(*meso*-5,7,7,12,14,14-Hexamethyl-1,4,8,11-tetraaza-cyclotetradecane)nickel(II) tetrachlorocuprate(II)

Zai-Shan Wei* and Guang-Ming Yu

School of Environmental Science and
Engineering, Sun Yat-Sen University,
Guangzhou 510275, People's Republic of China

Correspondence e-mail: ceswzs@yahoo.com.cn

In the title compound, $[Ni(C_{16}H_{36}N_4)][CuCl_4]$, the cation is centrosymmetric and the anion lies on a twofold rotation axis. The cation and anion are linked by weak N—H···Cl hydrogen bonds to form neutral supramolecular zigzag chains.
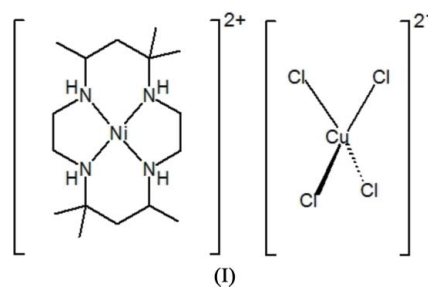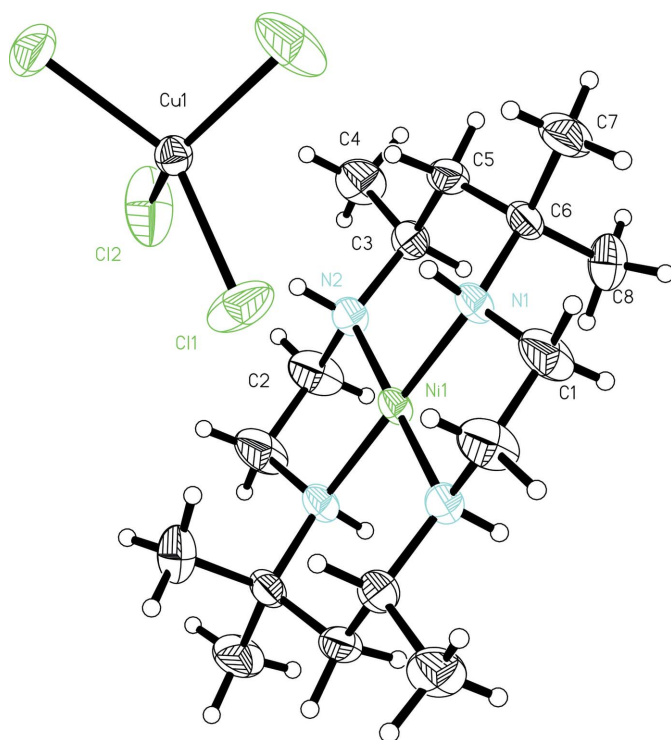
Comment

Cyanide wastes are found predominantly in industrial effluents generated by electroplating, photographic processes, metal processing and petroleum refineries. The toxicity of cyanide creates serious environmental problems and cyanide removal from waste water by ozonation is currently a well accepted process. References to this process span more than 50 years (Walker & Zabban, 1953).

Bubble-type ozonation methods have long been the most popular techniques in the application of ozone to waste water treatment (Andreozzi *et al.*, 2000). More recently, photo-oxidation processes using ultraviolet radiation in combination with various oxidants such as H_2O_2 and ozone, with metal ions as catalysts, have been used as a highly promising approach to the treatment of cyanide wastes (Sarla *et al.*, 2004)

CuO is used as a catalyst to treat waste water containing cyanide under highly alkaline conditions in a laboratory-scale electrochemical batch reactor (Szpyrkowicz *et al.*, 2000). The syntheses of macrocyclic metal complexes with tetrachloro-metallate anions were reported for the first time by Curtis *et al.* (1973). Subsequently, analogous complexes have been reported only once (Bencini *et al.*, 1988).

In the present study, we used a tetrachlorocuprate(II) anion in cooperation with a macrocyclic metal cation to oxidize cyanide in aqueous solution by means of a bubble-type ozonation process. The title compound appears to be a highly efficient oxidant. The tetrachlorocuprate anion facilitates the catalytic ability of the macrocyclic Ni[II] cation in the treatment of cyanide wastes. Further studies of the reaction mechanism are currently in progress and we now report the crystal structure of (I).

(I)

The constituent ions of (I) are shown in Fig. 1 and selected bond lengths are given in Table 1. The Ni atom lies on a centre

Figure 1
The structure of (I), shown with 30% probability displacement ellipsoids. Unlabelled atoms in the cation are related to labelled atoms by $(x + 1, y + 1, z)$. Unlabelled atoms in the anion are related to labelled atoms by $(\frac{1}{2} - x, \frac{3}{2} - y, z)$.
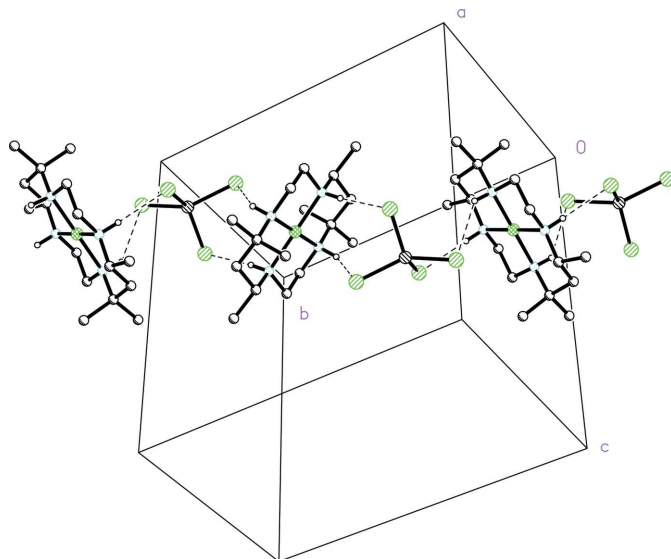
Figure 2
Part of the crystal structure of (I), showing the formation of a [110] double hydrogen-bonded chain. All H atoms attached to C atoms have been omitted for clarity.

of symmetry and the Cu atom on a twofold rotation axis. The Ni—N bond lengths are slightly shorter than expected. The $[CuCl_4]^{2-}$ anions are linked to the neighbouring $[Ni(meso)]^{2+}$ cations by means of two unique weak N—H$\cdots$Cl hydrogen bonds (Table 2), resulting in one-dimensional zigzag chains along [111].

Experimental

The macrocyclic ligand (*meso-L*) and its nickel(II) complex [Ni(*meso-L*)](ClO$_4$)$_2$ were prepared according to a previously reported method (Tait & Busch, 1976). Plate-shaped brown crystals of the title compound were obtained by slow evaporation of a concentrated HCl solution containing an approximately 1:1 molar ratio of NiL(ClO$_4$)$_2$ and CuCl$_2$·2H$_2$O in approximately 55% yield at room temperature. Elemental analysis calculated for C$_{16}$H$_{36}$N$_4$Cl$_4$CuNi: C 35.03, H 6.62, N 10.21%; found: C 35.07, H 6.55, N 10.18%.

Crystal data

[Ni(C$_{16}$H$_{36}$N$_4$)][CuCl$_4$]
$M_r = 548.54$
Orthorhombic, $Pccn$
$a = 9.7331 (14)$ Å
$b = 14.943 (2)$ Å
$c = 16.111 (2)$ Å
$V = 2343.2 (6)$ Å^3
$Z = 4$
$D_x = 1.555$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 3908
  reflections
$\theta = 2.5–26.5°$
$\mu = 2.18$ mm^{-1}
$T = 293 (2)$ K
Plate, brown
$0.45 \times 0.31 \times 0.12$ mm

Data collection

Bruker SMART CCD area-detector
  diffractometer
φ and ω scans
Absorption correction: multi-scan
  (*SADABS*; Sheldrick, 1996)
  $T_{min} = 0.441$, $T_{max} = 0.780$
11112 measured reflections

2295 independent reflections
1700 reflections with $I > 2\sigma(I)$
$R_{int} = 0.031$
$\theta_{max} = 26.0°$
$h = -9 \rightarrow 12$
$k = -18 \rightarrow 18$
$l = -19 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.102$
$S = 1.06$
2295 reflections
123 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0395P)^2$
  $+ 3.5285P]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.67$ e Å^{-3}
$\Delta\rho_{min} = -0.43$ e Å^{-3}

Table 1
Selected bond lengths (Å).

Cl1—Cu1	2.2118 (12)	Ni1—N2	1.953 (3)
Cl2—Cu1	2.2230 (13)	Ni1—N1	1.959 (3)

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N2—H2C$\cdots$Cl2	0.91	2.39	3.302 (4)	175
N1—H1C$\cdots$Cl1	0.91	2.60	3.329 (4)	137

The H atoms were positioned geometrically and treated as riding on their parent C and N atoms, with C—H distances in the range 0.96–0.98 Å, and N—H distances of 0.91 Å, and with U_{iso}(H) = 1.2–1.5U_{eq}(parent atom).

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT-Plus* (Bruker, 1999); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics:

SHELXTL (Bruker, 1999); software used to prepare material for publication: *SHELXTL*.

References

Andreozzi, R., Capiro, V., Insola, A., Marotta, R. & Sanchirco, R. (2000). *Water Res.* **34**, 620–628.

Bencini, A., Caneschi, A., Dei, A., Gatteschi, D., Zanchini, C. & Kahn, O. (1988). *Inorg. Chem.* **25**, 1374–1378.

Bruker (1999). *SMART* (Version 5.054), *SAINT-Plus* (Version 6.45) and *SHELXTL* (Version 6.14). Bruker AXS Inc., Madison, Wisconsin, USA.

Curtis, N. F., Swann, D. A. & Waters, T. N. (1973). *J. Chem. Soc. Dalton Trans.* pp. 1963–1974.

Sarla, M., Pandit, M., Tyagi, D. K. & Kapoor, J. C. (2004). *J. Hazard. Mater. B*, **116**, 49–56.

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

Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.

Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.

Szpyrkowicz, L., Kaul, S. N., Molga, E. & DeFaveri, M. (2000). *Electrochim. Acta*, **46**, 381–387.

Tait, A. M. & Busch, D. H. (1976). *Inorg. Synth.* **18**, 4–19.

Walker, C. A. & Zabban, W. (1953). *Plating*, **40**, 777–780.