

**[3,3',3''-(1,4,7-Triazacyclononane-1,4,7-triyl)-
tripropanamide]nickel(II) bis(perchlorate)****Rui Liu, Yi-Zhi Li, Zhong Zhang
and Zhi-Lin Wang***Coordination Chemistry Institute, State Key
Laboratory of Coordination Chemistry, Nanjing
University, Nanjing 210093, People's Republic
of China

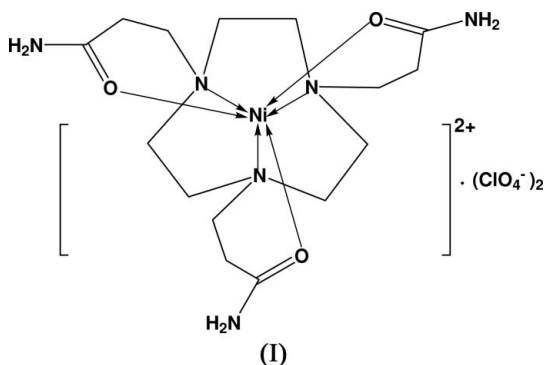
Correspondence e-mail: llyyz@nju.edu.cn

Received 5 April 2006
Accepted 12 April 2006

In the title compound, $[\text{Ni}(\text{C}_{15}\text{H}_{30}\text{N}_6\text{O}_3)](\text{ClO}_4)_2$, the Ni^{II} atom is coordinated by three N and three O atoms from the 3,3',3''-(1,4,7-triazacyclononane-1,4,7-triyl)tripropanamide (tcet) ligand in a pseudo-octahedral geometry. The $[\text{Ni}(\text{tcet})]^{2+}$ complex cations are linked by $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds to form zigzag chains, which are further connected into a three-dimensional network by $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds with ClO_4^- anions.

Key indicatorsSingle-crystal X-ray study
 $T = 298 \text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.007 \text{ \AA}$
 R factor = 0.055
 wR factor = 0.134
Data-to-parameter ratio = 15.0For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.**Comment**

Ligands with pendent amide groups are particularly interesting (Weyhermüller *et al.*, 1998) because they can form metal complexes in which the NH_2 groups can remain protonated and the CH_2CONH_2 groups coordinate to the metal atom through the carbonyl O atoms. This coordination behaviour is very similar to that of the CONH group in small peptides. We report here the structure of the title compound, $[\text{Ni}(\text{tcet})](\text{ClO}_4)_2$ [tcet = 3,3',3''-(1,4,7-triazacyclononane-1,4,7-triyl)tripropanamide], (I), the ligand being a new derivative of H_3tacn having pendent arms (H_3tacn = 1,4,7-triazacyclononane).



In (I), the coordination geometry around the Ni atom is pseudo-octahedral (Fig. 1). The twist angle, which is defined as 0° for a regular trigonal prism and 60° for an octahedron (Schlager *et al.*, 1995), is $53.2(2)^\circ$.

The complex cations are connected by $\text{N4}-\text{H4E}\cdots\text{O3}^{\text{i}}$ hydrogen bonds [Table 1; symmetry code (i) $x, \frac{3}{2} - y, z - \frac{1}{2}$], forming zigzag chains along the b axis (Fig. 2). $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds between the complex and ClO_4^- anions link these chains into a three-dimensional network.

Experimental

H_3tacn (10 mmol, 1.3 g), prepared according to the literature procedure of Bushnell *et al.* (1998), and acrylamide (40 mmol, 3 g)

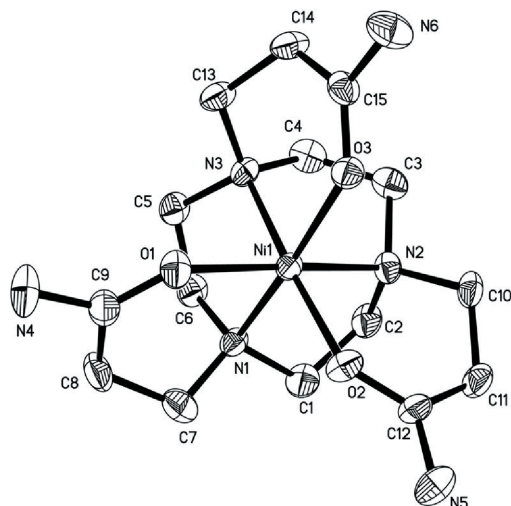


Figure 1

A view of the complex cation in (I), with displacement ellipsoids drawn at the 30% probability level. All H atoms have been omitted for clarity.

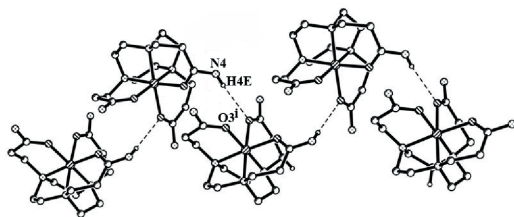


Figure 2

The hydrogen-bonded chain of the complex cation of (I), along the *b* axis. H atoms have been omitted except for those involved in the hydrogen bonding. Dashed lines indicate hydrogen bonds. [Symmetry code: (i) $x, \frac{3}{2} - y, z - \frac{1}{2}$]

were dissolved in MeOH (30 ml), and the mixture reacted at 333 K for 12 h. The tcet ligand was obtained as a colourless solid by evaporating the solvent and this was then recrystallized from a solution in methanol–diethyl ether (2:3 *v/v*) (yield of tcet 2.6 g, 75.8%). Elemental analysis found: C 52.86, H 8.53, N 24.34%; calculated for $C_{15}H_{30}N_6O_3$: C 52.61, H 8.83, N 24.54%. 1H NMR (500 Hz, CD_3CN , δ , p.p.m.): 2.8–2.9 (*m*, 12H, N–CH₂–CH₂–N), 2.26 (*t*, 6H, N–CH₂), 2.12 (*t*, 6H, CH₂–CONH₂).

To tcet (0.3 mmol, 103 mg) in MeOH (30 ml) was added $Ni(ClO_4)_2 \cdot 6H_2O$ (0.4 mmol, 146 mg), and the reaction mixture was stirred at boiling point. A purple precipitate formed quickly. Crystals of (I) suitable for X-ray diffraction were obtained by slow diffusion of diethyl ether into an acetonitrile solution [yield of (I) 102 mg, 57.2%]. Elemental analysis found: C 30.06, H 5.04, N 13.63%; calculated for $C_{15}H_{30}Cl_2N_6NiO_{11}$: C 30.03, H 5.06, N 14.01%; ESMS (*m/z*): 200 ($L+Ni^{2+}$), 501 ($L+Ni^{2+}+ClO_4^-$).

Crystal data

$[Ni(C_{15}H_{30}N_6O_3)](ClO_4)_2$
 $M_r = 600.06$
 Monoclinic, $P2_1/c$
 $a = 18.544$ (2) Å
 $b = 12.5781$ (14) Å
 $c = 10.7292$ (12) Å
 $\beta = 105.562$ (2)°
 $V = 2410.8$ (5) Å³

$Z = 4$
 $D_x = 1.653$ Mg m⁻³
 Mo $K\alpha$ radiation
 $\mu = 1.09$ mm⁻¹
 $T = 298$ K
 Block, purple
 $0.34 \times 0.33 \times 0.31$ mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Bruker, 2000)
 $T_{min} = 0.70$, $T_{max} = 0.72$

12942 measured reflections
 4726 independent reflections
 3802 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.041$
 $\theta_{max} = 26.0^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.055$
 $wR(F^2) = 0.134$
 $S = 1.05$
 4726 reflections
 316 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.07P)^2 + 1.9365P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 0.28$ e Å⁻³
 $\Delta\rho_{min} = -0.40$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Ni1–O2	2.039 (3)	Ni1–N3	2.078 (3)
Ni1–O1	2.071 (3)	Ni1–N2	2.081 (3)
Ni1–N1	2.077 (3)	Ni1–O3	2.111 (3)
O2–Ni1–N1	96.54 (13)	O1–Ni1–N2	176.18 (13)
O1–Ni1–N1	91.04 (13)	N1–Ni1–O3	176.02 (12)
O2–Ni1–N3	176.62 (14)	N3–Ni1–O3	90.89 (12)
O1–Ni1–N3	93.56 (13)	N2–Ni1–O3	95.08 (12)
O2–Ni1–N2	91.63 (14)		

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
N4–H4E···O3 ⁱ	0.89	2.55	3.405 (6)	160
N4–H4D···O21 ⁱⁱ	0.89	2.48	3.242 (5)	144
N5–H5D···O24 ⁱⁱⁱ	0.89	2.43	3.046 (5)	127
N5–H5E···O24	0.89	2.28	3.170 (5)	173
N5–H5E···O23	0.89	2.59	3.270 (5)	134
N6–H6C···O14	0.89	2.44	3.100 (5)	131
N6–H6D···O11 ^{iv}	0.89	2.30	3.181 (5)	168

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

All H atoms were placed in calculated positions and treated as riding atoms, with C–H = 0.97 Å and N–H = 0.89 Å, and with $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}(N)$.

Data collection: SMART (Bruker, 2000); cell refinement: SAINT (Bruker, 2000); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Bruker, 2000); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

This project was supported by the Natural Science Foundation of China (grant No. 20475026).

References

- Bruker (2000). SMART, SAINT, SADABS and SHELXTL. Bruker AXS inc., Madison, Wisconsin, USA.
 Bushnell, G. W., Fortier, D. G. & McAuley, A. (1998). *Inorg. Chem.* **27**, 2626–2634.
 Schlager, O., Wieghardt, K., Grondey, H., Rufinska, A. & Nuber, B. (1995). *Inorg. Chem.* **34**, 6440–6448.
 Weyhermüller, T., Wieghardt, K. & Chaudhuri, P. (1998). *J. Chem. Soc. Dalton Trans.* pp. 99–110.