Crystal structure of [9,22-(bisbutyloxy)hemiporphyrizinato]nickel(II), $C_{34}H_{30}N_8O_2Ni$

K. Haberoth^I, M. Hanack^I and C. Maichle-Mössmer^{*,II}^I Universität Tübingen, Institut für Organische Chemie II, Auf der Morgenstelle 18, D-72076 Tübingen, Germany^{II} Universität Tübingen, Institut für Anorganische Chemie I, Auf der Morgenstelle 18, D-72076 Tübingen, Germany

Received January 15, 2004, accepted and available on-line February 11, 2004; CCDC no. 1267/1207

Abstract

$C_{34}H_{30}N_8NiO_2$, monoclinic, $P12_1/n1$ (no. 14), $a = 14.048(4)$ Å, $b = 4.7256(1)$ Å, $c = 21.491(6)$ Å, $\beta = 99.10(1)^\circ$, $V = 1408.7$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.054$, $wR_{\text{ref}}(F) = 0.059$, $T = 293$ K.

Source of material

A suspension of 580 mg (1.0 mmol) 9,22-(bisbutyloxy)hemiporphyrizine [1] and 375 mg (1.5 mmol) $Ni(OAc)_2 \cdot 4H_2O$ in 5 ml DMF was stirred at 140 °C for 4 h. After cooling to room temperature water was added to the mixture. The greenish precipitate was filtered and the filtrate rinsed with water. Purification of the title compound was achieved by column chromatography on silica ($CHCl_3/MeOH$, 100:1, v/v; $R_f = 0.18$). A 0.01 M solution of the title compound in $CHCl_3$ was covered with the same volume of *n*-hexane and allowed to stand at room temperature under exclusion of light for one week, yielding bluish-black, needle-like crystals suitable for X-ray structure determination.

Discussion

The crystal structure of the title compound is built up by the centro-symmetric completely planar metal complex molecules, (the atoms N1/N1a/N21/N21a and N20/N20a/N30/N30a show

no deviation from the least-squares planes). The essential feature is the orthorhombic (compressed) environment around nickel with two *trans* metal to isoindole nitrogen distances $d(Ni-N1) = 2.077(3)$ Å and two *trans* metal to pyridine nitrogen distances $d(Ni-N21) = 1.887(3)$ Å. With respect to the bond distances of the four bridging nitrogen atoms N20/N20a/N30/N30a, e.g. $d(N30-C6) = 1.375(5)$ Å and $d(N30-C29) = 1.283(5)$ Å, the title compound should be described as a non-aromatic metal chelate, where two *trans* pyridine units are linked via a single bonds to two *trans* isoindole units.

Along the *b* axis a columnar structure is built up by stacks of tilt metal complexes, leading to a significantly enlarged intermolecular distance $d(Ni \cdots Ni) = 4.7256(1)$ Å. We predict that the pseudo-octahedral environment of the nickel atom (with respect to the additional intermolecular atoms N20 and N20a of the neighbouring metal complexes) stabilizes this stacking along the *b* axis. This new structure differs from the previously reported structure of hemiporphyrizinato nickel(II) [2], which shows cofacial stacking of the non-planar, distorted saddle-shaped molecules and an intermolecular $Ni \cdots Ni$ distance of 3.7637(4) Å.

* Correspondence author

(e-mail: caecilia.maichle-moessmer@uni-tuebingen.de)

Table 1. Data collection and handling.

Crystal:	bluish-black needle, size 0.2 × 0.2 × 0.6 mm
Wavelength:	Cu K α radiation (1.54056 Å)
μ :	13.95 cm ⁻¹
Diffraction, scan mode:	Enraf-Nonius CAD4, ω
$2\theta_{\max}$:	138°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	4444, 2270
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 3 \sigma(I_{\text{obs}})$, 1726
$N(\text{param})_{\text{refined}}$:	206
Programs:	SHELXS-86 [3], SDP [4], PLATON [5]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
H(24)	4e	0.2548	0.4432	0.2184	0.042
H(25)	4e	0.3719	0.7987	0.2142	0.047
H(26)	4e	0.3959	0.9976	0.1180	0.047
H(27)	4e	0.2977	0.8572	0.0227	0.044
H(3)	4e	-0.0558	0.1582	-0.2383	0.039
H(5)	4e	0.1628	0.6287	-0.1464	0.041
H(421)	4e	0.1992	0.6475	-0.2581	0.049
H(422)	4e	0.1355	0.8752	-0.2329	0.049
H(431)	4e	0.1578	1.0148	-0.3333	0.052
H(432)	4e	0.0502	0.9333	-0.3363	0.052
H(441)	4e	0.0817	0.4956	-0.3799	0.063
H(442)	4e	0.1879	0.5878	-0.3792	0.063
H(451)	4e	0.0999	0.6646	-0.4806	0.086
H(452)	4e	0.0295	0.8608	-0.4520	0.086
H(453)	4e	0.1356	0.9530	-0.4513	0.086

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
Ni(1)	2a	0	0	0	0.0454(7)	0.0398(5)	0.0394(4)	-0.0007(5)	0.0045(4)	-0.0017(5)
O(41)	4e	0.0630(2)	0.5228(8)	-0.2606(1)	0.042(2)	0.043(2)	0.026(1)	0.007(1)	0.006(1)	-0.014(2)
N(1)	4e	0.1234(3)	0.1234(8)	0.1234(2)	0.021(2)	0.028(2)	0.026(2)	-0.001(2)	0.004(1)	-0.002(2)
N(20)	4e	0.1024(3)	0.0971(8)	0.1522(2)	0.029(2)	0.032(2)	0.026(2)	-0.001(2)	0.003(2)	-0.006(2)
N(21)	4e	0.0980(3)	0.2319(8)	0.0434(2)	0.021(2)	0.026(2)	0.025(2)	0.000(2)	0.002(1)	-0.004(2)
N(30)	4e	0.1518(3)	0.4948(9)	-0.0405(2)	0.030(2)	0.040(2)	0.030(2)	0.002(2)	0.002(2)	-0.011(2)
C(2)	4e	-0.0300(3)	0.103(1)	-0.1430(2)	0.023(3)	0.029(2)	0.028(2)	-0.002(2)	0.003(2)	0.000(2)
C(3)	4e	-0.0158(4)	0.219(1)	-0.2000(2)	0.034(3)	0.032(2)	0.026(2)	0.002(2)	0.003(2)	-0.006(2)
C(4)	4e	0.0542(4)	0.421(1)	-0.2027(2)	0.030(3)	0.033(3)	0.027(2)	0.004(2)	0.006(2)	0.002(2)
C(5)	4e	0.1099(3)	0.497(1)	-0.1468(2)	0.028(3)	0.037(2)	0.029(2)	0.004(2)	0.006(2)	-0.004(2)
C(6)	4e	0.0908(3)	0.378(1)	-0.0902(2)	0.021(3)	0.033(2)	0.030(2)	-0.001(2)	0.002(2)	0.000(2)
C(22)	4e	0.1304(3)	0.237(1)	0.1079(2)	0.024(3)	0.024(2)	0.027(2)	-0.003(2)	0.001(2)	0.002(2)
C(23)	4e	0.2085(3)	0.447(1)	0.1225(2)	0.022(3)	0.028(2)	0.030(2)	-0.003(2)	0.002(2)	0.000(2)
C(24)	4e	0.2640(4)	0.527(1)	0.1790(2)	0.031(3)	0.034(3)	0.030(2)	-0.002(2)	0.000(2)	0.000(2)
C(25)	4e	0.3330(4)	0.736(1)	0.1758(2)	0.029(3)	0.038(3)	0.036(2)	-0.006(2)	-0.000(2)	-0.002(2)
C(26)	4e	0.3464(4)	0.855(1)	0.1187(2)	0.025(3)	0.038(3)	0.044(2)	-0.006(2)	0.004(2)	-0.007(2)
C(27)	4e	0.2901(4)	0.773(1)	0.0625(2)	0.030(3)	0.040(3)	0.036(2)	0.002(2)	0.004(2)	-0.009(2)
C(28)	4e	0.2221(3)	0.564(1)	0.0663(2)	0.023(3)	0.033(3)	0.031(2)	-0.002(2)	0.003(2)	-0.001(2)
C(29)	4e	0.1519(3)	0.426(1)	0.0172(2)	0.022(3)	0.029(2)	0.029(2)	-0.001(2)	0.005(2)	-0.001(2)
C(42)	4e	0.1358(4)	0.733(1)	-0.2647(2)	0.036(3)	0.042(3)	0.033(2)	0.006(2)	0.004(2)	-0.008(2)
C(43)	4e	0.1147(4)	0.859(1)	-0.3303(2)	0.043(3)	0.037(3)	0.036(2)	0.011(2)	0.008(2)	-0.002(3)
C(44)	4e	0.1228(4)	0.656(1)	-0.3833(2)	0.053(4)	0.050(3)	0.039(2)	0.007(2)	0.014(2)	0.010(3)
C(45)	4e	0.0941(5)	0.795(2)	-0.4473(3)	0.087(5)	0.080(5)	0.035(2)	0.012(3)	0.015(3)	0.015(4)

Acknowledgments. The authors gratefully acknowledge the financial support of the BASF AG Ludwigshafen and the German Ministry of Education and Research (BMBF).

References

- Hanack, M.; Haberth, K.; Rack, M.: Synthese und Charakterisierung von substituierten Nickelhemiporphyrinen. *Chem. Ber.* **126** (1993) 1201-1204.
- Peng, S. M.; Wang, Y.; Ho, T. P.; Chang, I. C.; Tang, C. P.; Wang C. J.: Structural Relationships between the Hemiporphyrine Macroyclic Ligand and its Metal Complexes. *J. Chin. Chem. Soc.* **33** (1986) 13-21.
- Sheldrick, G. M.: SHELXS-86. Program for the Solution of Crystal Structures. University of Göttingen, Germany 1986.
- Frenz, B. A.: SDP - Enraf-Nonius Structure Determination Package. Enraf-Nonius, Delft, The Netherlands 1989.
- Spek, A. L.: PLATON - A Multipurpose Crystallographic Tool. Utrecht University, The Netherlands 1998.