ω–θ scans with ω half-width $(1.05 + 0.35\tan\theta)^\circ$
Absorption correction: ψ scans (North *et al.*, 1968)
$T_{\rm min} = 0.846$, $T_{\rm max} = 0.934$
2515 measured reflections

$h = -9 \rightarrow 8$
$k = 0 \rightarrow 24$
$l = 0 \rightarrow 11$
3 standard reflections
frequency: 60 min
intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.079$
$S = 1.026$
2446 reflections
187 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.027P)^2 + 0.291P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} = 0.005$
$\Delta\rho_{\rm max} = 0.27$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.26$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected bond lengths (Å)*

Co1—O3	2.050 (2)	C31—C41	1.361 (5)
Co1—O1	2.112 (2)	C41—C51	1.402 (5)
Co1—Cl1	2.5011 (8)	C51—C61	1.343 (5)
N11—C21	1.365 (4)	C61—C1*M*	1.490 (5)
N11—C61	1.369 (4)	N12—C22	1.366 (4)
C21—O1	1.265 (4)	N12—C62	1.368 (4)
C21—C31	1.419 (4)		

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3*A*···O2$^{\rm i}$	0.77 (4)	2.02 (4)	2.758 (4)	161 (4)
O3—H3*B*···O2$^{\rm ii}$	0.86 (4)	1.86 (4)	2.712 (4)	176 (4)
N11—H11···Cl1$^{\rm ii}$	0.86 (4)	2.31 (4)	3.104 (3)	152 (4)
N12—H12···Cl1	0.79 (4)	2.49 (4)	3.229 (4)	157 (3)

Symmetry codes: (i) $x - 1, y, z$; (ii) $-x, -y, -z$.

The H atoms attached to sp^2-hybridized C atoms were allowed to ride on their parent atoms with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$; methyl groups were treated as rotating rigid groups with $U_{\rm iso}({\rm H}) = 1.5U_{\rm eq}({\rm C})$. The four H atoms attached to N11, N12 and O3 were refined freely.

Data collection: *DIF*4 (Stoe & Cie, 1990*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1990*b*). Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1995). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL* and *CAMERON* (Pearce *et al.*, 1994). Software used to prepare material for publication: *PLATON* (Spek, 1997).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: MU1364). Services for accessing these data are described at the back of the journal.

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Trimethylammonium Nickel(II) Chloride Dihydrate

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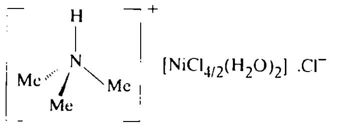
Abstract

catena-Poly[trimethylammonium [diaquanickel(II)-di-μ-chloro] chloride], $[(CH_3)_3NH][NiCl_2(H_2O)_2]Cl$, is built up by infinite chains of Cl-edge-sharing *trans*-$[NiCl_4(H_2O)_2]$ octahedra separated by trimethylammonium cations and discrete Cl^- anions. The compound is isostructural with the cobalt and manganese compounds, with negligible modifications caused by the difference in the ionic radii of the metal ions. The crystal structure is stabilized by hydrogen bonds between the discrete Cl^- ions and the water molecules, and also between the trimethylammonium ions and the water molecules.

Comment

The title compound is isostructural with the analogous manganese (Caputo *et al.*, 1976) and cobalt (Losee *et al.*, 1973) compounds; they consist of infinite chains of edge-sharing *trans*-$[MCl_4(H_2O)_2]$ octahedra (M = Mn, Co or Ni) running parallel to the *b* axis. These one-dimensional chains make the compounds useful for studying and testing the concepts of prediction of magnetic properties, established by the Ising or Heisenberg theory (De Jongh & Miedema, 1974). The magnetic susceptibilities of powder samples of the one-dimensional $S = 1$ system $[(CH_3)_3NH][NiCl_3].2H_2O$ (O'Brien *et al.*, 1981) have been measured and the data reveal strong ferromagnetic intra-chain spin correlations with the onset of a long-range order at T = 3.5 K. The earlier investigations of O'Brien *et al.* (1981) could not explain the anisotropy of the susceptibility, because single crystals of suitable size were lacking. We have obtained single crystals of the title compound, (I), allowing us to determine the crystal structure.



(I)

The infinite chains of edge-sharing octahedra in (I) are separated by layers of trimethylammonium cations in the *bc* plane. The decrease of the lattice constants, which is largest in the **b** direction, from those of the Mn compound (a = 16.779, b = 7.434 and c = 8.227 Å) *via* the Co compound (a = 16.671, b = 7.273 and c = 8.113 Å) to the Ni compound, can be explained by the decreasing radii of the metal ions. A comparison of (I) with $NiCl_2.2H_2O$ (Morosin, 1967) shows that in (I) the *trans*-$[NiCl_4(H_2O)_2]$ octahedra are slightly less elongated along the **b** direction. The formation of hydrogen bonds between the terminal H atom of each trimethylammonium group and O atoms of the octahedral chains [H1· · ·O = 2.49 (4) Å] leads to a tilt of the $[NiCl_4(OH_2)_2]$ octahedra towards one another. The deviation of the Ni—Cl—Ni bridge from linearity is smaller in the $NiCl_2.2H_2O$ compound (about 7.6°) than in (I) (about 8.9°). There are further hydrogen bonds between the Cl^- ions and the H atoms of the water moieties of the Cl-edge-sharing chains of octahedra [Cl3· · ·H3*A* = 2.32 (5) Å and Cl3· · ·H3*B* = 2.41 (4) Å], which contribute to the stabilization of the structure.

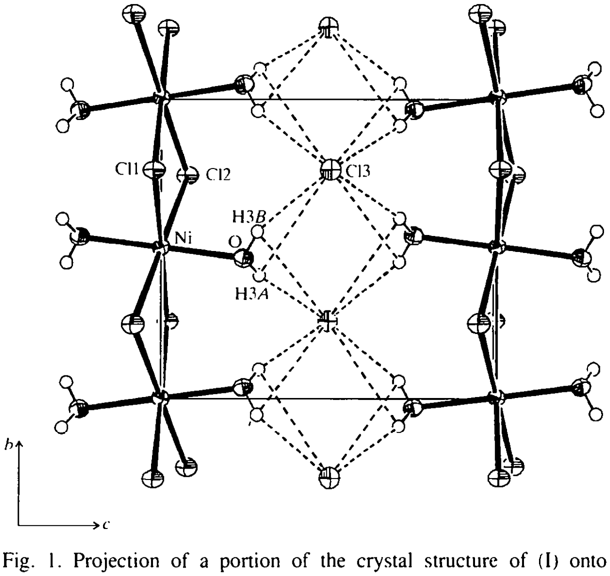


Fig. 1. Projection of a portion of the crystal structure of (I) onto the *bc* plane. The chains of Cl-edge-sharing *trans*-$[NiCl_4(H_2O)_2]$ octahedra, which run along the *b* axis, form hydrogen bonds between the discrete Cl^- ions and the water molecules in the **c** direction. (The probability level of the displacement ellipsoids is 50%.)

Experimental

The title compound was prepared by slow evaporation from a dilute hydrochloric acid solution containing equimolar amounts of $NiCl_2$ and $[(CH_3)_3NH]Cl$ under a nitrogen atmosphere. The yellow–green hygroscopic crystals grew as prisms, elongated along the *b* axis.

Crystal data

$(C_3H_{10}N)[NiCl_2(H_2O)_2]Cl$
M_r = 261.21
Orthorhombic
Pnma
a = 16.675 (3) Å
b = 7.163 (1) Å
c = 8.100 (2) Å
V = 967.5 (3) Å^3
Z = 4
D_x = 1.793 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 19 reflections
θ = 10.19–17.29°
μ = 2.783 mm^{-1}
T = 293 (2) K
Needle
0.3 × 0.1 × 0.1 mm
Yellow–green

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (Siemens, 1989)
T_{min} = 0.528, T_{max} = 0.757
1032 measured reflections
925 independent reflections
622 reflections with $I > 2\sigma(I)$

R_{int} = 0.076
θ_{max} = 24.97°
$h = 0 \rightarrow 19$
$k = -8 \rightarrow 0$
$l = -9 \rightarrow 0$
2 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.027
$wR(F^2)$ = 0.079
S = 1.097
925 reflections
85 parameters
Only coordinates of H atoms refined

$w = 1/[\sigma^2(F_o^2) + (0.0409P)^2 + 0.0764P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.578 e Å^{-3}
$\Delta\rho_{min}$ = −0.488 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Ni	0	0	0	0.0199 (2)
Cl1	0.09605 (7)	−1/4	0.06739 (16)	0.0247 (3)
Cl2	0.09687 (6)	1/4	0.00711 (14)	0.0234 (3)
O	0.02440 (17)	−0.0374 (4)	−0.2465 (3)	0.0262 (5)
Cl3	0.08792 (8)	1/4	−0.50303 (14)	0.0298 (3)

N	0.1825 (3)	−1/4	−0.3051 (5)	0.0273 (10)
C1	0.2255 (3)	−0.0790 (6)	−0.2521 (6)	0.0397 (10)
C2	0.1671 (4)	−1/4	−0.4853 (7)	0.0378 (14)

Table 2. *Selected geometric parameters (Å, °)*

Ni—O	2.055 (3)	N—C2	1.482 (8)
Ni—Cl2	2.4123 (8)	N—C1	1.483 (5)
Ni—Cl1	2.4637 (8)		
O—Ni—Cl2^{i}	90.72 (9)	Cl1—Ni—Cl1^{i}	180.0
O^{i}—Ni—Cl2^{i}	89.28 (9)	Ni^{ii}—Cl1—Ni	93.25 (4)
O—Ni—Cl1	89.53 (8)	Ni—Cl2—Ni^{iii}	95.86 (4)
O^{i}—Ni—Cl1	90.47 (8)	C2—N—C1	111.7 (3)
Cl2^{i}—Ni—Cl1	84.32 (3)	C1—N—C1^{iv}	111.4 (5)
Cl2—Ni—Cl1	95.68 (3)		

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

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O—H3*A*···Cl3	0.87 (5)	2.32 (5)	3.111 (3)	150 (4)
O—H3*B*···Cl3	0.77 (4)	2.41 (4)	3.153 (3)	163 (4)
N—H1···O	0.75 (5)	2.49 (4)	3.082 (5)	138 (4)
N—H1···Cl1	0.75 (5)	2.80 (5)	3.344 (4)	132 (5)

The quality of the single crystals, initial cell parameters and symmetry information were determined from DeJong and Buerger photographs taken at 293 K. The largest feature in the final difference electron-density map was 0.58 e Å^{-3} at a distance of 0.99 Å from Cl3. Every H atom was clearly resolved in the $\Delta\rho$ maps.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *CADFOR*/*CADSEX* (Keller, 1981). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *ORTEP*III (Johnson & Burnett, 1997).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AB1508). Services for accessing these data are described at the back of the journal. A projection of the structure onto the *ac* plane has also been deposited.

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Transition Metal Complexes with Thiosemicarbazide-Based Ligands. 33. [4-(2-Diphenylphosphino-α-ethoxybenzyl-*P*)-3-methyl-1-salicylideneisothiosemicarbazido-N^1,N^4,*O*]nickel(II)

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Abstract

The title compound, $[Ni(C_{30}H_{28}N_3O_2PS)]$, is the first example of a transition metal complex involving a thiosemicarbazide-based tetradentate ligand with a P atom in its coordination sphere. The Ni atom in the complex has a distorted square-planar configuration formed by N_2OP donor atoms. It can be concluded from the structure that the formation of the complex involved addition across the azomethine group, which is the first time this has been observed for this class of ligands.

Comment

A large number of complexes involving thiosemicarbazide-based ligands of different denticity with O, S and N as donor atoms have been described (Jensen & Rancke-Madsen, 1934; Campbell, 1975; Padhye & Kauffman, 1985; West *et al.*, 1991). In a recent paper (Leovac *et al.*, 1996), we described a nickel(II) complex of an *O,N,P*-tridentate 2-(diphenylphosphino)-thiosemicarbazone, the first thiosemicarbazide-derived ligand to contain a P atom. It is well known that the NH_2 group of the thiosemicarbazide and the *S*-alkylisothiosemicarbazide fragment of tridentate semicarbazones takes part in the common condensation reaction with carbonyl compounds only in the presence of a metal ion acting as template, the products being complexes with corresponding tetradentate ligands.

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