metal-organic papers

Aquabis(3,5-dicarboxybenzoato-κO)bis(hexamethylenetetramine-κN)nickel(II)

Shan Gao,[a] Li-Hua Huo,[a] Hui Zhao[a] and Seik Weng Ng[b]*

[a]College of Chemistry and Materials Science, Heilongjiang University, Harbin 150080, People's Republic of China, and [b]Department of Chemistry, University of Malaya, Kuala Lumpur 50603, Malaysia

Correspondence e-mail: seikweng@um.edu.my

The Ni atom in the title compound, $[Ni(C_9H_5O_6)_2(C_6H_{12}N_4)_2(H_2O)]$, is bonded to two monobasic 3,5-dicarboxybenzoate ions and datively bonded to two hexamethylenetetramine molecules; the apical position of the square-pyramidal geometry is occupied by a water molecule. The complex lies on a crystallographic twofold axis that passes through the Ni atom and the water molecule.

Comment

The reaction of trimesic (1,3,5-benzenetricarboxylic) acid with metal salts sometimes leads to the loss of only one of the three carboxyl H atoms, as for the manganese(II) (Chui *et al.*, 1999), cobalt(II) (Guillou *et al.*, 2000), cobalt(II) (Livage *et al.*, 2001) and iron(II) (Riou-Cavellec *et al.*, 2001) derivatives. The metal 3,5-dicarboxybenzoates are also Lewis-basic compounds that afford adducts with N-donor ligands, *e.g.* the 2-amino-5-methyl-1,3,4-thiadiazole adduct of the copper derivative (Lynch, 2002), the 1,4,7-triazacyclononane adducts of the copper derivative (Wang *et al.*, 2003), the 2-(1-methyl-1*H*-pyrazol-3-yl)pyridine adduct of the zinc derivative (Plater *et al.*, 2001) and the 1,4-diaminobenzene adduct of the nickel derivative (Prior & Rosseinsky, 2001). The title adduct, (I), with hexamine (see scheme) is another example of such adducts.

(I)
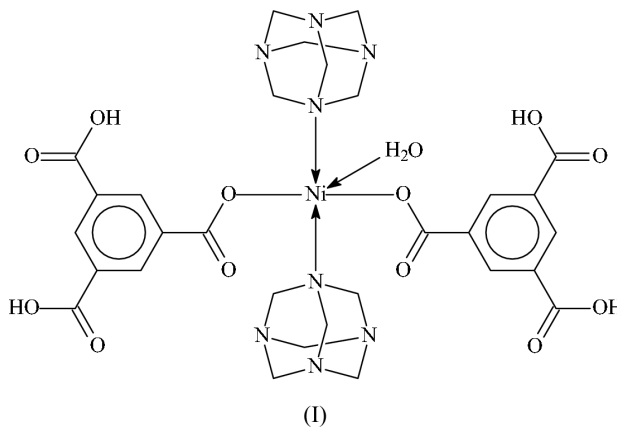
The Ni atom in (I) is covalently bonded to two monobasic carboxylate ions, and is datively bonded to two hexamine molecules; the pairs of O and N atoms form a square-planar coordination around the Ni atom, above which is the water molecule (Fig. 1). The complex lies on a crystallographic twofold axis that passes through the Ni atom and the water molecule. Adjacent formula units are linked by hydrogen bonds into a three-dimensional network structure (Table 2).

Experimental

Nickel nitrate hexahydrate (0.29 g, 1 mmol) and hexamethylenetetramine (0.14 g, 1 mmol) were added to trimesic acid (0.21 g, 1 mmol) dissolved in a small volume of dimethylformamide. Green prismatic crystals separated from the filtered solution after several weeks. Elemental analysis calculated for $C_{30}H_{36}N_8NiO_{13}$: C 46.47, H 4.68, N 14.45%; found: C 46.51, H 4.64, N 14.40%.

Crystal data

$[Ni(C_9H_5O_6)_2(C_6H_{12}N_4)_2(H_2O)]$
$M_r = 775.38$
Orthorhombic, $Pccn$
$a = 20.610$ (4) Å
$b = 12.246$ (2) Å
$c = 12.907$ (3) Å
$V = 3257$ (1) Å^3
$Z = 4$
$D_x = 1.581$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 28656 reflections
$\theta = 3.0–27.5°$
$\mu = 0.68$ mm^{-1}
$T = 295$ (2) K
Prism, green
$0.35 \times 0.24 \times 0.18$ mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)
$T_{min} = 0.730$, $T_{max} = 0.888$
28890 measured reflections

3732 independent reflections
3221 reflections with $I > 2\sigma(I)$
$R_{int} = 0.036$
$\theta_{max} = 27.5°$
$h = -26 \rightarrow 26$
$k = -15 \rightarrow 15$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.122$
$S = 1.11$
3732 reflections
248 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0693P)^2 + 1.6993P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.43$ e Å^{-3}
$\Delta\rho_{min} = -0.72$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ni1—O1	1.988 (2)	Ni1—N1	2.286 (2)
Ni1—O1w	2.072 (2)		
O1—Ni1—O1^i	173.2 (1)	O1^i—Ni1—N1^i	85.6 (1)
O1—Ni1—O1w	93.4 (1)	O1w—Ni1—N1^i	93.5 (1)
O1—Ni1—N1^i	94.0 (1)	N1^i—Ni1—N1	173.1 (1)

Symmetry code: (i) $\frac{1}{2} - x, \frac{3}{2} - y, z$.

Table 2
Hydrogen-bonding geometry (Å, °).

D—H$\cdots$A	D—H	H$\cdots$A	$D\cdots$A	D—H$\cdots$A
O4—H4o$\cdots$N2^{ii}	0.85 (1)	1.83 (1)	2.674 (2)	167 (3)
O6—H6o$\cdots$N4^{iii}	0.85 (1)	1.82 (1)	2.657 (2)	174 (3)
O1w—H1w$\cdots$O2^{iv}	0.84 (1)	1.92 (2)	2.688 (3)	152 (2)

Symmetry codes: (ii) $1 - x, \frac{1}{2} + y, -\frac{1}{2} - z$; (iii) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$; (iv) $\frac{1}{2} - x, y, \frac{1}{2} + z$.

H atoms bonded to C atoms were positioned geometrically and refined using a riding model. The C—H distances were set at 0.94 Å
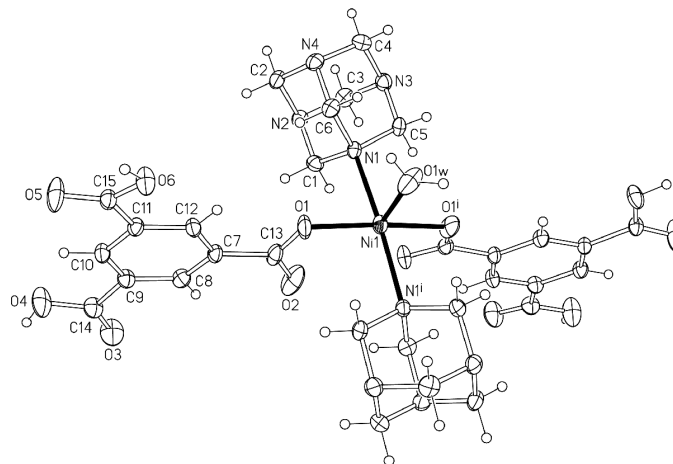
Figure 1
ORTEPII (Johnson, 1976) plot of (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are drawn as spheres of arbitrary radii. [Symmetry code: (i) $\frac{1}{2} - x, \frac{3}{2} - y, z$.]

for aromatic CH and at 0.97 Å for methylene groups. Their isotropic displacement parameters were fixed at 1.2 times U_{eq} of the parent atom. H atoms bonded to O atoms were freely refined.

Data collection: RAPID-AUTO (Rigaku, 1998); cell refinement: RAPID-AUTO; data reduction: CrystalStructure (Rigaku/MSC, 2002); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEPII (Johnson, 1976); software used to prepare material for publication: SHELXL97.

References

Chui, S. S.-Y., Lo, S. M.-F., Lo, Charmant, J. P. H. & Orpen, A. G. (1999). Science, **283**, 1148–1150.
Guillou, N., Livage, C., Marrot, J. & Ferey, G. (2000). Acta Cryst. C**56**, 1427–1428.
Higashi, T. (1995). ABSCOR. Rigaku Corporation, Tokyo, Japan.
Johnson, C. K. (1976). ORTEPII. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Livage, C., Guillou, N., Marrot, J. & Ferey, G. (2001). Chem. Mater. **13**, 4387–4392.
Lynch, D. E. (2002). Acta Cryst. E**58**, m577–m579.
Plater, M. J., Foreman, M. R. St J., Howie, R. A., Skakle, J. M. S., Coronado, E., Gomez-Garcia, C. J., Gelbrich, T. & Hursthouse, M. B. (2001). Inorg. Chim. Acta, **319**, 159–175.
Prior, T. & Rosseinsky, M. J. (2001). Chem. Commun. pp. 1222–1223.
Rigaku (1998). RAPID-AUTO. Rigaku Corporation, Tokyo, Japan.
Rigaku/MSC (2002). CrystalStructure. Rigaku/MSC Inc., 9009 New Trails Drive, The Woodlands, TX 77381-5209, USA.
Riou-Cavellec, M., Albinet, C., Greneche, J.-M. & Ferey, G. (2001). J. Mater. Chem. **11**, 3166–3171.
Sheldrick, G. M. (1997). SHELXL97 and SHELXS97. University of Göttingen, Germany.
Wang, Q.-L., Xie, C.-Z., Liao, D.-Z., Yan, S.-P., Jiang Z.-H. & Cheng, P. (2003). Transition Met. Chem. **28**, 16–20.