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Bis[chlorobis(1,10-phenanthroline-*N*,*N*′)(thiourea-*S*)nickel(II)] chloride nitrate diethanol solvate

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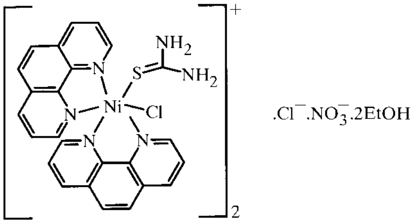
The crystal structure of the title compound, $[NiCl(C_{12}H_8N_2)_2(CH_4N_2S)]_2(NO_3)Cl\cdot 2C_2H_6O$, is formed by $[Ni(phen)_2(thiourea)Cl]^+$ cations (phen = 1,10-phenanthroline), chloride and nitrate counter-ions, and ethanol solvate molecules. The Ni atom is octahedrally coordinated to two bidentate phen ligands, a monodentate thiourea and a chloride ion. Both the chloride and nitrate anions, which provide charge balance, are located at special positions on a twofold symmetry axis. Hydrogen bonds play a key role in the packing and conformation of the cation and create a three-dimensional network.

Comment

Although structures where Ni is coordinated by both thiourea and anionic ligands have already been reported in the literature (Lopez-Castro & Truter, 1963; Nardelli *et al.*, 1966; Gasparri *et al.*, 1969), the title compound, (I), is the only known Ni compound coordinated by thiourea and a neutral ligand; no other Ni compound of this type could be found in the April 1999 release of the Cambridge Structural Database (CSD; 1999).



(I)

Compound (I) crystallizes in the polar space group *Fdd*2 with 16 $C_{27}H_{26}Cl_{1.5}N_{6.5}NiO_{2.5}S$ formula units per unit cell. The structure is composed of $[Ni(phen)_2(thiourea)Cl]^+$ cations, nitrate and chloride anions, and ethanol solvate molecules, in a 1:0.5:0.5:1 ratio. Each of the counter-ions is located on a twofold symmetry axis, thus halving their total number in the structure and allowing for the required charge balance.

The presence of a chloride ion in the coordination sphere of the Ni atom in (I) may play a role in the stabilization of the coordinated thiourea through the formation of an intramolecular hydrogen bond with one thiourea H atom (Table 2), and by reducing the formal charge of the complex. This phenomenon has also been observed in $[Co(phen)(thiourea)(H_2O)Cl_2]\cdot(thiourea)$ (Suescun, Mariezcurrena & Mombrú, 1999). The coordination sphere around Ni is a distorted octahedron, with the equatorial plane defined by three N atoms (N11 from phen1, and N21 and N22 from phen2) and a Cl atom (Cl1). The S (S31) and the remaining N atom from phen1 (N12) are located at apical positions. Table 1 shows all coordination distances and angles. The distortion becomes evident by examining the N11—Ni—N12 and N21—Ni—N22 angles, which are close to 80°. This is a usual feature in Ni–phen complexes that results from the rigid bite of the bidentate phen ligand and from the Ni—N bond distances, which are close to 2.1 Å. The decrease of the N—Ni—N intramolecular angles from the expected 90° of regular octahedral coordination leads to an increase in the other N—Ni—Cl and N—Ni—S *cis* angles, the largest observed being Cl1—Ni1—S31 [100.02 (7)°]. The Ni1—S31 coordination distance is 2.464 (2) Å, similar to the values found in other Ni–thiourea compounds (Lopez-Castro & Truter, 1963; Nardelli *et al.*, 1966; Gasparri *et al.*, 1969).

Both phen molecules in the asymmetric unit of (I) are planar, with maximum deviations of 0.070 (9) Å for C12 in phen1 and 0.030 (9) Å for C24 in phen2. No mirror or C_2 distortions from planarity are observed for these molecules in

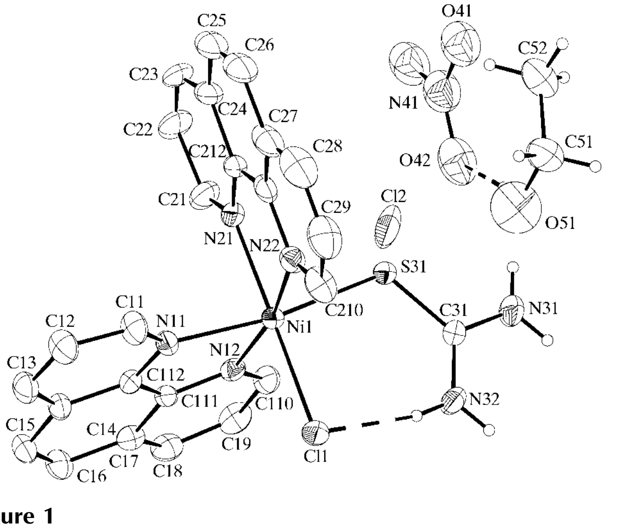


Figure 1
ZORTEP (Zsolnai & Pritzkow, 1995) drawing showing the $[Ni(phen)_2(thiourea)Cl]^+$ cation of (I), one nitrate and one chloride anion, and an ethanol molecule, together with the atom-labelling scheme. The hydrogen bond connecting the thiourea and the coordinated Cl atom is marked as a dashed line. Displacement ellipsoids are drawn at the 30% probability level. Most H atoms are excluded for clarity and the remainder are shown as spheres of arbitrary radii.

this complex (Frenz & Ibers, 1972; Nishigaki *et al.*, 1978). The thiourea molecule is also planar, with the Cl atom located 0.12 (3) Å from the mean molecular plane; this allows us to describe Cl1 as forming a plane with the thiourea molecule, since the two ligands are connected into a closed loop by the intramolecular hydrogen bond (Table 2). The dihedral angle between the two phen ligands is 87.54 (9)°, similar to those in $[Ni(phen)_3]^{2+}$ compounds (Marek *et al.*, 1995; Decurtins *et al.* 1996; Suescun, Mombrú & Mariezcurrena, 1999). This value, combined with the position of the nearly planar thiourea–Cl^- pair, demonstrates that the ligands occupy nearly the same position as the third missing phenanthroline in $[Ni(phen)_3]^{2+}$. The dihedral angles between the thiourea–Cl^- plane and phen1 and phen2 are 79.09 (18) and 75.61 (19)°, respectively. These values are quite comparable to those observed in other $[Ni(phen)_3]^{2+}$ compounds (Marek *et al.*, 1995; Decurtins *et al.*, 1996; Suescun, Mombrú & Mariezcurrena, 1999).

The packing of the structure of (I) is mainly governed by electrostatic forces and hydrogen bonds between the nitrate, chloride, thiourea and ethanol moieties. Table 2 shows all intra- and intermolecular hydrogen bonds. No stacking interactions between phen ligands are observed.

Experimental

Compound (I) was obtained together with $[Ni(phen)_3](NO_3)_2$·thiourea·H_2O, (II) (Suescun, Mombrú & Mariezcurrena, 1999), by preparing an aqueous hydrochloric acid solution (0.5 *M*, 50 ml) containing $Ni(NO_3)_2·6H_2O$ (1 mmol) to which an equal volume of an ethanolic solution of 1,10-phenanthroline (2 mmol) and thiourea (2 mmol) was added. The light-blue solution was allowed to rest. After a week, a crop of orange well shaped crystals of compound (II) began to grow, but it was not until three to four weeks had elapsed that the first blue octahedral crystals of compound (I) appeared.

Crystal data

$[Ni(CH_4N_2S)(C_{12}H_8N_2)_2Cl]_2(NO_3)$-
$Cl·2C_2H_6O$
M_r = 1250.98
Orthorhombic, *Fdd*2
a = 22.813 (4) Å
b = 29.024 (6) Å
c = 17.113 (4) Å
V = 11 331 (4) Å^3
Z = 8

D_x = 1.467 Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 25 reflections
θ = 19.28–21.93°
μ = 0.940 mm^{-1}
T = 293 (2) K
Octahedral, blue
0.33 × 0.24 × 0.20 mm

Table 1
Selected geometric parameters (Å, °).

Ni1—N12	2.096 (7)	Ni1—N21	2.111 (7)
Ni1—N22	2.099 (7)	Ni1—Cl1	2.405 (2)
Ni1—N11	2.102 (6)	Ni1—S31	2.464 (2)
N12—Ni1—N22	169.1 (2)	N11—Ni1—Cl1	90.37 (18)
N12—Ni1—N11	79.3 (3)	N21—Ni1—Cl1	173.4 (2)
N22—Ni1—N11	91.5 (3)	N12—Ni1—S31	96.02 (18)
N12—Ni1—N21	93.4 (3)	N22—Ni1—S31	91.9 (2)
N22—Ni1—N21	80.1 (3)	N11—Ni1—S31	168.81 (19)
N11—Ni1—N21	87.1 (2)	N21—Ni1—S31	83.04 (18)
N12—Ni1—Cl1	92.12 (18)	Cl1—Ni1—S31	100.02 (7)
N22—Ni1—Cl1	93.9 (2)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N31—H31*A*···Cl2^{i}	0.86	2.43	3.234 (8)	155
N31—H31*B*···O51	0.86	2.45	3.151 (18)	139
N32—H32*A*···Cl2^{i}	0.86	2.57	3.337 (7)	150
N32—H32*A*···Cl2^{ii}	0.86	2.57	3.337 (7)	150
N32—H32*B*···Cl1	0.86	2.26	3.112 (8)	170
O51—H51···O42	0.82	2.15	2.95 (2)	165

Symmetry codes: (i) $\frac{1}{4}+x, \frac{9}{4}-y, \frac{1}{4}+z$; (ii) $\frac{7}{4}-x, y-\frac{1}{4}, \frac{1}{4}+z$.

Data collection

Rigaku AFC-7*S* diffractometer
θ/2*θ* scans
Absorption correction: *ψ* scan (Molecular Structure Corporation, 1993)
T_{min} = 0.747, T_{max} = 0.834
3588 measured reflections
3369 independent reflections (plus 202 Friedel-related reflections)

3013 reflections with $I > 2\sigma(I)$
R_{int} = 0.066
θ_{max} = 27.50°
$h = -29 \rightarrow 29$
$k = -25 \rightarrow 37$
$l = -15 \rightarrow 22$
3 standard reflections
every 150 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.066
$wR(F^2)$ = 0.209
S = 1.096
3571 reflections
357 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1559P)^2 + 21.2516P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 2.289 e Å^{-3}
$\Delta\rho_{min}$ = −1.073 e Å^{-3}
Absolute structure: Flack (1983)
Flack parameter = 0.01 (3)

In spite of the fact that the crystals of (I) showed no external evidence of any deviation from regularity, some ill-shaped diffraction maxima were observed in all the specimens checked. Although this did not prevent either data collection or the solution of the structure, it resulted in some difficulties in the refinement. This was evidenced in the final *R* factor, as well as in the unusually high residual electron density around the nitrate ion and the ethanol solvate, which suggested disorder. Several attempts to refine a disordered model, which included additional positions for new water molecules as well as an alternate position for the ethanol molecule and an alternate distribution of the anions, did reduce the crystallographic residual, but also led to contacts with unacceptable molecular geometry. The disorder was therefore not included in the final refinement. Outside this disordered region, the final difference Fourier map appeared essentially featureless, with extreme values of residual electron density not larger than 0.90 e Å^{-3}. In order to prevent unrealistic shifts for groups positioned on crystallographic symmetry elements and in the disordered region, some metric as well as vibrational restraints were applied.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *MSC/AFC Diffractometer Control Software*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ZORTEP* (Zsolnai & Pritzkow, 1995); software used to prepare material for publication: *PLATON*98 (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SX1095). Services for accessing these data are described at the back of the journal.

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