Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

rac-[2,2′-Bis(1-ethylbenzimidazol-2-yl-κN^3)-biphenyl]dichloronickel(II)

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Key indicators

Single-crystal X-ray study
T = 297 K
Mean σ(C–C) = 0.009 Å
Disorder in main residue
R factor = 0.059
wR factor = 0.169
Data-to-parameter ratio = 13.9

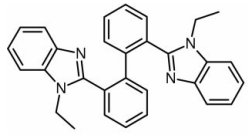
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 4 December 2003
Accepted 8 January 2004
Online 17 January 2004

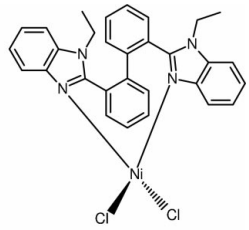
The title compound, $[NiCl_2(C_{30}H_{26}N_4)]$, is a monoclinic (purple) racemic polymorph of a previously reported orthorhombic (blue) form of the same compound. The complex exhibits pseudo-tetrahedral coordination geometry around the nickel(II) metal center. This geometry is enforced by the geometrically constraining ligand 2,2′-bis(1-ethylbenzimidazol-2-yl)biphenyl.

Comment

Bis(2-benzimidazol-2-yl) species bridged by various connecting moieties have attracted considerable interest (Stibrany *et al.*, 2003*b*). In the present study, we have examined a racemic polymorphic form of a 2,2′-biphenyl-bridged bis(2-benzimidazol-2-yl) species complexed to nickel(II). When the geometrically constraining ligand 2,2′-bis(1-ethylbenzimidazol-2-yl)biphenyl, (I) (Stibrany *et al.*, 2003*a*) is complexed to nickel(II) dichloride, a pseudo-tetrahedral coordination environment is adopted by the nickel metal center, (II). These nickel(II) pre-catalysts can be activated with methylaluminoxane to oligomerize ethylene (Stibrany *et al.*, 2002) and to polymerize norbornene (Patil *et al.*, 2003). The analogous copper(II) complexes can be activated with methylaluminoxane to polymerize ethylene and acrylates (Stibrany, Schulz *et al.*, 2003).



(I)



(II)

The monoclinic title compound, $(II)_m$, crystallizes as a racemate. Chirality is necessarily introduced by the 2,2′-biphenyl bridge. Facile interconversion of the biphenyl bridge in the free ligand is expected due to the low rotational barrier offered by the 6,6′-proton substitution. The crystal chosen of the polymorphic orthorhombic form $(II)_o$ was crystallographically determined to be the *R* enantiomer (Stibrany, Matturro *et al.*, 2003). It is not yet known if $(II)_m$ is the result of a solvent-induced racemization of *R*-$(II)_o$ or if $(II)_o$ exists as a mixture of *R* and *S* crystals. The nickel coordination varies only slightly in the two polymorphic forms. The nickel coordination parameters for $(II)_m$ are Ni—N = 2.000 (3)–2.005 (3) Å and Ni—Cl = 2.2310 (15)–2.2405 Å, and the angles are 98.55 (11)–125.90 (6)°. In $(II)_o$, the corresponding ranges are 1.999 (8)–2.008 (7) Å, 2.226 (2)–2.233 (3) Å and 101.0 (2)–

123.43 (11)°. In $(II)_m$, the phenyl–phenyl dihedral angle is 81.6 (2)°, compared with 83.9 (3)° in $(II)_o$.

Occupation of the calculated solvent-accessible void of 37 Å^3 for $(II)_m$ is unlikely. The complex was prepared in the presence of triethylorthoformate to ensure the removal of any adventitious water. The measured density of 1.34 (1) Mg m^{-3} is within experimental error of the value (1.359 Mg m^{-3}) calculated from the structure. The calculated density is 1.402 Mg m^{-3} if a water molecule occupies the void. The measured density of the blue form was found to be 1.37 (1) Mg m^{-3} which compares well with the calculated density of 1.372 Mg m^{-3}. The blue form, $(II)_o$, does not have a void large enough to accommodate a solvent molecule. This accounts for the slightly higher density. The measured density of the bulk blue form seems to indicate a uniform density. This indicates that either the *S* enantiomer has nearly the same density as the *R* enantiomer or the blue form exists entirely as the *R* enantiomer. In either case, a second method of separation of blue and purple forms is provided by flotation.

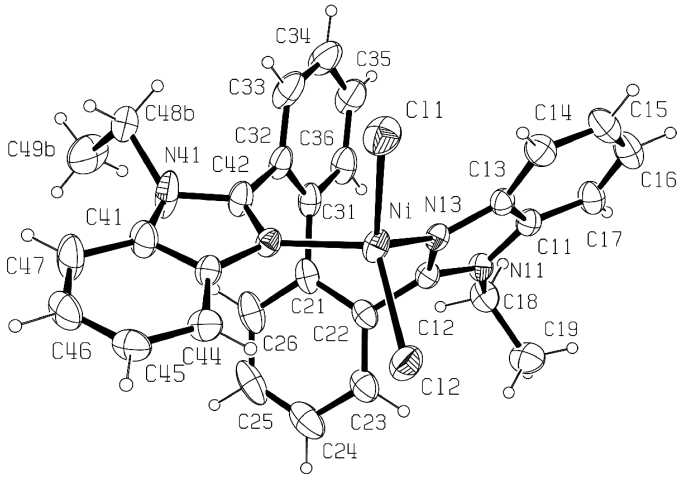


Figure 1
The molecular structure of $(II)_m$, showing 25% probability displacement ellipsoids. Only the minor component of the disordered ethyl group is shown.

Experimental

The blue orthorhombic crystalline form of the title compound, (II), was obtained as previously described in Stibrany *et al.* (2002). This solid was dissolved in a mixture of acetonitrile and triethylorthoformate with gentle reflux. The blue–purple solution was then sealed in a jar to allow diethyl ether diffusion. Overnight, a mixture of blue and purple crystals was obtained which could be physically separated.

Crystal data

$[NiCl_2(C_{30}H_{26}N_4)]$
M_r = 572.15
Monoclinic, $P2_1/n$
a = 9.1464 (5) Å
b = 18.6955 (10) Å
c = 16.4401 (10) Å
β = 95.806 (4)°
V = 2796.8 (3) Å^3
Z = 4
D_x = 1.359 Mg m^{-3}
D_m = 1.34 (1) Mg m^{-3}
D_m measured by flotation in CCl_4/cyclohexane
Mo $K\alpha$ radiation
Cell parameters from 765 reflections
θ = 2.5–21.3°
μ = 0.91 mm^{-1}
T = 297 (1) K
Rod, purple
0.46 × 0.12 × 0.04 mm

Data collection

Siemens *P*3 diffractometer with a Bruker SMART APEX CCD area-detector
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Blessing, 1995)
T_{min} = 0.787, T_{max} = 0.960
20111 measured reflections
4918 independent reflections
3033 reflections with $I > 2\sigma(I)$
R_{int} = 0.071
θ_{max} = 25.0°
$h = -10 \rightarrow 10$
$k = -22 \rightarrow 22$
$l = -15 \rightarrow 19$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.059
$wR(F^2)$ = 0.169
S = 1.00
4918 reflections
353 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0957P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.63 e Å^{-3}
$\Delta\rho_{min}$ = −0.43 e Å^{-3}

One of the ethyl groups C48–C49 was found to be disordered over two sites. The disorder also resulted in some unusually large deviations in the near neighbor displacement parameters.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2000); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*III (Burnett & Johnson, 1996) and *ORTEP*32 (Farrugia, 1997); software used to prepare material for publication: *SHELXTL* (Bruker, 2000).

The authors thank ExxonMobil Research and Engineering Company.

References

Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.
Bruker (2000). *SHELXTL* (Version 6.10), *SAINT-Plus* (Version 6.02) and *SMART* (Version 5.622). Bruker AXS Inc., Madison, Wisconsin, USA.
Burnett, M. N. & Johnson, C. K. (1996). *ORTEP*III. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Patil, A. O., Zushma, S., Stibrany, R. T., Rucker, S. P., & Wheeler, L. M. (2003). *J. Polymer Sci. Part A Polym. Chem.* **41**, 2095–2106.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.
Stibrany, R. T., Matturro, M. G., Zushma, S. & Patil, A. O. (2002). US Patent 6 501 000.
Stibrany, R. T., Matturro, M. G., Zushma, S. & Patil, A. O. (2003). Private Communication (deposition number CCDC 224191) to the Cambridge Structural Database. Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, England.
Stibrany, R. T., Schugar, H. J. & Potenza, J. A. (2003*a*). *Acta Cryst.* E**59**, o693–o695.
Stibrany, R. T., Schugar, H. J. & Potenza, J. A. (2003*b*). *Acta Cryst.* E**59**, o1448–o1450.
Stibrany, R. T., Schulz, D. N., Kacker, S., Patil, A. O., Baugh, L. S., Rucker, S. P., Zushma, S., Berluche, E. & Sissano, J. A. (2003). *Macromolecules*, **36**, 8584–8586.