Instrumental Achievements

Crystal Structure of [*N*,*N*′-Bis(3,5-dinitrosalicylidene)-1,3-propanediaminato)-bis(3,4-dimethylpyridine)]nickel(II)dioxane Solvate

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Nitro groups in organic molecules severely change the characteristics, such as the electron density, acidity and solubility. This situation can be observed very clearly in two hydroxy Schiff bases.[1,2] Due to the electron-withdrawing effect of the nitro group, the electron density of the iminic nitrogen decreases and an unexpected coordination arises.[3]

After a solution of bis-*N*,*N*′-3,5-dinitrosalicylidene-1,3-propanediamine (0.460 g, 1 mmol) in hot dioxane (50 ml) was added to 3,4-dimethylpyridine (0.7 ml), a solution of $NiCl_2 \cdot 6H_2O$ (0.238 g, 1 mmol) in hot MeOH (20 ml) was also added. The resulting mixture was set aside for three days, and light-brown crystals formed were filtered off and dried in air. A chemical diagram of the title compound is shown Fig. 1.

In this study, $[Ni(C_{17}H_{12}N_6O_{10})(C_7H_9N)_2] \cdot 1/2C_4H_8O_2$, the coordination polyhedron around the Ni^{II} atom, has an irregular octahedral environment with two O and two N atoms from the tetradentate *N*,*N*′-bis(dinitrosalicylidene)-(3,5-dinitro $SALPD^{2-}$)-1,3-propanediaminato ligand, forming the equatorial plane; the two N atoms from the two monodentate (4,5-dimethylpyridine) ligands in the apical positions. As shown in Fig. 2, the coordination around the metal atom is generally distorted square planar in these complexes. The Ni–N bond distances are 2.062(3)Å and 2.152(3)Å and the Ni–O bond distances range from 2.064(2) to 2.066(2)Å. The tetradentate ligand, 3,5-dinitro $SALPD^{2-}$, is not planar. The equatorial plane of the irregular octahedral is defined by atoms O1, O2, N1 and N2 [maximum deviation 0.163(2)Å]; the Ni atom is located 0.0554(4)Å from the coordination plane (O1, O2, N1, N2). Among the *cis* bond angles, O2–Ni–N4 [86.82(10)˚] has the greatest deviation from 90˚. Dioxane solvate has a chair conformation and lies on an inversion center. Atoms O11 and $O11^{i}$ [symmetry code: (i) $-x$, $-y$, $-z$] of the dioxane lie +0.5706(13)Å from the plane of the C atoms. The dioxane solvate bridges between the two complexes of the neighbouring unitcell. The Ni···O11 distance is 8.092(10)Å. The crystal structure of the tridentate ONO Schiff base ligand in the presence of some monodentate ligands was studied previously in our laboratory.[4-6]

The crystal and experimental data are given in Table 1. The final atomic parameters are listed in Table 2. Selected bond distances and angles are given in Table 3.

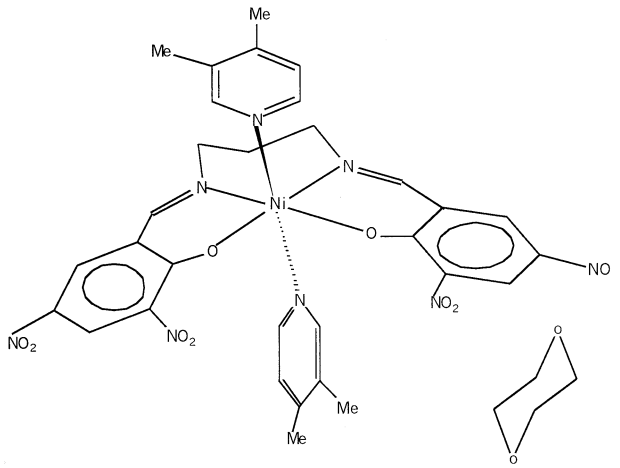

Fig. 1 Chemical diagram.

Table 1 Crystal and experimental data

Formula: $[Ni(C_{17}H_{12}N_6O_{10})(C_7H_9N)_2]1/2C_2H_4O$	
Formula weight = 755.37	
Space group: $P\bar{1}$	$Z = 2$
Crystal system: triclinic	
a = 7.9479(12)Å	α = 84.458(2)˚
b = 11.4217(11)Å	β = 85.842(3)˚
c = 19.9496(13)Å	γ = 82.393(2)˚
V = 1783.4(3)Å^3	
D_x = 1.407 g/cm^3	
μ (Mo K$_\alpha$) = 0.612 mm^{-1}	
T = 295 K	
Color: light brown	
Radiation Mo K$_\alpha$ (λ = 0.71073 Å)	
0.35 × 0.30 × 0.20 mm	
$2\theta_{max}$ = 51.9˚	
No. of reflection = 6984	
No. of reflection used = 5319 ($I > 2\sigma(I)$)	
No. of parameters = 467	
R = 0.045	Rw = 0.124
Goodness-of-fit = 1.07	
$(\Delta\rho)_{max}$ = 0.92 eÅ^{-3}	
$(\Delta\rho)_{min}$ = –0.27 eÅ^{-3}	
Measurement: Enraf-Nonius CAD-4	
Program system: SHELX97	
Structure determination: SHELXS97	
Refinement: full matrix least-square SHELXL97	
Treatment of hydrogen atoms: geometric calculation	

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Table 2 Final atomic coordinates and equivalent isotropic thermal parameters for non-hydrogen atoms

Atom	*x*	*y*	*z*	B_{eq}
Ni	-0.14154(5)	0.16753(3)	-0.272706(18)	2.46(2)
O1	0.0204(3)	0.26622(19)	-0.33273(11)	3.1(5)
O2	0.0206(3)	0.1388(2)	-0.19471(10)	2.9(5)
O3	0.3550(4)	0.4848(3)	-0.3900(2)	7.6(5)
O4	0.2709(5)	0.3867(5)	-0.3038(3)	10.9(8)
O5	-0.0899(5)	0.7686(3)	-0.4845(2)	7.4(5)
O6	-0.3253(4)	0.7081(3)	-0.50414(16)	5.5(5)
O7	0.2728(4)	0.2520(4)	-0.15562(18)	8.0(6)
O8	0.3557(4)	0.1655(4)	-0.0624(2)	7.5(5)
O9	-0.0952(5)	0.1817(3)	0.11427(14)	6.4(5)
O10	-0.3256(5)	0.1133(3)	0.09643(14)	6.1(5)
O11*	0.3564(18)	0.4476(12)	0.0006(8)	16.4(6)
N1	-0.3040(3)	0.2040(2)	-0.35126(12)	2.8(3)
N2	-0.3045(3)	0.0710(2)	-0.21202(13)	2.8(3)
N3	-0.2328(3)	0.3316(2)	-0.22982(13)	2.9(3)
N4	-0.0026(3)	0.0148(2)	-0.31203(13)	3.0(3)
N5	0.2413(4)	0.4426(3)	-0.3538(2)	5.2(4)
N6	-0.1877(5)	0.6930(3)	-0.47859(17)	4.6(4)
N7	0.2451(4)	0.1984(3)	-0.10265(18)	4.7(3)
N8	-0.1882(5)	0.1453(3)	0.07696(15)	4.3(3)
C1	-0.0305(4)	0.3627(3)	-0.36561(15)	2.9(2)
C2	0.0731(4)	0.4576(3)	-0.37926(18)	3.5(3)
C3	0.0228(5)	0.5631(3)	-0.41517(19)	3.8(3)
C4	-0.1359(4)	0.5815(3)	-0.44082(17)	3.5(3)
C5	-0.2405(4)	0.4931(3)	-0.43246(16)	3.2(3)
C6	-0.1929(4)	0.3866(3)	-0.39575(15)	2.8(2)
C7	-0.3088(4)	0.2973(3)	-0.39179(15)	2.9(3)
C8	-0.4314(5)	0.1242(3)	-0.35919(17)	3.6(4)
C9	-0.5330(4)	0.0944(3)	-0.29381(18)	3.8(5)
C10	-0.4314(5)	0.0126(3)	-0.24240(18)	3.8(4)
C11	-0.3073(4)	0.0615(3)	-0.14769(15)	2.9(3)
C12	-0.1911(4)	0.1048(3)	-0.10625(15)	2.8(3)
C13	-0.2376(4)	0.1048(3)	-0.03783(16)	3.1(3)
C14	-0.1328(4)	0.1402(3)	0.00627(15)	3.3(3)
C15	0.0256(5)	0.1692(3)	-0.01558(17)	3.5(4)
C16	0.0754(4)	0.1680(3)	-0.08282(16)	3.2(3)
C17	-0.0287(4)	0.1388(3)	-0.13314(15)	2.7(3)
C18	-0.1161(5)	0.3963(3)	-0.2134(2)	3.9(4)
C19	-0.1520(6)	0.5103(4)	-0.1953(3)	5.3(4)
C20	-0.3198(7)	0.5623(4)	-0.1928(3)	5.8(6)
C21	-0.4394(6)	0.4949(4)	-0.2089(2)	5.5(5)
C22	-0.3933(4)	0.3810(3)	-0.22662(19)	3.9(4)
C23	-0.0089(9)	0.5754(6)	-0.1778(5)	10.9(8)
C24	-0.3695(11)	0.6892(5)	-0.1748(4)	10.9(8)
C25	0.0578(5)	-0.0752(3)	-0.26875(18)	3.7(4)
C26	0.1855(5)	-0.1603(3)	-0.2864(2)	4.3(3)
C27	0.2572(5)	-0.1577(3)	-0.3512(2)	4.0(4)
C28	0.1929(5)	-0.0684(3)	-0.39772(18)	3.7(3)
C29	0.0640(5)	0.0158(3)	-0.37502(16)	3.4(4)
C30	0.4100(7)	-0.2464(4)	-0.3703(3)	6.7(6)
C31	0.2588(7)	-0.0582(4)	-0.4705(2)	5.8(6)
C32*	0.3593(17)	0.5669(13)	-0.0192(8)	10.6(8)
C33*	0.4801(15)	0.6065(11)	0.0230(6)	8.2(8)

$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* (\boldsymbol{a}_i \cdot \boldsymbol{a}_j)$.
* These atoms are refined isotropically and the multiplicity is 0.5.

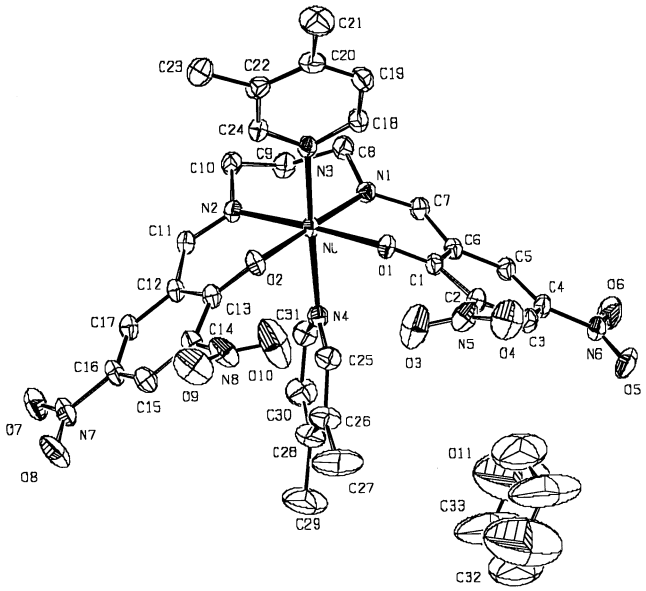

Fig. 2 Molecular structure of the title compound, showing 30% probability displacement ellipsoids. The H atoms have been omitted for clarity.

Table 3 Selected bond distances (Å) and angles (°)

Ni-O1	2.064(2)			Ni-O2	2.066(2)		
Ni-N1	2.079(3)			Ni-N2	2.062(3)		
Ni-N3	2.152(3)			Ni-N4	2.123(4)		
O11-C32	1.385(9)			C32-C33	2.463(9)		
N2	Ni	O2	87.21(9)	N1	Ni	N4	94.99(10)
O1	Ni	O2	92.64(9)	N2	Ni	N3	94.19(10)
N1	Ni	N1	94.25(10)	O1	Ni	N3	85.02(10)
O1	Ni	N1	85.87(9)	O2	Ni	N3	85.02(9)
O2	Ni	N1	177.59(10)	N1	Ni	N3	92.96(10)
N2	Ni	N4	93.50(10)	N4	Ni	N3	168.49(10)

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