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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1540). Services for accessing these data are described at the back of the journal.

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Di-μ-chloro-bis{[tris(2-pyridylmethyl)amine-κ⁴N]nickel(II)} bis(triethylammonium) tetraperchlorate

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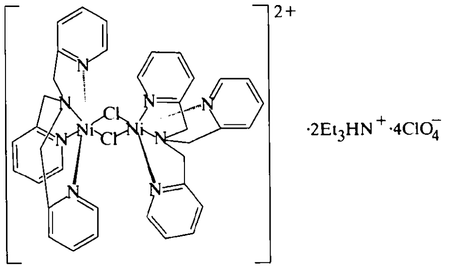
Abstract

The title compound, $(C_6H_{16}N)_2[Ni_2Cl_2(C_{18}H_{18}N_4)_2](ClO_4)_4$ or $[\{Ni(TPA)Cl\}_2](ClO_4)_2\cdot 2HN(CH_2CH_3)_3\cdot ClO_4$, where TPA is tris(2-pyridylmethyl)amine, consists of a centrosymmetric dimeric nickel(II) center bridged asymmetrically by Cl^- ions. The difference in the Ni—Cl distances [0.141 Å for 2.3655 (8) and 2.507 (1) Å] is the largest thus far reported. Each Ni atom is pseudo-octahedral six-coordinate. Triethylammonium perchlorate cocrystallizes with the metal complex.

Comment

We have considerable interest in metal complexes of TPA [tris(2-pyridylmethyl)amine] and upon reading the introduction of a recent article (Bebout *et al.*, 1997), we noted that Ni^{II} complexes of TPA were not mentioned in a list of known TPA–metal complexes. After we had synthesized the title complex, (I), we found that the crystal structures of three Ni^{II}–TPA complexes had been reported previously (Ito & Takita, 1996; Zhang *et al.*, 1996).



(I)

The cationic portion of the title complex is a centrosymmetric unit of two Ni atoms bridged unsymmetrically by two Cl atoms. The separation of the two Ni atoms is 3.525 (1) Å, and the Cl separation is 3.367 (2) Å. The Ni atoms are pseduo-octahedral six-coordinate, with four N atoms from the TPA ligand completing the coordination environment. The difference in the Ni—Cl distances (0.141 Å) is the largest of any Ni_2Cl_2 core reported (see, for example, Bkouche-Waksman *et al.*, 1981; Ianelli *et al.*, 1991; Blake *et al.*, 1996; Di Vaira *et al.*, 1997). As expected, in the reported structures, the greatest differences are observed for cases in which the types of donor atoms *trans* to the bridges are the most different. In the present case, the difference in Lewis basicity of the tertiary amine compared to that of pyridine is quite pronounced, as reflected in the Ni—Cl distances. The shortest Ni—Cl distance [2.3655 (8) Å] is *trans* to the tertiary amine of TPA. In many structures, the Lewis basicity difference between the tertiary amine and pyridine of TPA further manifests itself as a longer metal-to-nitrogen distance for the tertiary amine (see, for example, Norman *et al.*, 1990; Dalley *et al.*, 1996). That is not the case here where the Ni—N distances are all similar. The distances and angles within the dimeric Ni^{II} unit are the same within experimental error as those reported previously for $[\{Ni(TPA)Cl\}_2](ClO_4)_2\cdot H_2O$ (Zhang *et al.*, 1996).

We found five examples of triethylammonium perchlorate cocrystallizing with a metal complex (Kato & Ito, 1986; Gomez-Romero *et al.*, 1988; Das & Nag, 1991; Gluziński *et al.*, 1993; Thuéry *et al.*, 1995). The metrical parameters in the title complex are unremarkable. The triethylammonium ion hydrogen bonds to a perchlorate; the separation of O6 to N5 of a triethyl-

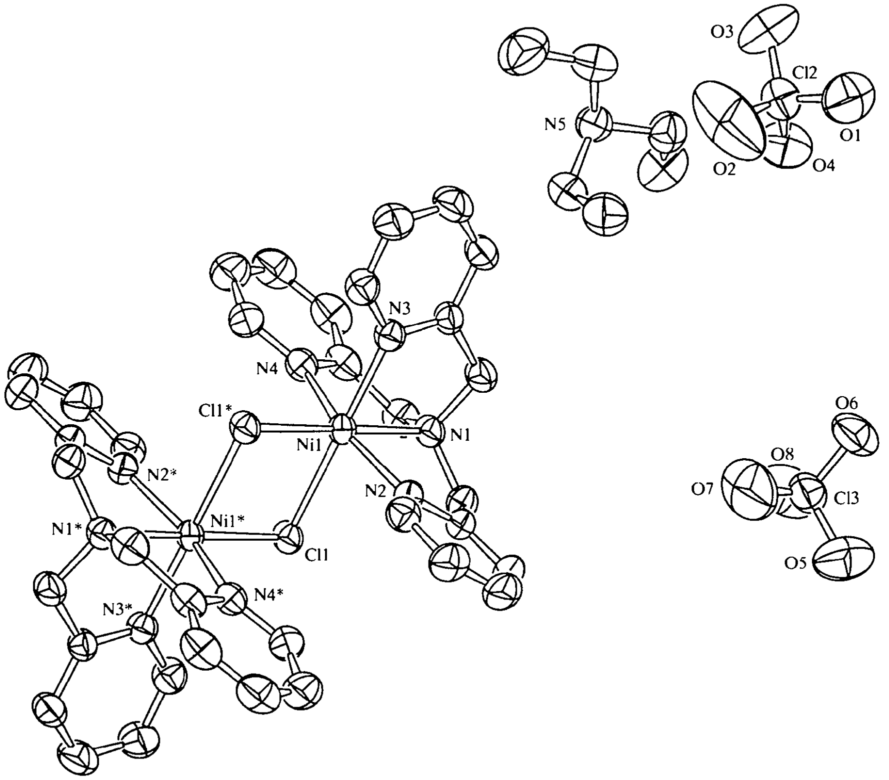


Fig. 1. The asymmetric unit of (I) with the nickel dimer expanded. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted. The C atoms are numbered sequentially starting from N1 towards N2 (and analogously towards N3 and N4), ending with C18 bound to N4. Additionally, C19, C21 and C23 are the methylene C atoms of $HNEt_3^+$. [The asterisks represent symmetry code $-x$, $-1-y$, $-z$.]

ammonium cation in a neighboring cell (x, y, $z-1$) is 2.929 (4) Å.

Experimental

TPA·$HClO_4$ (0.1954 g) was dissolved in methanol (20 ml) followed by the addition of triethylamine (105 ml). $Ni(ClO_4)_2$·$6H_2O$ (0.1829 g) was added to the resulting solution, followed by $HN(CH_2CH_3)_3Cl$ (0.0689 g). This solution was stirred for 30 min and then allowed to stand at room temperature covered with parafilm in which a small hole had been punched. After 7 d, bright-blue rectangular prismatic crystals of the title complex were obtained [observed (uncorrected) m.p. 535–538 K]. **Caution:** the perchlorate salts in this study are all potentially explosive and should be handled with care.

Crystal data

$(C_6H_{16}N)_2[Ni_2Cl_2(C_{18}H_{18}N_4)_2](ClO_4)_4$
$M_r = 1371.24$
Monoclinic
$P2_1/c$

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 20.0$–$22.5°$

$a = 11.511$ (4) Å
$b = 22.022$ (3) Å
$c = 12.521$ (2) Å
$\beta = 107.71$ (2)°
$V = 3024$ (1) Å^3
$Z = 2$
$D_x = 1.506$ Mg m^{-3}
D_m not measured

$\mu = 0.960$ mm^{-1}
$T = 294$ K
Rectangular prism
0.55 × 0.30 × 0.30 mm
Blue

Data collection

Rigaku AFC-7*R* diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.691$, $T_{max} = 0.750$
9991 measured reflections
9210 independent reflections

5429 reflections with $I > 2\sigma(I)$
$R_{int} = 0.039$
$\theta_{max} = 30.0°$
$h = 0 \rightarrow 16$
$k = 0 \rightarrow 30$
$l = -23 \rightarrow 23$
3 standard reflections every 150 reflections intensity decay: 1.25%

Refinement

Refinement on F
$R = 0.045$
$wR = 0.054$
$S = 1.960$

$w = 1/[\sigma^2(F_o) + 0.00013|F_o|^2]$
$(\Delta/\sigma)_{max} = 0.027$
$\Delta\rho_{max} = 0.62$ e Å^{-3}

5429 reflections
370 parameters
H-atom parameters not refined

$\Delta\rho_{\min} = -0.79$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Ni1—Cl1	2.507 (1)	Ni1—N2	2.070 (3)
Ni1—Cl1^i	2.3655 (8)	Ni1—N3	2.085 (3)
Ni1—N1	2.086 (2)	Ni1—N4	2.084 (3)
Cl1—Ni1—Cl1^i	87.37 (3)	Cl1^i—Ni1—N4	99.76 (8)
Cl1—Ni1—N1	93.16 (7)	N1—Ni1—N2	80.0 (1)
Cl1—Ni1—N2	87.98 (7)	N1—Ni1—N3	83.4 (1)
Cl1—Ni1—N3	175.38 (7)	N1—Ni1—N4	81.5 (1)
Cl1—Ni1—N4	90.76 (7)	N2—Ni1—N3	94.4 (1)
Cl1^i—Ni1—N1	178.66 (8)	N2—Ni1—N4	161.3 (1)
Cl1^i—Ni1—N2	98.81 (8)	N3—Ni1—N4	85.7 (1)
Cl1^i—Ni1—N3	96.15 (7)	Ni1—Cl1—Ni1^i	92.63 (3)

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

H atoms were placed in idealized positions (C—H 0.95 Å and N—H 0.97 Å), with $U_{\rm iso} = 1.2U_{\rm eq}$ of the attached atom.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1997). Program(s) used to solve structure: *PATTY* in *DIRDIF*92 (Beurskens *et al.*, 1992). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

We are grateful to the Kresge Foundation for providing the funds for the purchase of the diffractometer used in this work.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1198). Services for accessing these data are described at the back of the journal.

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A three-dimensional host framework with small tetragonal and large hexagonal channels

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Abstract

Bis(cyclohexylamine-*N*)cadmium(II)bis{tricyanocadmate(II)}–toluene (1/1), $[Cd(C_6H_{11}NH_2)_2\{Cd(CN)_3\}_2]\cdot C_6H_5CH_3$ {or, alternatively, bis(cyclohexylamine-*N*)-hexacyanotricadmium(II) toluene solvate, $[Cd_3(CN)_6(C_6H_{13}N)_2]_n\cdot nC_7H_8$}, is a three-dimensional framework made up of octahedral and tetrahedral Cd sites (in a 1:2 ratio) bridged by cyanide groups. The octahedral Cd centers are coordinated by four cyano groups and two *trans* cyclohexylamine ligands, and the tetrahedral Cd centers are coordinated by four cyano groups. The host structure provides small tetragonal and large hexagonal channels, which are occupied, respectively, by the toluene guest molecules and the cyclohexylamine ligands coordinated to the octahedral Cd site.

Comment

Inorganic supramolecular chemistry and the construction of polymeric multi-dimensional frameworks are ideas which currently garner much interest. As part of their strategy for designing novel supramolecular systems using cyanometallate complex hosts and organic