0) center with a neutral non-cleaved diphenyl disulfide ligand cannot be excluded for the compound. Analytical and spectroscopic data do not give a definite conclusion. Thus the crystals have been subjected to X-ray analysis, and the structure of the bis(benzenethiolato) complex formed by the S—S bond cleavage has been unequivocally confirmed.

Experimental. Dark-brown prisms (from a mixture of methanol-d₄ and D₂O), 0.5 × 0.5 × 0.3 mm, Rigaku automated four-circle diffractometer, graphite-monochromated Cu $K\alpha$ radiation, unit-cell dimensions by

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least squares from the 2θ values of 40 reflections; intensities in the range $3^\circ < 2\theta < 120^\circ$ measured with $\omega/2\theta$ scan technique, scan rate $8^\circ (2\theta) \text{ min}^{-1}$, scan width $1.75^\circ (\omega)$ plus α_1 - α_2 divergence; five reference reflections monitored periodically showed no significant intensity deterioration; 4596 measured independent reflections, 530 with no net intensities; no absorption correction; observation threshold value $|F_{\text{lim}}| = 2.44$; standard deviations estimated by $\sigma^2(F_o) = \sigma_p^2(F_o) + qF_o^2$ with $\sigma_p(F_o)$ evaluated from counting statistics and q (3.14×10^{-4}) from variations of monitored reflections; structure solved by direct methods, anisotropic block-diagonal least-squares refinement, $\sum w(|F_o| - |F_c|)^2$ minimized with $w = 1/\sigma^2(F_o)$; 23 H atoms from a difference map, isotropic; 3 H atoms of a phenyl ring (and also deuteriums of D₂O) were not located and were assumed as being present at a distance of 1.00 Å from the attached carbon with sp^2 hybridization; zero reflections (with $|F_c| > |F_{\text{lim}}|$) included in least-squares calculation by assuming $F_o = F_{\text{lim}}$ and $w = 1/\sigma^2(F_{\text{lim}})$; final $R = 0.077$ for 3973 reflections with $F_o \geq 3\sigma$ ($R_w = 0.086$, $S = 2.737$); final $(\Delta/\sigma)_{\text{max}} = 0.2$, final $\Delta\rho$ excursions from +0.53 [near S(2)] to -0.90 (near Ni) e Å⁻³; atomic scattering factors from *International Tables for X-ray Crystallography* (1974); programs: *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), *TBLS* (Takenaka & Sasada, 1972, unpublished), *LISTUP* (Takenaka & Sasada, 1983, unpublished) and *DCMS82* (Takenaka & Sasada, 1982, unpublished).

Discussion. Atomic parameters are listed in Table 1.* As the crystals are centrosymmetric, they contain the Δ and Λ isomers, the structure of the former being shown in Fig. 1. The Ni^{II}-center coordination is a distorted octahedron, and the two S atoms of the thiophenolates occupy *cis* positions in the octahedron.

Bond lengths and angles are listed in Table 2. Bond angles N(1)-Ni-N(2) [$77.3(2)^\circ$] and N(3)-Ni-N(4) [$77.8(2)^\circ$] are very small and four Ni-N-C angles in the chelates are large in comparison with those of the other related nickel bipyridine complexes already reported (Wada, Katayama & Tanaka, 1976; Arora, Carter, Fernando & Seff, 1977), although the four Ni-N bond lengths are similar. No structures of octahedral nickel thiophenolato complexes have, to our knowledge, been reported and the Ni-S bond distances of the present complex are larger than those of [Ni(SC₆H₅)₄]²⁻ or S-bridged [Ni(SC₂H₅)₂]₆ with tetrahedral structures (Swenson, Baenziger &

Coucovanis, 1978; Woodward, Dahl, Abel & Crosse, 1965).

Both bipyridine ligands are essentially planar; maximum shifts of carbons and nitrogens are 0.10 Å. Both thiophenolate anions including S atoms are within 0.05 Å. Most of the bond angles in the bipyridine deviate from 120° . In the six-membered rings small and large angles alternate around the ring and C-N-C angles are noticeably small. Such features have also been observed in uncoordinated bipyridine (Nakatsu, Yoshioka, Matsui, Koda & Ooi, 1982).

The three H atoms bonded to C(3), C(4) and C(5) could not be found, probably due to the large thermal vibration of the molecule.

S(2) forms a hydrogen bond with the deuterated water molecule with S...O 3.220 (8) Å and angle C(1)-S(2)-O 143.7 (2)° as shown in Fig. 2. The distance is similar to those of S...HO bonds reported in other compounds (Kuleshova & Zorkii, 1981).

Table 1. Fractional coordinates and isotropic temperature factors

The B values are the equivalent isotropic temperature factors calculated from the anisotropic thermal parameters using the equation $B = 8\pi^2 (U_1 + U_2 + U_3)/3$, where U_1 , U_2 , and U_3 are the principal components of the mean-square-displacement matrix U . Values in brackets are the anisotropy defined by $[\sum(B - 8\pi^2 U_i)^2/3]^{1/2}$, and those in parentheses are e.s.d.'s; they refer to last decimal places.

	x	y	z	B(Å ²)
Ni	0.5628 (1)	0.2219 (1)	0.3391 (1)	4.76 (38)
S(1)	0.6389 (1)	0.0491 (1)	0.3576 (1)	4.46 (168)
S(2)	0.4326 (1)	0.1204 (1)	0.2590 (1)	4.67 (144)
N(1)	0.5243 (2)	0.2185 (3)	0.4580 (3)	3.2 (8)
N(2)	0.4926 (2)	0.3665 (3)	0.3314 (3)	3.2 (4)
N(3)	0.6770 (2)	0.3088 (3)	0.3960 (3)	3.3 (5)
N(4)	0.6071 (3)	0.2529 (3)	0.2262 (3)	3.8 (7)
C(1)	0.3406 (3)	0.1874 (4)	0.2743 (4)	4.3 (16)
C(2)	0.3071 (4)	0.1537 (7)	0.3451 (4)	7.0 (43)
C(3)	0.2370 (5)	0.2100 (11)	0.3599 (6)	12.9 (117)
C(4)	0.2022 (5)	0.2929 (11)	0.3051 (8)	14.7 (142)
C(5)	0.2324 (5)	0.3242 (7)	0.2352 (7)	10.3 (83)
C(6)	0.3021 (4)	0.2712 (5)	0.2200 (4)	5.7 (28)
C(7)	0.7508 (4)	0.0759 (4)	0.3779 (4)	4.3 (15)
C(8)	0.8070 (4)	0.0831 (6)	0.4683 (5)	6.4 (20)
C(9)	0.8963 (5)	0.1015 (7)	0.4814 (6)	9.0 (40)
C(10)	0.9286 (5)	0.1117 (7)	0.4096 (7)	9.1 (36)
C(11)	0.8756 (4)	0.1090 (6)	0.3230 (5)	7.0 (27)
C(12)	0.7879 (4)	0.0898 (4)	0.3087 (4)	4.7 (14)
C(13)	0.5415 (3)	0.1391 (4)	0.5197 (4)	4.0 (7)
C(14)	0.5083 (4)	0.1366 (5)	0.5924 (4)	4.7 (12)
C(15)	0.4561 (4)	0.2177 (5)	0.6029 (4)	5.2 (14)
C(16)	0.4372 (4)	0.3004 (4)	0.5423 (4)	4.4 (9)
C(17)	0.4720 (3)	0.2988 (4)	0.4692 (3)	3.3 (8)
C(18)	0.4537 (3)	0.3824 (4)	0.3975 (3)	3.2 (7)
C(19)	0.4000 (4)	0.4705 (4)	0.3961 (4)	4.5 (7)
C(20)	0.3864 (4)	0.5440 (5)	0.3251 (4)	5.1 (16)
C(21)	0.4276 (4)	0.5286 (5)	0.2590 (4)	4.7 (14)
C(22)	0.4796 (3)	0.4395 (4)	0.2646 (4)	4.1 (5)
C(23)	0.7097 (3)	0.3345 (4)	0.4823 (4)	4.3 (8)
C(24)	0.7868 (4)	0.3924 (5)	0.5197 (4)	5.5 (17)
C(25)	0.8311 (4)	0.4212 (6)	0.4572 (5)	6.8 (29)
C(26)	0.7991 (4)	0.3963 (5)	0.3658 (5)	5.7 (17)
C(27)	0.7221 (3)	0.3382 (4)	0.3384 (4)	3.8 (11)
C(28)	0.6842 (4)	0.3048 (4)	0.2436 (4)	4.2 (16)
C(29)	0.7272 (4)	0.3184 (5)	0.1774 (4)	5.8 (30)
C(30)	0.6867 (6)	0.2778 (6)	0.0916 (5)	7.9 (45)
C(31)	0.6092 (5)	0.2250 (6)	0.0728 (4)	6.7 (26)
C(32)	0.5717 (4)	0.2158 (5)	0.1417 (4)	5.6 (12)
O	0.4934 (5)	-0.0728 (6)	0.1510 (6)	14.1 (57)

* Lists of structure factors, anisotropic thermal parameters of Ni, N, C and O atoms, atomic parameters of H atoms, and the least-squares planes for the thiophenolates and bipyridines have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38886 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 2. Bond lengths (Å) and angles (°) with their standard deviations in parentheses

Ni-S(1)	2.444 (2)	Ni-S(2)	2.445 (2)
Ni-N(1)	2.088 (4)	Ni-N(2)	2.104 (4)
Ni-N(3)	2.086 (4)	Ni-N(4)	2.086 (4)
S(1)-C(7)	1.758 (6)	S(2)-C(1)	1.765 (6)
N(1)-C(13)	1.340 (7)	N(1)-C(17)	1.344 (6)
N(2)-C(18)	1.348 (6)	N(2)-C(22)	1.339 (7)
N(3)-C(23)	1.316 (7)	N(3)-C(27)	1.342 (6)
N(4)-C(28)	1.348 (7)	N(4)-C(32)	1.340 (8)
C(1)-C(2)	1.406 (9)	C(1)-C(6)	1.365 (8)
C(2)-C(3)	1.393 (13)	C(3)-C(4)	1.346 (15)
C(4)-C(5)	1.352 (14)	C(5)-C(6)	1.371 (11)
C(7)-C(8)	1.424 (9)	C(7)-C(12)	1.368 (8)
C(8)-C(9)	1.403 (11)	C(9)-C(10)	1.350 (13)
C(10)-C(11)	1.358 (12)	C(11)-C(12)	1.377 (10)
C(13)-C(14)	1.366 (8)	C(14)-C(15)	1.347 (9)
C(15)-C(16)	1.361 (8)	C(16)-C(17)	1.387 (7)
C(17)-C(18)	1.480 (7)	C(18)-C(19)	1.388 (7)
C(19)-C(20)	1.390 (8)	C(20)-C(21)	1.373 (8)
C(21)-C(22)	1.373 (8)	C(23)-C(24)	1.402 (8)
C(24)-C(25)	1.393 (10)	C(25)-C(26)	1.384 (10)
C(26)-C(27)	1.386 (8)	C(27)-C(28)	1.466 (8)
C(28)-C(29)	1.390 (9)	C(29)-C(30)	1.385 (11)
C(30)-C(31)	1.359 (11)	C(31)-C(32)	1.361 (10)
S(1)-Ni-S(2)	86.0 (1)	S(1)-Ni-N(1)	98.2 (1)
S(1)-Ni-N(2)	175.3 (1)	S(1)-Ni-N(3)	93.3 (1)
S(1)-Ni-N(4)	89.0 (1)	S(2)-Ni-N(1)	90.4 (1)
S(2)-Ni-N(2)	92.7 (1)	S(2)-Ni-N(3)	174.7 (1)
S(2)-Ni-N(4)	97.0 (1)	N(1)-Ni-N(2)	77.3 (2)
N(1)-Ni-N(3)	94.9 (2)	N(1)-Ni-N(4)	170.1 (2)
N(2)-Ni-N(3)	88.4 (2)	N(2)-Ni-N(4)	95.6 (2)
N(3)-Ni-N(4)	77.8 (2)	Ni-S(1)-C(7)	107.6 (2)
Ni-S(2)-C(1)	108.3 (2)	Ni-N(1)-C(13)	125.4 (3)
Ni-N(1)-C(17)	116.5 (3)	C(13)-N(1)-C(17)	117.8 (4)
Ni-N(2)-C(18)	115.9 (3)	Ni-N(2)-C(22)	125.8 (3)
C(18)-N(2)-C(22)	118.2 (4)	Ni-N(3)-C(23)	126.6 (4)
Ni-N(3)-C(27)	115.9 (3)	C(23)-N(3)-C(27)	117.6 (4)
Ni-N(4)-C(28)	115.6 (3)	Ni-N(4)-C(32)	126.2 (4)
C(28)-N(4)-C(32)	117.8 (5)	S(2)-C(1)-C(2)	118.6 (5)
S(2)-C(1)-C(6)	121.8 (5)	C(2)-C(1)-C(6)	119.6 (6)
C(1)-C(2)-C(3)	118.6 (7)	C(2)-C(3)-C(4)	119.4 (10)
C(3)-C(4)-C(5)	122.6 (10)	C(4)-C(5)-C(6)	119.2 (9)
C(1)-C(6)-C(5)	120.6 (6)	S(1)-C(7)-C(8)	120.8 (5)
S(1)-C(7)-C(12)	122.2 (4)	C(8)-C(7)-C(12)	117.0 (5)
C(7)-C(8)-C(9)	119.0 (7)	C(8)-C(9)-C(10)	120.6 (8)
C(9)-C(10)-C(11)	121.3 (8)	C(10)-C(11)-C(12)	118.9 (7)
C(7)-C(12)-C(11)	123.2 (6)	N(1)-C(13)-C(14)	122.9 (5)
C(13)-C(14)-C(15)	118.7 (6)	C(14)-C(15)-C(16)	120.5 (6)
C(15)-C(16)-C(17)	118.7 (5)	N(1)-C(17)-C(18)	121.4 (5)
N(1)-C(17)-C(18)	115.1 (4)	C(16)-C(17)-C(18)	123.5 (5)
N(2)-C(18)-C(17)	114.9 (4)	N(2)-C(18)-C(19)	121.4 (5)
C(17)-C(18)-C(19)	123.7 (5)	C(18)-C(19)-C(20)	119.2 (5)
C(19)-C(20)-C(21)	119.2 (6)	C(20)-C(21)-C(22)	118.4 (5)
N(2)-C(22)-C(21)	123.6 (5)	N(3)-C(23)-C(24)	126.0 (5)
C(23)-C(24)-C(25)	114.3 (6)	C(24)-C(25)-C(26)	121.8 (6)
C(25)-C(26)-C(27)	117.6 (6)	N(3)-C(27)-C(28)	122.8 (5)
N(3)-C(27)-C(28)	115.4 (5)	C(26)-C(27)-C(28)	121.9 (5)
N(4)-C(28)-C(27)	115.3 (5)	N(4)-C(28)-C(29)	121.9 (5)
C(27)-C(28)-C(29)	122.6 (5)	C(28)-C(29)-C(30)	117.1 (6)
C(29)-C(30)-C(31)	121.9 (7)	C(30)-C(31)-C(32)	116.9 (7)
N(4)-C(32)-C(31)	124.4 (6)		

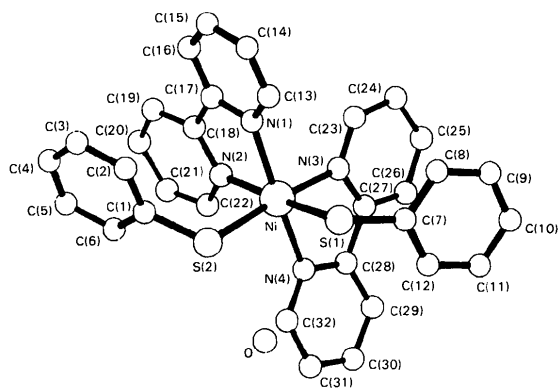


Fig. 1. Atomic numbering and molecular structure.

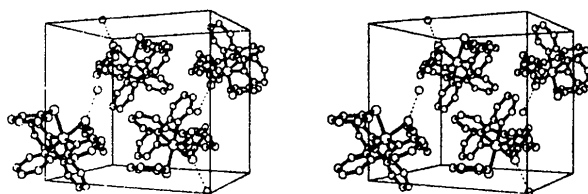


Fig. 2. Crystal structure.

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