metal-organic compounds

Poly[chlorido-μ_3-1,2,4-triazolato-nickel(II)]

Yu-Xiang Gao,* Li-Bin Wang and Xiang-Rong Hao

Department of Chemistry, Tonghua Teachers' College, Tonghua 134002, People's Republic of China
Correspondence e-mail: yxgao_tonghua@yahoo.com.cn

The title compound, $[\text{Ni}(\text{C}_2\text{H}_2\text{N}_3)\text{Cl}]_n$, has been prepared by the hydrothermal reaction of nickel(II) chloride and 1,2,4-triazole. The nickel cation is coordinated in a slightly distorted tetrahedral environment, by one Cl atom and three N atoms from different triazolate ligands. The polymeric layer is formed by the triply bridging nature of the 1,2,4-triazolate bonded to three different Ni atoms through its three N atoms. The layer contains both binuclear units and tetranuclear cavities. In the binuclear unit, two Ni atoms are bridged by two nearly coplanar triazolate groups through the 1,2-positions, affording a six-membered ring around an inversion center. Each binuclear unit is further connected to four parallel units through the 4-positions of the triazolate groups. Four adjacent units, which are parallel in pairs, afford 16-membered tetranuclear cavities. In such a cavity, the two nearest-neighbor Ni atoms are bridged by a single triazolate group through the 1,4-positions.

Related literature

For background information, see: Evans *et al.* (2001); Evans & Lin (2001); Honma *et al.* (2001); Jannasch (2003); Javaid *et al.* (2001); Sudik *et al.* (2005); Kitaura *et al.* (2002); Ngo *et al.* (2004); Rowsell *et al.* (2004); Sanchez *et al.* (2003); Suzuki *et al.* (2002); Vioux *et al.* (2004). For related structures, see: Jonas *et al.* (1995); Wayne *et al.* (2006).
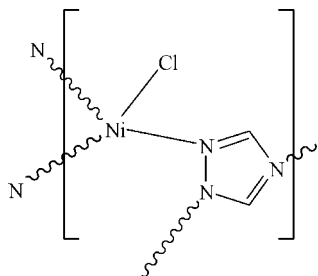
Experimental

Crystal data

$[\text{Ni}(\text{C}_2\text{H}_2\text{N}_3)\text{Cl}]$	V = 524.1 (2) Å³
M_r = 162.23	Z = 4
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
a = 6.1455 (18) Å	μ = 4.07 mm⁻¹
b = 9.764 (2) Å	T = 293 (2) K
c = 8.857 (2) Å	0.10 × 0.10 × 0.10 mm
β = 99.542 (2)°	

Data collection

Bruker SMART CCD diffractometer	1024 independent reflections
	923 reflections with $I > 2\sigma(I)$
Absorption correction: none	R_{int} = 0.028
44136 measured reflections	

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.022	65 parameters
$wR(F^2)$ = 0.065	H-atom parameters not refined
S = 1.00	$\Delta\rho_{max}$ = 0.27 e Å⁻³
1024 reflections	$\Delta\rho_{min}$ = −0.43 e Å⁻³

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SHELXTL* (Bruker, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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supplementary materials

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Y.-X. Gao, L.-B. Wang and X.-R. Hao

Comment

Hybrid organic-inorganic materials occupy a prominent position by virtue of their applications to catalysis, optical materials, membranes, and sorption (Ngo *et al.*, 2004; Evans *et al.*, 2001; Vioux *et al.*, 2004; Sanchez *et al.*, 2003; Evans & Lin, 2001; Jannasch, 2003; Javaid *et al.*, 2001; Honma *et al.*, 2001; Sudik *et al.*, 2005; Rowsell *et al.*, 2004; Kitaura *et al.*, 2002). The design of organic-inorganic hybrid materials is conceived of the metal, metal cluster, or metal oxide substructure as a node from which rigid or flexible multitopic organic ligands radiate to act as tethers to adjacent nodes in the bottom-up construction of complex extended architectures. While a variety of organic molecules have been investigated as potential tethers, materials incorporating multitopic carboxylates and pyridine ligands have witnessed the most significant development. However, ligands offering alternative tether lengths, different charge-balance requirements, and orientations of donor groups may afford advantages in the design of materials. One such ligand is 1,2,4- triazole, a member of the polyazaheteroaromatic family of compounds, which exhibit an extensively documented ability to bridge metal ions to afford polynuclear compounds. Triazole is an attractive ligand for the design of novel hybrid materials because of the unusual structural diversity associated with the di- and trinucleating properties of the neutral and anionic ligand forms, respectively. Herein, one new complex,[(1,2,4-triazolato) nickel(II) chloride]$_n$ (I), obtained from 1,2,4-triazole and nickel chloride under hydrothermal reaction is reported, which is iso-structural to reported ones (Wayne *et al.*, 2006; Jonas *et al.*, 1995).

The coordination polyhedron of the nickel atom is shown in Fig. 1 which can be described as a slightly distorted tetrahedron. The nickel cation is surrounded by three crystallographically independent nitrogen atoms belonging to three different triazolato ligands, and a chlorine atom. The Ni—N bond lengths are in the range of 2.004–2.006 Å, very close to each other. The Ni—C1 bond length is 2.216. The bond angles around the nickel atom are in the range of 106.21 to 113.19 Å. The polymeric layers as shown in Fig. 2 is formed due to the triply bridging nature of the 1,2,4-triazolato. The 1,2,4-triazolato ligand is simultaneously bonded to three different nickel atoms through its three nitrogen atoms, and its symmetry is very close to C2v. A layer contains both binuclear units and tetranuclear cavities. In the binuclear unit two nickel atoms are bridged by two nearly coplanar triazolato groups through the 1,2-positions, affording a six-membered ring around an inversion center; the Ni⋯Ni separation within the binuclear unit is equal to 3.756 Å. The chlorine atoms bonded to the metals of a binuclear unit point out in opposite parallel directions. Each binuclear unit is further connected to four parallel units through the four positions of the triazolato groups. Four adjacent units, which are pairwise parallel, afford sixteen-membered tetranuclear cavities. In such a cavity the two nearest neighbor nickel atoms are bridged by a single triazolate group through the 1,4 positions with Ni⋯Ni separations of 5.957 and 6.070 Å.

Experimental

All chemicals were used as purchased from Shanghai Chemical Co. Ltd. A mixture of nickel(II) chloride (0.5 mmol), potassium hydroxide (0.5 mmol), 1,2,4-triazole (0.5 mmol) and H2O (8 ml) in a 25 ml Teflon-lined stainless steel autoclave was kept at 413 K for 2 d, and then cooled to room temperature. Green, block-shaped crystals of (I) were obtained in a yield of 36%. Anal. Calc. for $C_2H_2ClN_3Ni$: C 14.81, H 1.24, N 25.91, Ni 36.18%; Found: C 14.76, H 1.27, N 25.87, Ni 36.17%.

supplementary materials

Refinement

H atoms were placed in calculated positions with a C—H bond distance of 0.93%A and $U_{iso}(H) = 1.2U_{eq}$ of the respective carrier atom.

Figures
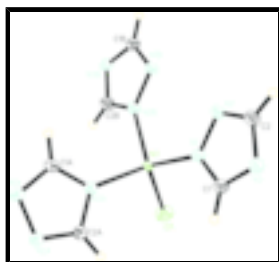

Fig. 1. A view of the structure of (I), showing 30% probability displacement ellipsoids. Atoms labeled with A are at the symmetry position$(-x + 2,-y + 1,-z + 2)$ and those labeled B at $(-x + 3/2,y + 1/2,-z + 3/2)$.
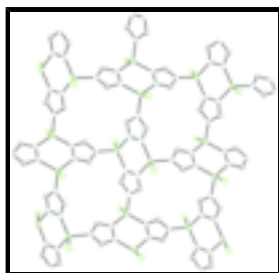

Fig. 2. View of a layer showing both the binuclear units and the tetranuclear cavities.

Poly[chlorido-µ$_3$-1,2,4-triazolato-nickel(II)]

Crystal data

[Ni(C$_2$H$_2$N$_3$)Cl]	$F_{000} = 320$
$M_r = 162.23$	$D_x = 2.056$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
Hall symbol: -P 2yn	Cell parameters from 2213 reflections
$a = 6.1455$ (18) Å	$\theta = 2.9–26.4°$
$b = 9.764$ (2) Å	$\mu = 4.07$ mm^{-1}
$c = 8.857$ (2) Å	$T = 293$ (2) K
$\beta = 99.542$ (2)°	Block, green
$V = 524.1$ (2) Å^3	$0.10 \times 0.10 \times 0.10$ mm
$Z = 4$	

Data collection

Bruker P4 diffractometer	923 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	$R_{int} = 0.028$
Monochromator: graphite	$\theta_{max} = 26.0°$

$T = 293(2)$ K	$\theta_{min} = 3.1°$
ω scans	$h = -7 \rightarrow 7$
Absorption correction: none	$k = -12 \rightarrow 12$
44136 measured reflections	$l = -10 \rightarrow 10$
1024 independent reflections	

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters not refined
$R[F^2 > 2\sigma(F^2)] = 0.022$	$w = 1/[\sigma^2(F_o^2) + (0.0426P)^2 + 0.2251P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.065$	$(\Delta/\sigma)_{max} = 0.021$
$S = 1.00$	$\Delta\rho_{max} = 0.27$ e Å^{-3}
1024 reflections	$\Delta\rho_{min} = -0.43$ e Å^{-3}
65 parameters	Extinction correction: SHELXL97, $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.036 (3)
Secondary atom site location: difference Fourier map	

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	$U_{iso}*/U_{eq}$
Ni1	1.04409 (5)	0.58054 (3)	0.81491 (3)	0.01943 (16)
Cl1	1.30630 (14)	0.55345 (9)	0.67321 (9)	0.0469 (2)
N1	0.8721 (4)	0.4084 (2)	0.8360 (3)	0.0294 (5)
C1	0.7601 (4)	0.3316 (3)	0.7286 (3)	0.0319 (6)
H1	0.7529	0.3475	0.6244	0.038*
N3	0.6573 (4)	0.2276 (2)	0.7863 (3)	0.0304 (5)
C2	0.7132 (5)	0.2456 (3)	0.9381 (3)	0.0352 (7)
H2	0.6665	0.1887	1.0106	0.042*
N2	0.8407 (4)	0.3522 (2)	0.9727 (2)	0.0314 (5)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.0242 (2)	0.0181 (2)	0.0153 (2)	−0.00054 (11)	0.00114 (13)	0.00152 (10)
Cl1	0.0453 (5)	0.0556 (5)	0.0437 (5)	0.0037 (4)	0.0191 (4)	−0.0021 (4)
N1	0.0364 (13)	0.0288 (12)	0.0222 (11)	−0.0032 (9)	0.0024 (9)	0.0037 (8)
C1	0.0416 (16)	0.0320 (15)	0.0215 (13)	−0.0040 (13)	0.0032 (11)	−0.0011 (11)
N3	0.0363 (12)	0.0259 (11)	0.0277 (11)	−0.0041 (9)	0.0020 (9)	−0.0022 (9)
C2	0.0467 (17)	0.0317 (15)	0.0254 (14)	−0.0120 (13)	0.0009 (12)	0.0026 (12)
N2	0.0407 (13)	0.0304 (12)	0.0215 (11)	−0.0042 (10)	0.0006 (9)	0.0029 (9)

Geometric parameters (Å, °)

Ni1—N2^i	2.007 (2)	C1—H1	0.9300
Ni1—N3^{ii}	2.007 (2)	N3—C2	1.343 (3)
Ni1—N1	2.011 (2)	N3—Ni1^{iii}	2.007 (2)
Ni1—Cl1	2.2164 (9)	C2—N2	1.308 (3)
N1—C1	1.313 (3)	C2—H2	0.9300
N1—N2	1.371 (3)	N2—Ni1^i	2.007 (2)
C1—N3	1.341 (3)		
N2^i—Ni1—N3^{ii}	106.27 (10)	N3—C1—H1	123.8
N2^i—Ni1—N1	107.19 (9)	C2—N3—C1	102.9 (2)
N3^{ii}—Ni1—N1	110.16 (10)	C2—N3—Ni1^{iii}	125.28 (19)
N2^i—Ni1—Cl1	113.15 (7)	C1—N3—Ni1^{iii}	131.76 (18)
N3^{ii}—Ni1—Cl1	106.55 (7)	N2—C2—N3	112.5 (2)
N1—Ni1—Cl1	113.31 (8)	N2—C2—H2	123.8
C1—N1—N2	106.1 (2)	N3—C2—H2	123.7
C1—N1—Ni1	129.08 (19)	C2—N2—N1	106.2 (2)
N2—N1—Ni1	124.73 (16)	C2—N2—Ni1^i	125.75 (18)
N1—C1—N3	112.3 (2)	N1—N2—Ni1^i	128.08 (17)
N1—C1—H1	123.8		

Symmetry codes: (i) −*x*+2, −*y*+1, −*z*+2; (ii) −*x*+3/2, *y*+1/2, −*z*+3/2; (iii) −*x*+3/2, *y*−1/2, −*z*+3/2.

Fig. 1

Fig. 2