Crystal Structure of {2-[(2-Hydroxyphenyl)iminomethyl]-4,6-dinitrophenolato-*O,N,O′*}tris(3-ethylpyridine-*N*)nickel(II)

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Metal-chelate Schiff base complexes have continued to play the role of one of the most important stereochemical models in main-group and transition-metal coordination chemistry due to their preparative accessibility, diversity and structural variability.[1] The behavior of tridentate ONO and ONS Schiff-base ligands in the presence of monodentate ligands have been studied previously with four-coordinate nickel(II). In such complexes, the coordination of nickel is square planar or distorted square planar.[2-4] The title complex, shown in Fig. 1, was studied to determine the effect on coordination when the tridentate ligand has nitro substituents.

The crystalline ligand 3,5-dinitrosalicylaldehyde (0.212 g, l mmol) and 2-aminophenol (0.106 g, 1 mmol) were dissolved in MeCN (50 ml). This solution was heated to boiling point and 3-ethylpyridine (0.75 ml) was added. The resulting solution was mixed with a solution of $NiCl_2 \cdot 6H_2O$ (0.238 g, 1 mmol) in hot MeOH (30 ml) and set aside for 1 h at room temperature.

Table 1 shows the crystal and experimental data. All non-H atoms were refined with anisotropic displacement parameters. H atoms were placed geometrically at 0.95 Å from their parent atoms. For all H atoms, riding model was used with $U_{iso}(H)=1.3U_{eq}(C)$.

The final atomic coordinates, the bond distances and angles are given in Tables 2 and 3. The average Ni–O and Ni–N bond lengths are [2.016(2) and 2.13(3)Å], respectively. The bond lengths and angles are in agreement with values reported previously for Ni(II) complexes.[2-7] All distances and angles are generally as expected. The coordination about the nickel ion is not completely regular; *cis* bond angles at Ni(II) atom range from 82.6(9) to 94.4(9)˚. The best plane is defined by atoms N1, N2, N3 and N4 [maximum deviation 0.042(12)Å] and Ni(II) deviated only 0.009(10)Å from this plane. The dihedral angles between the planes of the two chelating moieties (O1, C1, C6, C7, N1 and N1, C8, C13, O2) has a value of 7.0(2)˚. We attribute this to the inductive effects of the nitro groups, whereby the ability of the tridentate ligands to donate

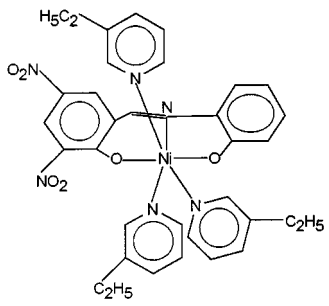

Fig. 1 Chemical structure.

Table 1 Crystal and experimental data

Formula: $C_{34}H_{34}N_6O_6Ni$	
Formula weight=681.38	
Crystal system: triclinic	
Space group: $P\bar{1}$	Z=2
a=11.475(3)Å	α=76.910(15)˚
b=12.930(2)Å	β=65.280(17)˚
c=13.245(2)Å	γ=64.287(15)˚
V=1605.9(5)Å^3	
D_x=1.409 g/cm^3	
μ(Mo K$_\alpha$)=0.66 mm^{-1}	
T=293 K	
Dark red	
F(0 0 0)=712	
Crystal size: 0.40×0.35×0.25 mm	
Radiation=Mo K$_\alpha$	
R=0.0509	
wR=0.1386	
Δ/σ =0.001	
$(\Delta\rho)_{max}$=0.843 eÅ^{-3}	
$(\Delta\rho)_{min}$=0.698 eÅ^{-3}	
$2\theta_{max}$=51.38˚	
No. of reflection used=5170	
No. of parameters=427	
Goodness-of-fit: 1.094	
Measurements: Enraf-Nonius CAD-4 diffractometer	
Program system: CAD-4-EXPRESS software	
Structure determination: SHELXS-86	
Treatment of hydrogen atoms: geometric calculation	
Refinement: full matrix least-squares(SHELXL-97)	

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

Atom	*x*	*y*	*z*	U_{eq}/Å^2
Ni	0.26910(3)	0.76018(3)	0.71302(3)	0.03641(15)
O1	0.4154(2)	0.66793(17)	0.78054(16)	0.0398(4)
O2	0.1421(2)	0.84357(18)	0.62713(17)	0.0453(5)
O3	0.5038(3)	0.6798(3)	0.9369(2)	0.0738(8)
O4	0.6369(3)	0.5097(3)	0.9732(2)	0.0712(7)
O5	1.0267(3)	0.3196(2)	0.6577(3)	0.0838(9)
O6	1.0159(3)	0.3616(3)	0.4944(3)	0.0777(8)
N1	0.4069(2)	0.6954(2)	0.5619(2)	0.0365(5)
N2	0.1158(3)	0.8222(2)	0.8664(2)	0.0425(6)
N3	0.2050(3)	0.6152(2)	0.7520(2)	0.0418(6)
N4	0.3343(3)	0.9043(2)	0.6799(2)	0.0420(6)
N5	0.5868(3)	0.5832(3)	0.9100(2)	0.0514(7)
N6	0.9640(3)	0.3731(3)	0.5946(3)	0.0591(8)
C1	0.5423(3)	0.6056(2)	0.7339(2)	0.0361(6)
C2	0.6339(3)	0.5542(3)	0.7950(2)	0.0418(6)
C3	0.7685(3)	0.4769(3)	0.7519(3)	0.0451(7)
C4	0.8219(3)	0.4527(3)	0.6420(3)	0.0473(7)
C5	0.7430(3)	0.5033(3)	0.5756(3)	0.0482(7)
C6	0.6060(3)	0.5786(2)	0.6178(2)	0.0401(6)
C7	0.5330(3)	0.6239(3)	0.5408(2)	0.0431(7)
C8	0.3420(3)	0.7351(2)	0.4829(2)	0.0385(6)
C9	0.4044(3)	0.7040(3)	0.3724(3)	0.0467(7)
C10	0.3299(4)	0.7455(3)	0.3032(3)	0.0558(8)
C11	0.1911(4)	0.8194(3)	0.3439(3)	0.0551(8)
C12	0.1276(3)	0.8520(3)	0.4519(3)	0.0511(8)
C13	0.2010(3)	0.8130(2)	0.5247(2)	0.0403(6)
C14	0.1332(3)	0.7785(3)	0.9624(2)	0.0529(8)
C15	0.0276(4)	0.8142(3)	1.0636(3)	0.0623(9)
C16	-0.0970(4)	0.8967(4)	1.0659(3)	0.0701(11)
C17	-0.1165(4)	0.9459(4)	0.9683(3)	0.0760(12)
C18	-0.0074(4)	0.9033(3)	0.8702(3)	0.0606(9)
C19	-0.2485(6)	1.0531(5)	0.9655(5)	0.1081(19)
C20	-0.3513(10)	1.0141(9)	0.9744(10)	0.196(5)
C21	0.1142(4)	0.6163(3)	0.7126(3)	0.0517(8)
C22	0.0771(5)	0.5243(4)	0.7289(3)	0.0665(10)
C23	0.1334(5)	0.4272(3)	0.7885(3)	0.0653(10)
C24	0.2247(4)	0.4246(3)	0.8327(3)	0.0518(8)
C25	0.2570(3)	0.5207(3)	0.8112(3)	0.0463(7)
C26	0.2831(5)	0.3234(3)	0.9046(3)	0.0682(10)
C27	0.1832(6)	0.3295(5)	1.0242(4)	0.0876(14)
C28	0.2706(4)	1.0035(3)	0.6329(3)	0.0519(8)
C29	0.3112(4)	1.0948(3)	0.6061(3)	0.0622(10)
C30	0.4230(4)	1.0843(3)	0.6284(3)	0.0624(10)
C31	0.4909(4)	0.9834(3)	0.6766(4)	0.0616(9)
C32	0.4407(4)	0.8971(3)	0.7019(3)	0.0536(8)
C33	0.6142(6)	0.9694(5)	0.7007(7)	0.111(2)
C34	0.7232(6)	0.8605(6)	0.6942(6)	0.126(2)

$U_{eq}=(1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*(\boldsymbol{a}_i\cdot\boldsymbol{a}_j)$.

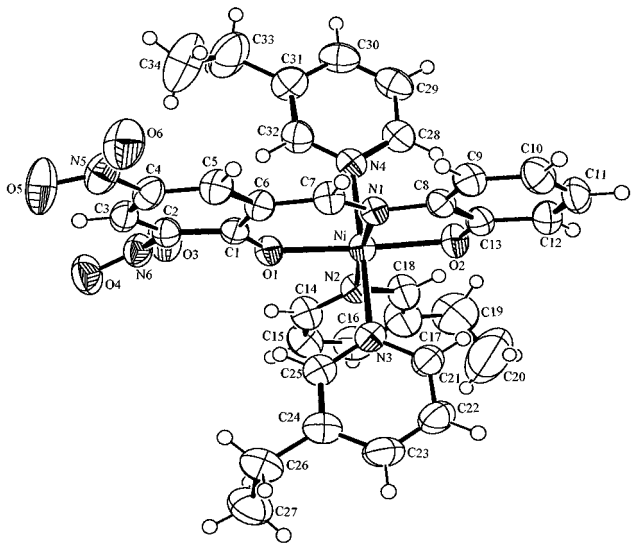

Fig. 2 ORTEP drawing of the title compound with atom labeling.

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

Ni	O1		2.019(2)
Ni	O2		2.012(2)
Ni	N1		2.041(2)
Ni	N2		2.095(2)
Ni	N3		2.183(3)
Ni	N4		2.188(3)
O1	C1		1.268(3)
O2	C13		1.304(3)
O3	N6		1.216(4)
O4	N6		1.225(4)
O5	N5		1.226(4)
O6	N5		1.220(4)
N1	C7		1.283(4)
N1	C8		1.413(4)
N2	C14		1.328(4)
N2	C18		1.334(4)
N3	C25		1.337(4)
N3	C21		1.341(4)
N4	C28		1.331(4)
N4	C32		1.331(4)
N5	C4		1.447(4)
N6	C2		1.466(4)
O1	Ni	N1	90.08(9)
O1	Ni	N2	92.92(9)
O1	Ni	N3	89.38(9)
O1	Ni	N4	88.99(8)
O2	Ni	N2	94.42(9)
O2	Ni	O1	172.65(8)
O2	Ni	N1	82.57(9)
O2	Ni	N3	90.67(9)
O2	Ni	N4	91.11(9)
N1	Ni	N2	175.11(9)
N1	Ni	N3	89.19(9)
N1	Ni	N4	92.17(9)
N2	Ni	N3	86.98(10)
N2	Ni	N4	91.75(10)
N3	Ni	N4	177.89(9)

electron density through their O and N atom is reduced; the increase in the coordination number of the Ni(II) center offsets this potential electron deficit. The coordination number of the previously studied similar structure which does not include nitro group has been reported to be four.[5,6]

The authors wish to acknowledge the purchase of the CAD4 diffractometer under Grant DPT/TBAG1 of the Scientific and Technical Research Council of Turkey.

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(Received August 26, 1998)
(Accepted December 21, 1998)