Crystal structure of *N,O*-(1-methyl-3-oxobutyliden)-*N'*,*N''*-(1-methyl-2-isonitroso-3-oxo-3-phenyl-propyliden)ethylenediaminonickel(II), $Ni(C_{17}H_{19}N_3O_3)$

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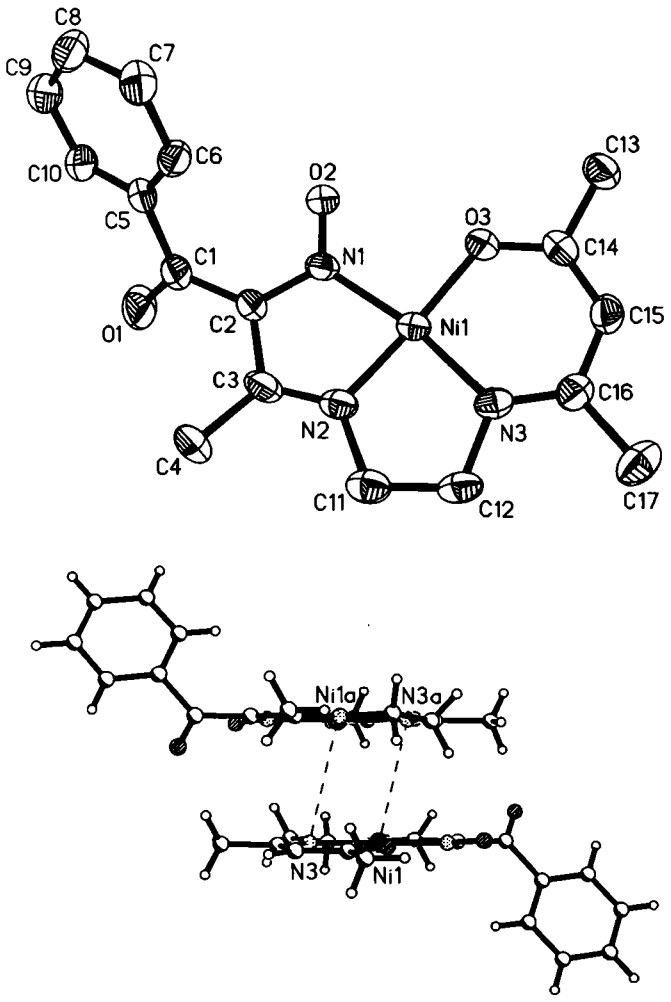
Received December 20, 2004, accepted and available on-line January 15, 2005; CCDC no. 1267/1449



Abstract

$C_{17}H_{19}N_3NiO_3$, trigonal, $R\bar{3}$ (no. 148), $a = 23.241(3)$ Å, $c = 17.080(3)$ Å, $V = 7989.8$ Å^3, $Z = 6$, $R_{gt}(F) = 0.088$, $wR_{ref}(F^2) = 0.243$, $T = 293$ K.

Source of material

Isonitrosobenzoylacetoacetate was prepared according to the method reported in [1]. 1.0 mmol isonitrosobenzoylacetoacetate and 1.0 mmol $Ni(CH_3COO)_2 \cdot 4H_2O$ in 20 mL of ethyl alcohol were mixed and stirred at room temperature for 15 minutes. The resulting solution was added to a solution of 1.0 mmol acetylacetone and 0.5 mL ethylenediamine in 20 mL of ethyl alcohol, and stirred for 3 h under reflux. The red orange precipitate was washed with hot EtOH, and recrystallized from trichloromethane giving dark-red prismatic crystals. It was difficult to grow better single crystals suitable for X-ray analysis by tried conventional solution method.

Discussion

Oxime derivatives are interesting ligands since the ketoximes are found to chelate transition metals through the N (oxime) and/or O (ketone) atoms. In view of the general interest in the factors determining the geometries and structures of ketoximato complexes, we have investigated the structure of the complex with ketoxime ligand [1-3]. Here we will report the structure of a new nickel(II) complex with unsymmetric quadridentate Schiff base with oxime group.

The crystal structure consists of discrete complex molecules. The double deprotonated Schiff base ligand is quadridentate and binds to the Ni(II) via the oximo nitrogen (N1), the two imine nitrogens (N2, N3), and the carbonyl oxygen (O3) (figure, top). This multidentate binding leads to the formation of two adjacent five-membered chelate rings and one six-membered chelate ring (5–5–6). The oximo group coordinates to the central atom through its oximo-nitrogen atom, not through the oximo-oxygen atom, such as it does in a Cu(II) complex with similar ligand [4]. The bond lengths of Ni1—N1, Ni1—N2, Ni1—N3 and Ni1—O3 are 1.873(5) Å, 1.798(5) Å, 1.852(5) Å and 1.817(4) Å, respectively. Except atoms C1, C5, C6, C7, C8, C9, C10 and O1 of benzoyl, the non-hydrogen atoms of the compound are planar (r.m.s. deviation 0.0615 Å). The distances between the molecule plane and the adjacent molecule (a) [symmetry code (a) $\frac{2}{3}-x,\frac{1}{3}-y,\frac{1}{3}-z$] plane is 3.378(8) Å (figure, bottom). It indicates that strong face-to-face π-π stacking interactions exist between these two molecules.

Table 1. Data collection and handling.

Crystal:	dark-red prism, size 0.20 × 0.20 × 0.40 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	11.12 cm^{-1}
Diffractometer, scan mode:	Rigaku R-AXIS RAPID, ω
$2\theta_{max}$:	54.96°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	23967, 4045
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2114
$N(param)_{refined}$:	217
Programs:	SHELXS-97 [5], SHELXL-97 [6]

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Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{iso}
H(4A)	6f	0.5144	0.1945	0.0119	0.190
H(4B)	6f	0.5518	0.2670	0.0434	0.190
H(4C)	6f	0.5303	0.2535	–0.0442	0.190
H(6)	6f	0.4080	0.3237	–0.0980	0.095
H(7)	6f	0.3996	0.3877	–0.1981	0.122
H(8)	6f	0.4814	0.4994	–0.2096	0.134
H(9)	6f	0.5648	0.5476	–0.1181	0.132
H(10)	6f	0.5721	0.4844	–0.0184	0.122
H(11A)	6f	0.4027	0.1026	–0.0057	0.116
H(11B)	6f	0.4294	0.1135	0.0793	0.116
H(12A)	6f	0.3351	0.0479	0.1246	0.113
H(12B)	6f	0.3122	0.0272	0.0393	0.113
H(13A)	6f	0.1655	0.2090	0.1008	0.128
H(13B)	6f	0.1256	0.1497	0.1576	0.128
H(13C)	6f	0.1118	0.1405	0.0678	0.128
H(15)	6f	0.1351	0.0457	0.1151	0.112
H(17A)	6f	0.2322	–0.0303	0.1033	0.139
H(17B)	6f	0.1632	–0.0453	0.0719	0.139
H(17C)	6f	0.1789	–0.0334	0.1612	0.139

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni(1)	6f	0.32793(4)	0.18246(4)	0.06813(4)	0.0721(6)	0.0708(5)	0.0619(5)	0.0453(4)	–0.0013(3)	–0.0001(3)
O(1)	6f	0.5516(3)	0.3806(4)	0.0479(4)	0.062(3)	0.169(6)	0.182(7)	0.029(4)	–0.014(4)	0.068(5)
O(2)	6f	0.3692(2)	0.3188(2)	0.0577(3)	0.077(3)	0.074(3)	0.102(3)	0.042(2)	0.004(2)	0.013(2)
O(3)	6f	0.2557(2)	0.1913(2)	0.0863(3)	0.073(3)	0.083(3)	0.089(3)	0.047(3)	0.005(2)	0.004(2)
N(1)	6f	0.3838(2)	0.2733(3)	0.0493(3)	0.071(3)	0.076(3)	0.076(3)	0.047(3)	–0.003(3)	0.005(3)
N(2)	6f	0.4016(3)	0.1785(3)	0.0463(3)	0.093(4)	0.092(4)	0.074(3)	0.065(4)	0.006(3)	0.004(3)
N(3)	6f	0.2864(3)	0.0913(3)	0.0813(3)	0.094(4)	0.068(3)	0.065(3)	0.047(3)	–0.013(3)	–0.009(2)
C(1)	6f	0.4994(3)	0.3584(4)	0.0140(5)	0.061(4)	0.112(6)	0.112(6)	0.041(4)	0.006(4)	0.028(5)
C(2)	6f	0.4466(3)	0.2907(4)	0.0300(4)	0.061(4)	0.095(5)	0.092(5)	0.043(4)	0.010(3)	0.024(4)
C(3)	6f	0.4548(4)	0.2332(5)	0.0302(5)	0.087(5)	0.127(7)	0.106(6)	0.075(5)	0.017(4)	0.018(5)
C(4)	6f	0.5184(5)	0.2373(6)	0.0081(8)	0.105(7)	0.18(1)	0.23(1)	0.103(7)	0.074(8)	0.082(9)
C(5)	6f	0.4914(3)	0.3990(3)	–0.0508(5)	0.056(4)	0.082(5)	0.114(5)	0.031(3)	0.020(4)	0.019(4)
C(6)	6f	0.4400(3)	0.3697(3)	–0.1026(4)	0.078(4)	0.078(4)	0.074(4)	0.033(4)	0.007(4)	0.012(3)
C(7)	6f	0.4354(4)	0.4070(4)	–0.1617(5)	0.085(5)	0.108(6)	0.098(6)	0.039(5)	0.010(4)	0.006(5)
C(8)	6f	0.4828(5)	0.4732(4)	–0.1674(6)	0.122(7)	0.101(6)	0.114(6)	0.057(6)	0.039(6)	0.037(5)
C(9)	6f	0.5332(4)	0.5014(4)	–0.1150(6)	0.079(5)	0.088(5)	0.146(8)	0.028(5)	0.008(5)	0.022(6)
C(10)	6f	0.5369(4)	0.4646(4)	–0.0556(5)	0.067(4)	0.085(5)	0.138(7)	0.027(4)	0.006(4)	0.022(5)
C(11)	6f	0.3961(4)	0.1131(4)	0.0464(5)	0.123(7)	0.110(6)	0.090(5)	0.083(6)	0.004(5)	–0.002(4)
C(12)	6f	0.3311(4)	0.0638(4)	0.0746(5)	0.131(7)	0.087(5)	0.094(5)	0.076(5)	0.010(5)	0.003(4)
C(13)	6f	0.1452(4)	0.1621(4)	0.1069(5)	0.081(5)	0.128(7)	0.124(6)	0.062(5)	0.020(4)	0.028(5)
C(14)	6f	0.1972(4)	0.1422(4)	0.0997(4)	0.071(4)	0.107(6)	0.084(4)	0.050(4)	–0.001(4)	0.001(4)
C(15)	6f	0.1805(4)	0.0770(4)	0.1051(5)	0.069(4)	0.085(5)	0.107(5)	0.024(4)	–0.009(4)	0.011(4)
C(16)	6f	0.2245(4)	0.0524(4)	0.0987(4)	0.088(5)	0.076(4)	0.076(4)	0.032(4)	–0.016(4)	–0.003(3)
C(17)	6f	0.1970(5)	–0.0209(4)	0.1097(5)	0.143(8)	0.073(5)	0.111(6)	0.038(5)	–0.024(5)	–0.004(4)

Acknowledgment. This project was supported by Education Department of Zhejiang Province (grant no. 20030710).

References

1. Feng, Y.-L.; Liu, S.-X.: Syntheses and Crystal Structures of Three Palladium(II) Complexes with Isonitrosobenzoylacetoneimine Ligand. Chin. J. Chem. **20** (2002) 841-845.
2. Feng, Y.-L.; Liu, S.-X.: Syntheses, Spectral Properties of Palladium(II) Complexes with Isonitrosoethylacetoacetate Imine Ligands, and Crystal Structure of *trans* $Pd(p\text{-}CH_3C_6H_4\text{-}IEAI)_2$. Chin. J. Inorg. Chem. **18** (2002) 229-232.
3. Feng, Y.-L.; Liu, S.-X.: Syntheses and Characterization of Two Palladium Complexes of Isonitrosoacetylacetoneimine. Acta Chim. Sinica **60** (2002) 947-949.
4. Cingi, M. B.; Villa, A. C.; Manfredotti, A. G.; Guastini, C.; Nardelli, M.: The Crystal and Molecular Structure of *N*-(1-methyl-3-oxo-butyliden)-*N'*-(1-methyl-2-isonitroso-3-oxobutyliden)ethylenediaminecopper(II), $Cu(II)(C_{12}H_{17}N_3O_3)$. Acta Crystallogr. B**28** (1972) 1075-1079.
5. Sheldrick, G. M.: Phase Annealing in SHELX-90: Direct Methods for Larger Structures. Acta Crystallogr. A**46** (1990) 467-473.
6. Sheldrick, G. M.: SHELXL-97. Program for the Refinement of Crystal Structures. University of Göttingen, Germany 1997.