Structure of a Tetrahedral Ni^{II} Dibromo Complex with a 6,6'-Disubstituted Bipyridine

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Abstract. Dibromo{dimethyl α,α'-bis(methoxycarbonyl)-[2,2'-bipyridine]-6,6'-dipropionate}nickel(II) hemibenzene solvate, [NiBr$_2$(C$_{22}$H$_{24}$N$_2$O$_8$)].0·5C$_6$H$_6$, $M_r = 702·0$, monoclinic, $P2_1/n$, $a = 11·948$ (2), $b = 15·867$ (5), $c = 16·277$ (6) Å, $\beta = 109·83$ (2)°, $V = 2902·8$ Å^3, $Z = 4$, $D_x = 1·61$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0·71073$ Å, $\mu = 34·43$ cm^{-1}, $F(000) = 1412$, $T = 292$ K, $R = 0·055$ for 2880 observations with $I > \sigma(I)$ (of 5093 unique data). The crystals were obtained from the reaction of the free ligand and anhydrous NiBr$_2$ in dichloromethane. The planar pyridine rings [maximum deviations 0·006 (7) and 0·008 (6) Å, respectively] form a dihedral angle of 5·9 (8)°, while the dihedral angle between the NiN$_2$ plane and NiBr$_2$ plane is 94·98 (14)° yielding an overall distorted tetrahedral molecular geometry. Ni—Br distances are 2·322 (1) and 2·336 (1) Å, and the Br—Ni—Br angle is 122·87 (4)°. The Ni—N distances are 1·981 (4) and 2·004 (4) Å. High thermal parameters exhibited by the methyl ester substituents and the solvent molecule suggest unresolved disorder. The benzene molecule lies on a center of symmetry.

Experimental. The title compound (I) was obtained as the hemibenzene solvate by slow evaporation of a dilute benzene solution of the complex, yielding purple crystals, dimensions of sample 0·12 × 0·28 × 0·32 mm. Space group from systematic absences $h0l$ with $h + l$ odd, and $0k0$ with k odd. Enraf–Nonius CAD-4 diffractometer with graphite monochromator and Mo $K\alpha$ radiation. Cell dimensions from setting

(I), R = CO$_2$CH$_3$
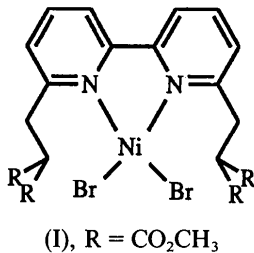
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angles of 25 reflections having $20 < 2\theta < 23°$. Data collection by ω–2θ scans designed for $I = 50\sigma(I)$, subject to 120 s maximum scan time. Scan rates varied 0·39–4·0° min^{-1}. Reflections having $1 < \theta < 25°$, $0 \le h \le 14$, $0 \le k \le 18$, $-19 \le l \le 19$ measured, corrected for background, Lorentz and polarization effects. Absorption correction by ψ scans, minimum relative transmission 71%. Standard reflections 600, 040, 004, ±2·6% maximum variation. Redundant $0kl$ and $0k\bar{l}$ data averaged to give 5093 unique reflections, $R_{int} = 0·025$. Structure solved by heavy-atom methods, refined by full-matrix least squares based on F using data for which $I > \sigma(I)$, 2213 unobserved reflections, $w = \sigma^{-2}(F_o)$, with Enraf–Nonius *SDP* (Frenz & Okaya, 1980). Non-H atoms anisotropic; H

Table 1. *Coordinates and equivalent isotropic thermal parameters*

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{eq}(\text{Å}^2)$
Ni	0·63565 (6)	0·18119 (5)	0·60603 (4)	3·48 (2)
Br1	0·82153 (6)	0·24608 (5)	0·64131 (4)	5·78 (2)
Br2	0·46855 (6)	0·25011 (5)	0·61466 (4)	6·20 (2)
N1	0·6862 (4)	0·0715 (3)	0·6652 (3)	3·3 (1)
N2	0·6143 (4)	0·1125 (3)	0·4984 (3)	3·6 (1)
O1	0·6578 (3)	0·1725 (3)	1·0099 (2)	4·9 (1)
O2	0·6920 (4)	0·2581 (3)	0·9141 (2)	6·5 (1)
O3	0·6514 (3)	−0·0138 (2)	0·9536 (2)	5·1 (1)
O4	0·5141 (4)	0·0481 (3)	0·8405 (2)	5·6 (1)
O5	0·8056 (4)	0·2660 (3)	0·3679 (2)	6·1 (1)
O6	0·6373 (4)	0·2512 (4)	0·2611 (3)	10·3 (2)
O7	0·6554 (5)	0·4285 (3)	0·3639 (3)	8·4 (2)
O8	0·5001 (5)	0·4014 (4)	0·4051 (4)	10·7 (2)
C1	0·7230 (5)	0·0569 (3)	0·7512 (3)	3·7 (1)
C2	0·7701 (6)	−0·0199 (4)	0·7849 (4)	5·2 (2)
C3	0·7805 (6)	−0·0821 (4)	0·7288 (4)	5·7 (2)
C4	0·7419 (6)	−0·0675 (4)	0·6406 (4)	5·2 (2)
C5	0·6939 (5)	0·0099 (3)	0·6095 (3)	3·8 (1)
C6	0·6500 (5)	0·0322 (4)	0·5172 (3)	3·8 (1)
C7	0·6415 (6)	−0·0261 (4)	0·4523 (4)	5·2 (2)
C8	0·5961 (6)	0·0001 (5)	0·3668 (4)	6·4 (2)
C9	0·5591 (6)	0·0803 (5)	0·3471 (4)	5·6 (2)
C10	0·5692 (5)	0·1375 (4)	0·4145 (3)	4·4 (2)
C11	0·7091 (5)	0·1308 (4)	0·8056 (3)	4·2 (2)
C12	0·7092 (5)	0·1095 (4)	0·8969 (3)	3·7 (1)
C13	0·6113 (5)	0·0443 (4)	0·8927 (3)	3·9 (1)
C14	0·6848 (5)	0·1896 (4)	0·9394 (3)	4·0 (1)
C15	0·5650 (6)	−0·0780 (4)	0·9533 (4)	7·3 (2)
C16	0·6292 (6)	0·2438 (4)	1·0548 (4)	6·2 (2)
C17	0·5313 (5)	0·2264 (5)	0·3964 (3)	5·2 (2)
C18	0·6332 (6)	0·2883 (4)	0·4011 (3)	5·0 (2)
C19	0·6900 (5)	0·2662 (5)	0·3344 (4)	5·4 (2)
C20	0·5853 (6)	0·3781 (5)	0·3906 (4)	6·4 (2)
C21	0·8681 (6)	0·2509 (6)	0·3076 (5)	9·1 (3)
C22	0·6228 (9)	0·5161 (5)	0·3509 (6)	11·6 (4)
C1S	0·9239 (9)	0·0266 (7)	0·4198 (7)	13·6 (4)
C2S	0·9287 (7)	0·0689 (6)	0·4949 (6)	11·6 (3)
C3S	1·0006 (8)	0·0467 (7)	0·5756 (6)	13·2 (4)

Table 2. *Bond distances* (Å), *bond angles* (°), *and selected torsion angles* (°)

Ni	Br1	2·336 (1)	C1	C2	1·376 (8)
Ni	Br2	2·322 (1)	C1	C11	1·513 (8)
Ni	N1	1·981 (4)	C2	C3	1·377 (9)
Ni	N2	2·004 (4)	C3	C4	1·371 (8)
N1	C1	1·337 (6)	C4	C5	1·377 (8)
N1	C5	1·358 (7)	C5	C6	1·457 (7)
N2	C6	1·346 (7)	C6	C7	1·382 (8)
N2	C10	1·348 (6)	C7	C8	1·376 (8)
O1	C14	1·320 (7)	C8	C9	1·35 (1)
O1	C16	1·450 (8)	C9	C10	1·396 (9)
O2	C14	1·176 (7)	C10	C17	1·481 (9)
O3	C13	1·319 (6)	C11	C12	1·524 (8)
O3	C15	1·448 (8)	C12	C13	1·546 (8)
O4	C13	1·185 (6)	C12	C14	1·521 (8)
O5	C19	1·302 (7)	C17	C18	1·545 (9)
O5	C21	1·44 (1)	C18	C19	1·50 (1)
O6	C19	1·169 (6)	C18	C20	1·52 (1)
O7	C20	1·33 (1)	C1S	C2S	1·38 (2)
O7	C22	1·44 (1)	C1S	C3S	1·46 (2)
O8	C20	1·18 (1)	C2S	C3S	1·35 (1)
Br1	Ni	Br2	122·87 (4)	N2	C6	C5	116·1 (5)
Br1	Ni	N1	99·2 (1)	N2	C6	C7	121·6 (5)
Br1	Ni	N2	106·4 (1)	C5	C6	C7	122·3 (5)
Br2	Ni	N1	120·7 (1)	C6	C7	C8	118·3 (6)
Br2	Ni	N2	116·9 (1)	C7	C8	C9	120·6 (6)
N1	Ni	N2	82·8 (2)	C8	C9	C10	119·6 (5)
Ni	N1	C1	126·8 (4)	N2	C10	C9	120·2 (6)
Ni	N1	C5	112·7 (3)	N2	C10	C17	118·2 (5)
C1	N1	C5	120·0 (4)	C9	C10	C17	121·6 (5)
Ni	N2	C6	112·3 (3)	C1	C11	C12	115·8 (5)
Ni	N2	C10	127·9 (4)	C11	C12	C13	110·8 (4)
C6	N2	C10	119·8 (5)	C11	C12	C14	108·7 (5)
C14	O1	C16	116·6 (5)	C13	C12	C14	108·7 (5)
C13	O3	C15	114·4 (4)	O3	C13	O4	126·3 (6)
C19	O5	C21	115·9 (4)	O3	C13	C12	111·0 (4)
C20	O7	C22	117·3 (7)	O4	C13	C12	122·8 (5)
N1	C1	C2	121·0 (5)	O1	C14	O2	124·2 (6)
N1	C1	C11	114·5 (4)	O1	C14	C12	111·4 (5)
C2	C1	C11	124·4 (5)	O2	C14	C12	124·4 (6)
C1	C2	C3	119·2 (5)	C10	C17	C18	114·4 (5)
C2	C3	C4	119·9 (6)	C17	C18	C19	110·9 (5)
C3	C4	C5	119·1 (6)	C17	C18	C20	109·2 (6)
N1	C5	C4	120·7 (5)	C19	C18	C20	112·4 (6)
N1	C5	C6	115·5 (5)	O5	C19	O6	123·7 (7)
C4	C5	C6	123·7 (5)	O5	C19	C18	111·9 (4)
O6	C19	C18	124·5 (6)	C2S	C1S	C3S	120·3 (8)
O7	C20	O8	123·9 (7)	C1S	C2S	C3S	123·8 (9)
O7	C20	C18	110·1 (6)	C1S	C3S	C2S	115·9 (9)
O8	C20	C18	125·9 (7)				
N2	Ni	N1	C5	6·3 (4)	N2	C10	C17	C18	83·2 (7)
N1	Ni	N2	C6	−4·1 (4)	C1	C11	C12	C13	−56·2 (7)
Ni	N1	C5	C6	−7·4 (6)	C1	C11	C12	C14	−175·6 (5)
Ni	N2	C6	C5	1·3 (6)	C11	C12	C13	O3	137·2 (5)
C16	O1	C14	C12	−178·3 (5)	C11	C12	C14	O1	166·1 (5)
C15	O3	C13	C12	−179·4 (5)	C13	C12	C14	O2	−136·4 (6)
C21	O5	C19	C18	−176·2 (6)	C10	C17	C18	C19	61·3 (6)
C22	O7	C20	C18	−179·9 (6)	C10	C17	C18	C20	−174·2 (5)
N1	C1	C11	C12	160·1 (5)	C17	C18	C19	O5	−133·1 (6)
N1	C5	C6	N2	4·1 (8)	C17	C18	C20	O7	−158·2 (5)
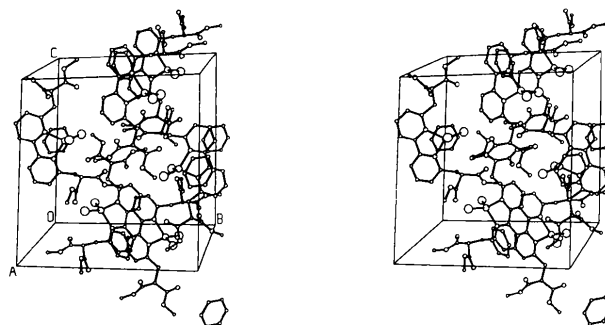
Fig. 2. Stereoview of the unit cell.

atoms were located in difference maps and included as fixed contributions with C—H 0·95 Å and $B = 1·3 \times B_{eq}$ for the bonded C atom. Solvent H atoms were ignored. Atomic scattering factors of Cromer & Waber (1974), anomalous coefficients of Cromer (1974). Final $R = 0·055$, $wR = 0·041$, $S = 1·646$ for 344 variables, extinction coefficient $g = 8·2$ (9) $\times 10^{-8}$ where the correction factor $(1 + gI_c)^{-1}$ was applied to F_c, maximum shift in final cycle $0·11\sigma$, maximum residual density 0·39, minimum $-0·32\,e\,Å^{-3}$. Atomic coordinates and equivalent isotropic thermal parameters are given in Table 1,* bond distances, angles, and selected torsion angles in Table 2. Fig. 1 shows the atom-numbering scheme, Fig. 2 illustrates the molecular packing.

Related literature. Crystal structures of (2,2′-biquinolyl)dibromonickel(II) and (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline)diiodonickel(II), which also contain tetrahedral Ni^II: Butcher & Sinn (1977); crystal structure of the PdCl_2 complex of the analogous phenanthroline ligand: Fronczek, Kahwa, Lu, Newkome, Ollino, Pitts, Sittattrakul, Wang & Watkins (1988).

* Lists of H-atom coordinates, anisotropic thermal parameters, least-squares planes, and structure-factor amplitudes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52321 (32 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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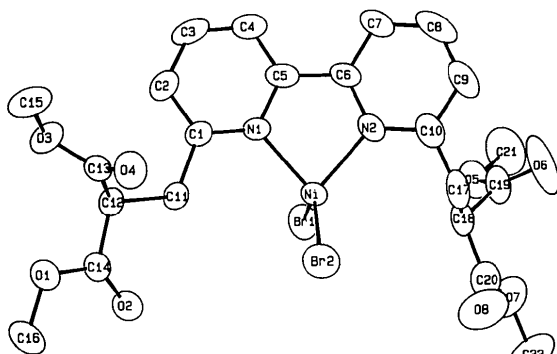
Fig. 1. The molecular structure of (I), with thermal ellipsoids drawn at the 40% probability level, and H atoms omitted.