trans-Diaquatetrakis(imidazole)nickel(II) dichloride

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Key indicators

Single-crystal X-ray study
$T = 295$ K
Mean σ(C–C) = 0.003 Å
R factor = 0.027
wR factor = 0.063
Data-to-parameter ratio = 19.4

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

The title compound, trans-[Ni(C$_3$H$_4$N$_2$)$_4$(H$_2$O)$_2$]Cl$_2$, was obtained by the reaction of nickel chloride, succinic acid, imidazole, and NaOH (molar ratio 4:2:8:3) in water. The compound contains a six-coordinate Ni^{II} ion lying on an inversion center, which is bonded to four imidazole N atoms and two water O atoms. Intermolecular hydrogen-bonding interactions are present, linking the nickel complex cations and chloride anions in the crystal structure.

Comment

Self-assembly reactions of organic ligands with metal ions or related complexes have been a subject of great interest in the field of supramolecular chemistry (Yaghi et al., 1998; Eddaoudi et al., 2001). Multidentate linkers such as di- or poly-carboxylates usually allow for the formation of aggregates with open frameworks, which are potentially useful in selective inclusion and chemical transformation. However, efficient crystallization techniques are usually lacking, since too many parameters, such as the experimental temperature, the pH value etc., are involved.
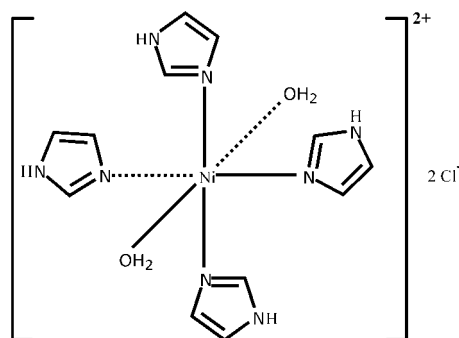
(I)

From a mixture of nickel chloride, succinic acid, imidazole, and NaOH in water, a heteroleptic compound, (I), was obtained as blue crystals. The succinic acid molecules in either the acid or any deprotonated conjugate form are not incorporated in the crystal structure. However, the cation, trans-[Ni(C$_3$H$_4$N$_2$)$_4$(H$_2$O)$_2$]$^{2+}$, was previously reported to crystallize with the terephthalate anion, [1,4-C$_6$H$_4$(CO$_2$)$_2$]$^{2-}$ (Niu et al., 1999).

It appears that rigid moieties such as that anion, compared with the flexible succinate anion, are selected preferentially as construction units, because of the easy packing. In (I), atom Ni1 lies on an inversion center and is octahedrally coordinated by four imidazole N atoms (N1, N3, N1A and N3A) and two water O atoms in trans positions (O1 and O1A) (Fig. 1). For the two symmetry-unrelated Ni—N bond lengths, we might
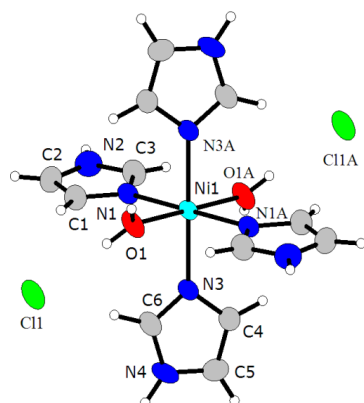
Figure 1
The molecular structure of (I), showing the atom-numbering scheme and displacement ellipsoids at the 50% probability level. [Symmetry code: A $\frac{1}{2}-x, \frac{3}{2}-y, -z$.]
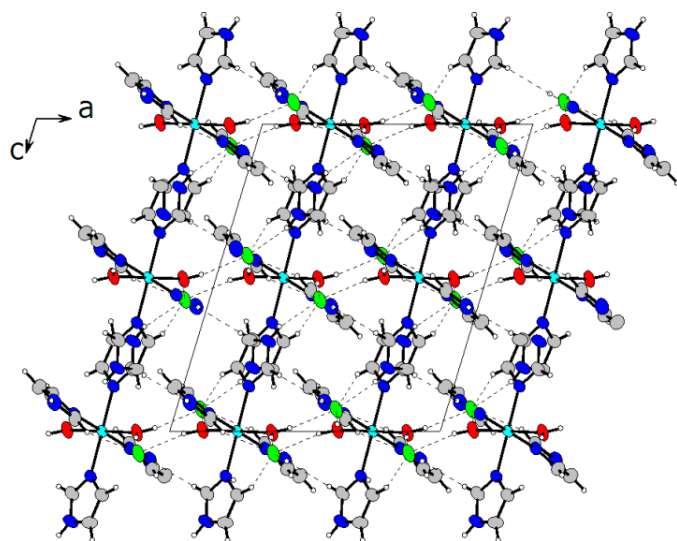

Figure 2
The crystal packing diagram of (I), with hydrogen bonds shown as dashed lines, viewed along the b axis.

expect to observe two similar values; in fact, they are quite different [Ni1—N1 = 2.132 (1) Å *versus* Ni1—N3 = 2.071 (2) Å]. This is apparently caused by many inter-molecular hydrogen-bonding interactions between H atoms of the coordinated imidazole and water molecules and the chloride ions (Fig. 2). The hydrogen-bonding interactions are weak (Steed & Atwood, 2000), based on H···A distances of 2.28–2.99 Å, D···A distances of 3.135 (2)–3.844 (2) Å and angles of 134–176° (Table 2).

Experimental

Succinic acid (0.239 g, 2.00 mmol), nickel chloride hexahydrate (0.951 g, 4.00 mmol), imidazole (0.550 g, 8.00 mmol), and NaOH (0.120 g, 3.00 mmol) were stirred in 10 ml of water until dissolved. The solution was placed in two test tubes. After three months, blue single crystals of (I) were collected and dried in air (yield 50%).

Crystal data

[Ni(C$_3$H$_4$N$_2$)$_4$(H$_2$O)$_2$]Cl$_2$	$D_x = 1.567$ Mg m^{-3}
$M_r = 437.97$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 2924
$a = 12.4020$ (12) Å	reflections
$b = 10.9759$ (11) Å	$\theta = 2.5–25°$
$c = 14.2847$ (14) Å	$\mu = 1.36$ mm^{-1}
$\beta = 107.323$ (2)°	$T = 295$ (2) K
$V = 1856.3$ (3) Å^3	Blockt, blue
$Z = 4$	$0.20 \times 0.15 \times 0.15$ mm

Data collection

Bruker SMART CCD area-detector diffractometer	2231 independent reflections
	1833 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.026$
Absorption correction: multi-scanl (*SADABS*; Sheldrick, 1995)	$\theta_{max} = 28.2°$
	$h = -16 \rightarrow 14$
$T_{min} = 0.774, T_{max} = 0.817$	$k = -14 \rightarrow 10$
5720 measured reflections	$l = -16 \rightarrow 19$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.032P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.027$	$+ 0.0266P]$
$wR(F^2) = 0.063$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.02$	$(\Delta/\sigma)_{max} < 0.001$
2231 reflections	$\Delta\rho_{max} = 0.31$ e Å^{-3}
115 parameters	$\Delta\rho_{min} = -0.21$ e Å^{-3}
H-atom parameters not refined	

Table 1
Selected geometric parameters (Å, °).

Ni1—N3	2.0709 (13)	Ni1—N1	2.1321 (12)
Ni1—O1	2.1296 (11)		
N3—Ni1—O1	90.73 (5)	O1—Ni1—N1	89.91 (5)
N3—Ni1—N1	88.30 (5)		

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1A···Cl1	0.84	2.31	3.147 (1)	176
O1—H1B···Cl1^i	0.87	2.28	3.135 (2)	169
C1—H1C···Cl1^{ii}	0.94	2.97	3.844 (2)	154
N2—H2A···Cl1^{iii}	0.88	2.45	3.311 (3)	165
C3—H3A···Cl1^i	0.95	2.99	3.739 (4)	136
N4—H4A···Cl1^{iv}	0.92	2.40	3.251 (2)	154
C6—H6A···Cl1	0.99	2.76	3.689 (3)	158

Symmetry codes: (i) $-x, 1-y, -z$; (ii) $\frac{1}{2}-x, \frac{3}{2}-y, -z$; (iii) $x, 1-y, \frac{1}{2}+z$; (iv) $\frac{1}{2}-x, \frac{1}{2}-y, -z$.

The H atoms were located in difference Fourier maps, but were not refined; their U_{iso} values were set at 0.05 Å^2.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXTL*.

References

Bruker (1997). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.

Bruker (1998). *SHELXTL.* Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.

Eddaoudi, M., Moler, D. B., Li, H., Chen, B., Reineke, T. M., O'Keeffe, M. & Yaghi, O. M. (2001). *Acc. Chem. Res.* **34**, 319–330.

Niu, S.-Y., Yang, Z.-Z., Yang, Q.-C., Hou, Y.-Y., Yang, G.-D. & Bu, W.-M. (1999). *Chem. J. Chin. Univ.* **20**, 1671–1676.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1995). *SADABS.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.

Steed, J. W. & Atwood, J. L. (2000). *Supramolecular Chemistry*. New York: Wiley.

Yaghi, O. M., Li, H., Davis, C., Richardson, D. & Groy, T. L. (1998). *Acc. Chem. Res.* **31**, 474–484.