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Di-μ-chlorido-bis[chlorido(4′-*p*-tolyl-2,2′:6′,2′′-terpyridine-κ^3N,N',N'')-nickel(II)]: a supramolecular system constructed by C—H···Cl interactions

Ying-Lin Chen, Ben-Zhen Li, Ping Yang and Jian-Zhong Wu*

School of Chemistry and Environment, South China Normal University, Guangzhou 510006, People's Republic of China
Correspondence e-mail: wujzh@scnu.edu.cn

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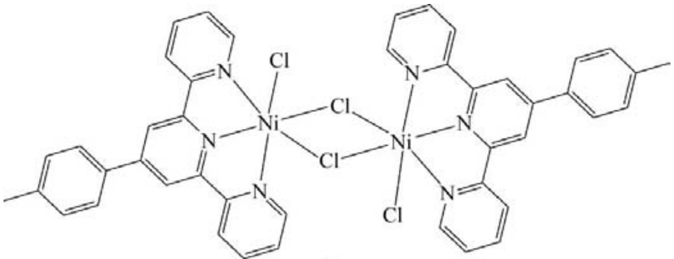
The title complex, $[Ni_2Cl_4(C_{22}H_{17}N_3)_2]$, was synthesized solvothermally. The molecule is a centrosymmetric dimer with the unique Ni^{II} centre in a distorted octahedral N_3Cl_3 coordination environment. The chloride bridges are highly asymmetric. In the 4′-*p*-tolyl-2,2′:6′,2′′-terpyridine ligand, the *p*-tolyl group is perfectly coplanar with the attached pyridine ring, and this differs from the situation found in previously reported compounds; however, there are no π–π interactions between the ligands. The terminal Cl atom forms four intermolecular C—H···Cl hydrogen bonds with one methyl and three methine groups. The methyl group also forms intermolecular C—H···π interactions with a pyridine ring. These nonclassical hydrogen bonds extend the molecule into a three-dimensional network.

Comment

2,2′:6′,2′′-Terpyridine and its derivatives are well known multidentate ligands. Among this ligand family, 4′-*p*-tolyl-2,2′:6′,2′′-terpyridine (ttp) plays an important role because it is quite easy to prepare and derivatize *via* bromination and oxidation, and the electron-donor nature of the terminal methyl group is useful in certain cases. Hence, a number of transition metal (*M*) complexes of ttp have been studied for a variety of interesting properties, such as photophysics (Yoshikawa *et al.*, 2007; Abrahamsson *et al.*, 2005), photochemistry (Beley *et al.*, 1991; Wilkinson *et al.*, 2004), electrochemistry (Al-Noaimi *et al.*, 2004; Chamchoumis & Potvin, 1999; Barigelletti *et al.*, 2000; Collin *et al.*, 1997; Mikel & Potvin, 2001), magnetism (Duboc *et al.*, 2006; Yu *et al.*, 2007), DNA binding (Uma *et al.*, 2005; Jain *et al.*, 2008; Bertrand *et al.*, 2007; Jiang *et al.*, 2008) and supramolecular assembly (Zhou *et al.*, 2007; Liu *et al.*, 2007; Messina *et al.*, 2001; Yutaka *et al.*, 2005; Hartshorn & Zibaseresht, 2006; Bray *et al.*, 2008; Yucesan *et al.*, 2005). All the complexes exist in the form of mononuclear $[M(ttp)_2]^{n+}$, except for the dinuclear manganese complex $[Mn_2(\mu_{1,1}\text{-}N_3)_2(N_3)_2(ttp)_2]$ (Yu *et al.*, 2007). Many metalloenzymes, including nickel enzymes, employ a dinuclear active site (Halcrow & Christou, 1994; Holm *et al.*, 1996; Solomon *et al.*, 1996; Wilcox, 1996). Lack of one Ni atom in the dinuclear active site can cause a reduction in catalytic activity or even complete deactivation of the enzyme. Halide-bridged dinuclear nickel complexes with nitrogen- and oxygen-containing ligands are occasionally utilized in ethylene oligomerization catalysis (Zhang *et al.*, 2007; Sun *et al.*, 2007). We present here the first structure of a dinuclear nickel(II) complex constructed with ttp and chloride ligands, namely di-μ-chlorido-bis[chlorido(4′-*p*-tolyl-2,2′:6′,2′′-terpyridine)nickel(II)], (I).



(I)

Complex (I) was obtained *via* a solvothermal reaction, but no solvent molecule could be detected in the structure. The complex molecule is arranged around an inversion centre and exhibits a planar $Ni_2(\mu\text{-}Cl)_2$ diamond-like framework (Fig. 1). The intramolecular Ni···Ni interatomic distance of 3.6565 (6) Å is typical of a binuclear nickel(II) complex and virtually excludes any specific interaction between these atoms. The coordination sphere of the Ni^{II} centre can be interpreted as a distorted octahedron (Table 1), with ttp atoms N1, N2 and N3 and the bridging atom Cl1 in the equatorial plane and the other bridging atom Cl1^i [symmetry code: (i) $-x, -y + 1, -z$] and the terminal atom Cl2 in axial positions. The tridentate chelation results in the three ttp pyridine rings being nearly coplanar, with the angles between the planes of the two outer pyridine rings and that of the central pyridine

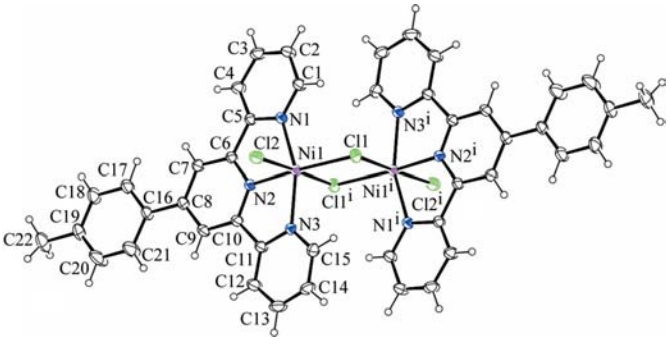


Figure 1
A view of the dinuclear unit of (I), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 40% probability level and H atoms are represented as small spheres of arbitrary radii. [Symmetry code: (i) $-x, -y + 1, -z$.]

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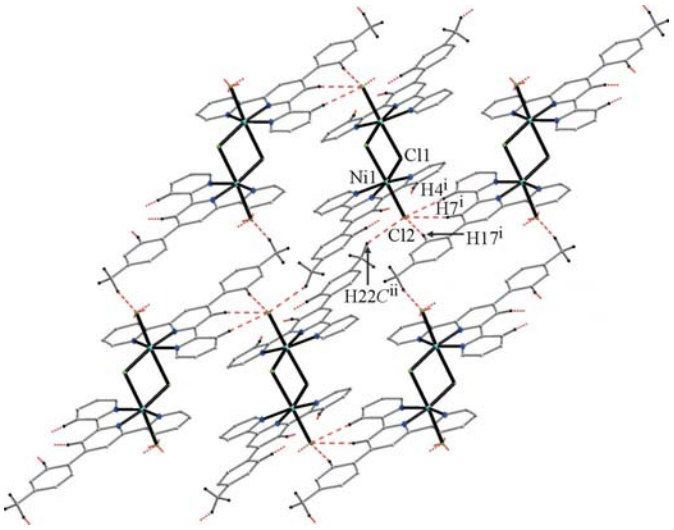

Figure 2
The packing in (I), showing the C—H···Cl (red dashed lines in the electronic version of the paper) interactions. [Symmetry codes: (i) $x, \frac{3}{2} - y, -\frac{1}{2} + z$; (ii) $1 - x, 1 - y, 1 - z$.]

ring being 5.69 (13) and 4.22 (13)°, which is common for ttp complexes. Compared to other ttp complexes, it is very unusal that the substituent *p*-tolyl group is almost in the same plane as the central pyridine ring; the torsion angles C7—C8—C16—C17 and C9—C8—C16—C21 are 1.7 (5) and 2.4 (5)°, respectively. The corresponding angles in previously reported complexes involving ttp are significantly larger and only a few are less than 10° [*cf* 4.58, 6.94 and 9.46° in Yucesan *et al.* (2005), and 9.39° in Mikel & Potvin (2001)].

Of the two bridging Cl1 atoms around an Ni^{II} centre, that *trans* to the central ttp pyridine ring is much closer to the Ni atom than that *trans* to the terminal Cl2 atom (Table 1). This reflects the difference in *trans* influence between pyridine and chloride, which are π-acid and π-donor ligands in nature, respectively. A similar difference in Ni—Cl distances is also found in other $Ni_2(\mu\text{-}Cl)_2Cl_2$ complexes in which the Ni atom is hexacoordinated and which contain a pyridine ring opposite one of two bridging Cl atoms [the two examples to date are: 2.367 *versus* 2.531 Å (Constable *et al.*, 2002) and 2.356 *versus* 2.520 Å (Zhang *et al.*, 2007)], but the difference in Ni—Cl distances found in (I) is the largest, possibly as a result of the good conjugation of all the ttp rings mentioned above. However, although ttp is a good extended π-system, there is no π–π stacking between the ttp planes in the crystal lattice in (I). Instead, some nonclassical intermolecular hydrogen bonds as secondary interactions play a crucial role in self-assembling the molecules into a three-dimensional network, as discussed below.

As shown in Table 2 and the packing view (Fig. 2), the terminal Cl2 atom acts as an acceptor of four intermolecular C—H···Cl interactions with three aromatic CH groups from the same neighboring molecule and one methyl group from another adjacent molecule. One of the H···Cl distances is quite short at 2.59 Å, suggesting a significant hydrogen bonding interaction, while the remaining three H···Cl distances fall slightly below the sum of van der Waals radii (2.95 Å) and the C—H···Cl angles are fairly linear, consistent with criteria for C—H···Cl interactions (Aakeröy *et al.*, 1999; Freytag *et al.*, 2000). Atoms H4, H7 and H17 from the same ttp ligand surround atom Cl2 in a manner reminiscent of chelation. The Ni—Cl coordination bond provides both charge assistance and directionality for strengthening the C—H···Cl interactions. The four Ni—Cl···H angles are in the range 94–105°, compatible with other C—H···Cl cases assisted by terminal *M*—Cl bonds (Balamurugan *et al.*, 2004).

Experimental

4′-*p*-Tolyl-2,2′:6′,2″-terpyridine (ttp) was prepared by an improved Kröhnke condensation method (Wang *et al.*, 2007; Collin *et al.*, 1991). A mixture of $NiCl_2{\cdot}6H_2O$ (0.2 mmol, 0.0476 g), ttp (0.2 mmol, 0.0646 g) and EtOH (10 ml) was placed in a 23 ml Teflon-lined stainless steel vessel and heated under autogenous pressure at 412 K for 3 d, followed by cooling to room temperature at a rate of 5 K h^{-1}. Light-green block-shaped crystals of (I) were obtained.

Crystal data

$[Ni_2Cl_4(C_{22}H_{17}N_3)_2]$
M_r = 905.99
Monoclinic, $P2_1/c$
a = 14.2218 (11) Å
b = 12.7866 (10) Å
c = 10.8659 (8) Å
β = 102.219 (1)°
V = 1931.2 (3) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 1.29 mm^{-1}
T = 298 (2) K
0.45 × 0.35 × 0.20 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
T_{min} = 0.594, T_{max} = 0.782
10824 measured reflections
3965 independent reflections
2507 reflections with $I > 2\sigma(I)$
R_{int} = 0.055

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.079
S = 0.86
3965 reflections
254 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.35 e Å^{-3}
$\Delta\rho_{min}$ = −0.35 e Å^{-3}

All H atoms were positioned geometrically and allowed to ride on their parent C atoms, with C—H distances of 0.93 or 0.96 Å and $U_{iso}(H)$ = 1.2 or $1.5U_{eq}(C)$ for aromatic and methyl H atoms, respectively.

Table 1
Selected geometric parameters (Å, °).

Cl1—Ni1	2.3449 (7)	N2—Ni1	1.976 (2)
Cl2—Ni1	2.3980 (8)	N3—Ni1	2.089 (2)
N1—Ni1	2.077 (2)	Ni1—Cl1^i	2.6231 (8)
N2—Ni1—N1	78.89 (9)	N3—Ni1—Cl2	89.31 (6)
N2—Ni1—N3	78.37 (9)	Cl1—Ni1—Cl2	98.78 (3)
N1—Ni1—N3	157.26 (9)	N2—Ni1—Cl1^i	85.07 (7)
N2—Ni1—Cl1	170.45 (7)	N1—Ni1—Cl1^i	87.10 (6)
N1—Ni1—Cl1	100.69 (6)	N3—Ni1—Cl1^i	90.60 (6)
N3—Ni1—Cl1	101.67 (6)	Cl1—Ni1—Cl1^i	85.38 (3)
N2—Ni1—Cl2	90.77 (7)	Cl2—Ni1—Cl1^i	175.77 (3)
N1—Ni1—Cl2	91.36 (6)		

Symmetry code: (i) $-x, -y + 1, -z$.

Table 2
Selected geometric parameters for intermolecular interactions (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C4—H4···Cl2^{ii}	0.93	2.59	3.512 (3)	171
C7—H7···Cl2^{ii}	0.93	2.91	3.837 (2)	170
C17—H17···Cl2^{ii}	0.93	2.93	3.851 (3)	170
C22—H22C···Cl2^{iii}	0.96	2.82	3.693 (3)	151

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

Data collection: *APEX2* (Bruker, 2004); cell refinement: *APEX2*; data reduction: *APEX2*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DN3115). Services for accessing these data are described at the back of the journal.

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