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}
Au1	0	1/2	1/2	0.02106 (13)
S1	−0.1380 (4)	0.61139 (13)	0.3035 (3)	0.0203 (4)
C11	0.0191 (13)	0.6174 (5)	0.1586 (10)	0.0195 (17)
N11	−0.0072 (12)	0.6813 (5)	0.0372 (9)	0.0266 (17)
C12	0.1373 (12)	0.6658 (6)	−0.0807 (9)	0.0235 (17)
C13	0.2829 (12)	0.5919 (6)	0.0079 (11)	0.0228 (18)
N12	0.1742 (11)	0.5606 (5)	0.1414 (9)	0.0250 (16)
Au2	1/2	1/2	1/2	0.02429 (13)
I	0.44663 (9)	0.34110 (4)	0.34810 (7)	0.02635 (14)

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

Au1—S1	2.318 (2)	S1—C11	1.698 (8)
Au1—Au2	3.2701 (6)	Au2—I	2.5558 (6)
S1—Au1—S1^{i}	180	I—Au2—I^{iii}	180
S1—Au1—Au2	105.78 (6)	I—Au2—Au1	86.895 (15)
Au2—Au1—Au2^{ii}	180	Au1—Au2—Au1^{iv}	180
C11—S1—Au1	107.9 (3)		

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

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

D—H···A	D—H	H···A	D···A	D—H···A
N11—H11···I^{i}	0.89 (5)	3.08 (6)	3.889 (7)	153 (6)
N12—H12···I	0.88 (5)	3.05 (6)	3.818 (7)	147 (7)

Symmetry code: (i) $-x, \frac{1}{2}+y, \frac{1}{2}-z$.

H atoms bonded to nitrogen were located from Fourier syntheses and refined freely, but with the N—H distances restrained to be equal using a *SADI* instruction (Sheldrick, 1997). Other H atoms were placed in calculated positions and refined using a riding model.

Data collection: *XSCANS* (Siemens, 1991). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *XP* (Siemens, 1994*b*). Software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1346). Services for accessing these data are described at the back of the journal.

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Complexation of ω-thiocaprolactam with heavy metals: terminal and bridging coordination modes in cadmium and silver compounds

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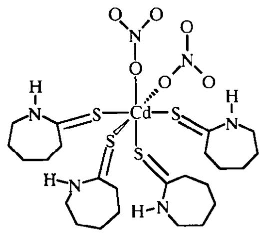
Abstract

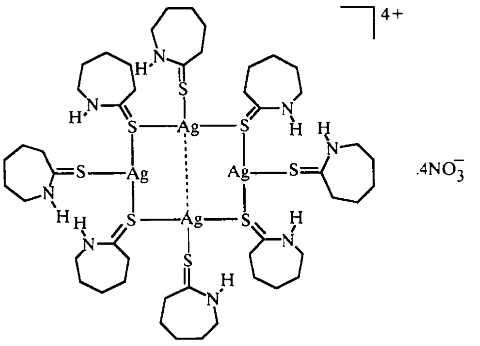
The soft base ω-thiocaprolactam (1-azacycloheptane-2-thione, Hthcl) reacts with Cd^{II} and Ag^{I} nitrate salts, giving two new coordination complexes, [Cd(NO$_3$)$_2$(C$_6$H$_{11}$NS)$_4$] and [Ag$_4$(C$_6$H$_{11}$NS)$_8$](NO$_3$)$_4$. The first compound, tetrakis(1-azacycloheptane-2-thione-*S*)bis(nitrate-*O*)cadmium(II), presents a slightly distorted octahedral coordination geometry, with two η^1-NO$_3$ fragments in a *cis* arrangement and four Hthcl molecules bonded *via* the S atom of the thiocarbonyl group; coordination bond lengths involving S atoms range from 2.5768 (19) to 2.6828 (18) Å. The cationic moiety of the silver compound, tetrakis[μ-(1-azacycloheptane-2-thione-*S*)]tetrakis[(1-azacycloheptane-2-thione-*S*)silver(I)] tetranitrate, is a centrosymmetric tetranuclear cluster containing eight Hthcl molecules, four of which are in terminal positions [coordination distances 2.4850 (19) and 2.478 (2) Å], as in the Cd complex, while the other four bridge two metallic ions each, with coordination distances in the range 2.4608 (17)–2.6976 (18) Å.

Comment

Solvent extraction is one of the most important methods for the isolation and separation of metal ions. It is well known (Huheey *et al.*, 1993) that metals classified as the so-called soft acids, such as Hg^{II}, Ag^{I} and Cd^{II}, are extracted selectively and effectively by extractants containing sulfur as the donor atom, which are classified as soft bases. Various sulfur extractants have been developed mainly for analytical purposes (Sato *et al.*, 1986; Inoue *et al.*, 1992). However, a limited number of compounds containing both sulfur and nitrogen have been studied. We report here the crystal structures of complexes of Cd^{II} and Ag^{I} with ω-thiocaprolactam (abbreviated Hthcl) as the ligand, with the aim of contributing to structure–reactivity investigations of this ligand with heavy metals in solvent extraction processes.



(I)



(II)

Hthcl reacts with nitrate salts of Cd^{II} and Ag^{I}, both of which have a $4d^{10}$ electronic configuration. Nevertheless, different compositions are obtained; Cd^{II} gives a mononuclear molecular complex, while Ag^{I} yields a tetranuclear cationic cluster.

The neutral mononuclear complex (I) results from the coordination to the Cd^{II} ion of four monodentate Hthcl fragments *via* their S atoms and of two terminal nitrate ligands in an unexpected *cis* configuration (Fig. 1). The metal centre presents a slightly distorted octahedral geometry, common for Cd^{II} complexes. The Cd—O distances [Cd1—O41 2.543 (5) and Cd1—O51 2.535 (5) Å] are substantially longer than those observed for related complexes, *e.g.* 2.290 (4) and 2.299 (4) Å in a tetrahedral Cd^{II} complex containing a thiourea derivative (Griffith *et al.*, 1983). This discrepancy could denote a weak coordination of the η^1-NO_3 moieties. Another feature of the η^1-NO_3 ligands is that somewhat obtuse angles are observed around the coordinated O atoms [N41—O41—Cd1 137.4 (5) and N51—O51—Cd1 134.1 (5)°], probably because of steric hindrance arising from the adjacent Hthcl ligands.

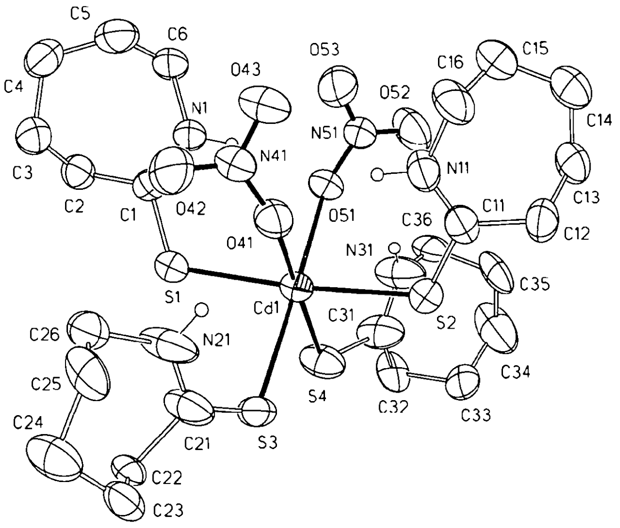


Fig. 1. The molecular structure of (I) showing 30% probability displacement ellipsoids. For clarity, H atoms bonded to C atoms have been omitted and only one position of the disordered Hthcl ligands is shown.

For the four Hthcl ligands, the C=S bond lengths lie in a short range [1.645 (9)–1.703 (8) Å] and are close to that observed for the free molecule (Mozzhukhin *et al.*, 1993; Nuñez, 1997). As reported previously for the $HgCl_2(Hthcl)_2$ complex (Nuñez *et al.*, 1998), Hthcl seems to coordinate weakly to heavy soft metals. Another striking feature of (I) is the strong *trans* effect arising from the nitrate ligands; the Cd—S bond lengths for the Hthcl fragments adjacent to nitrate [2.578 (2) and 2.5768 (19) Å] are significantly shorter than those for the *trans* ligands [2.6828 (18) and 2.658 (2) Å]. This *trans* effect is also indicated for the thiocarbonyl groups; although each of the C—S bonds are formally double bonds, the C—S bond for the *trans* ligands [S3—C21 1.645 (9) and S4—C31 1.669 (9) Å] are significantly shorter than those for the adjacent ligands [S1—C1 1.695 (7) and S2—C11 1.703 (8) Å]. Finally, the four H atoms from the amine groups participate in intramolecular hydrogen bonds with the six O atoms of the nitrate groups, with H···O contacts in the range 2.12–2.55 Å. This point confirms that the thio–enol tautomer for Hthcl is not present in the complex in the solid state. No significant intermolecular contacts are observed in the packing of (I).

The asymmetric unit of compound (II) contains two Ag atoms, four Hthcl ligands and two nitrate ions, one of which is disordered. In contrast to (I), the nitrate ions do not coordinate in (II). The cationic moiety lies on an in-version centre, which yields a dimeric centrosymmetric cation of formula [Ag$_4$(Hthcl)$_8$]$^{4+}$ (Fig. 2). The central core of the cation is an eight-membered ring which approximates a chair (double-puckered) conformation, as deduced from the torsion angles S3—Ag1—S4—Ag2^{i} of 170.38 (6)° and S4—Ag1—S3—Ag2 of 26.62 (10)° [symmetry code: (i) $1-x$, $1-y$, $-z$]. This central core is reminiscent of that of the recently reported compound obtained by reaction of zinc isomaleonitrile dithiolate with 4-methylpyridine (Xiong *et al.*, 1997), which yields a zinc dimer containing the eight-membered Zn$_2$S$_4$C$_2$ ring. It is also worth noting that complex (II) may be a good model for the tetrameric gold–thiomalate complex suggested recently, on the basis of mass spectral data, to be a component of the anti-arthritic drug myochrysine (Howard-Lock *et al.*, 1996). The recent report of the crystal structure of a polymeric form of gold thiomalate (Bau, 1998) shows that tetramers could result from intramolecular attack of a terminal thiolate of the polymer chain on a nearby Au atom.

The most interesting feature of the cation is that the eight Hthcl ligands exhibit two coordination modes: η^1-terminal, as in (I), for S1 and S2, and η^2-bridged for S3 and S4. This latter mode of coordination, to the best of our knowledge, has not been reported previously for Hthcl. As for (I), the C—S bond lengths are in a small range [1.682 (7)–1.710 (7) Å], consistent with a formal double bond for the thiocarbonyl functionalities. For the η^1-coordinated ligands, the C—S—Ag angles [C1—S1—Ag1 111.4 (3) and C11—S2—Ag2 107.3 (3)°] are consistent with the expected sp^3 hybridization for sulfur. For the η^2-coordinated ligands, the S atoms have a distorted tetrahedral environment, with Ag—S—Ag angles ranging from 94.77 (6) to 122.82 (7)°. The bridges are asymmetric, with short bond lengths [Ag2—S2 2.478 (2) and Ag2—S4^{i} 2.4608 (17) Å] and long bond lengths [Ag1—S4 2.6976 (18) and Ag2—S3 2.6660 (18) Å]. A weak transannular metal–metal interaction is observed [Ag2$\cdots$Ag2^{i} 3.2548 (11) Å], which can not be considered a covalent metal–metal bond because of the d^{10} electronic configuration of both metal ions. Nevertheless, this interaction may contribute to the difference noted for the geometries around the two crystallographically independent metals; in spite of similar trigonal environments for both Ag atoms, the mean plane around Ag2 is nearly planar, with a maximum deviation of −0.0423 (9) Å for Ag2, while Ag1 has a deviation of 0.3486 (9) Å from the mean plane formed by Ag1, S1, S3 and S4. Strong nearly linear intra- and intermolecular hydrogen bonds are observed between the H atoms of the amine groups and O43, O51 and O53 of the nitrate ions, with O$\cdots$H contacts in the range 1.99–2.66 Å.

Further studies on the coordination properties of Hthcl with heavy metals, including solution characterization experiments, are underway in an effort to determine and rationalize the extractive properties of this molecule.

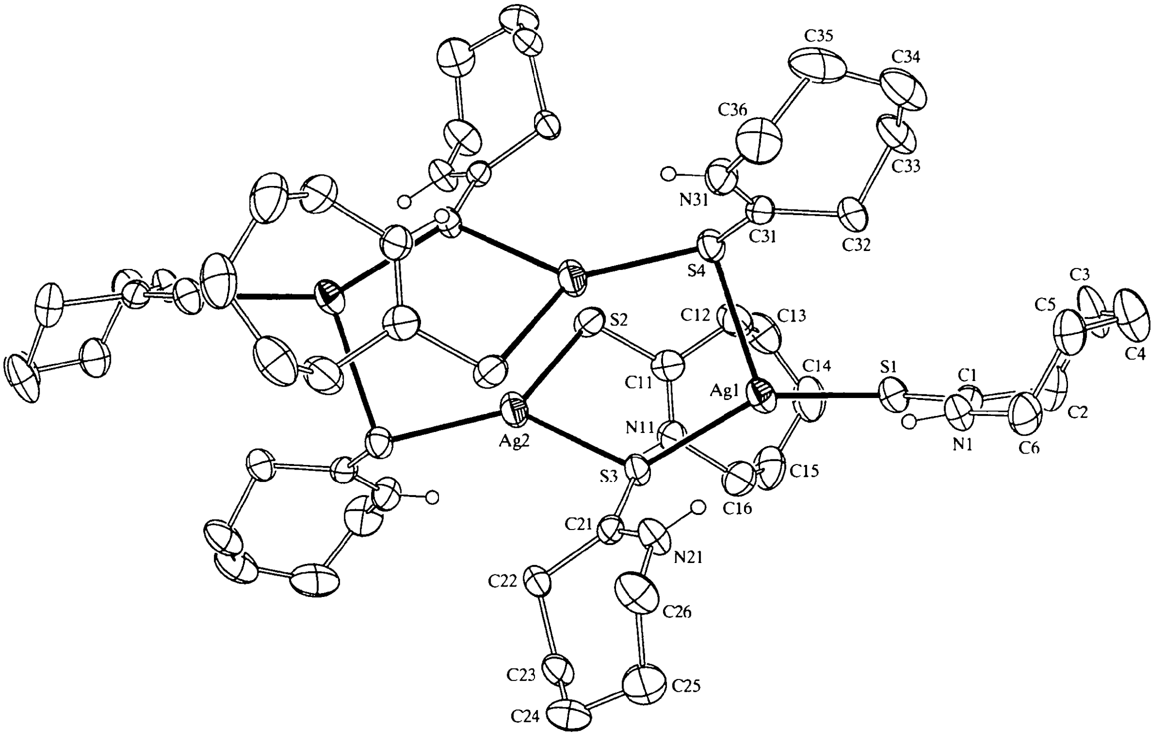


Fig. 2. The structure of the cation in (II) showing 30% probability displacement ellipsoids. H atoms bonded to C atoms have been omitted for clarity.

Experimental

To a solution (25 ml) of Hthcl (5 mmol l^{-1} in chloroform), a suitable amount of the desired metal salt was added in order to obtain a 1:1 stoichiometry, *i.e.* $Cd(NO_3)_2\cdot 4H_2O$ for (I) (0.0384 g, 0.125 mmol) and $AgNO_3$ for (II) (0.0213 g, 0.125 mmol). After a short period of stirring at room temperature [0.5 h and 1 h for (I) and (II), respectively], the solution was filtered and reduced in volume by slow evaporation at normal pressure. The solid collected was recrystallized [twice for (I)] from acetone, which afforded crystals suitable for X-ray analysis for both compounds in low yields.

Compound (I)

Crystal data

$[Cd(NO_3)_2(C_6H_{11}NS)_4]$
$M_r = 753.29$
Monoclinic
$P2_1/n$
$a = 15.4891\ (14)$ Å
$b = 12.2319\ (9)$ Å
$c = 18.2654\ (18)$ Å
$\beta = 97.694\ (7)°$
$V = 3429.4\ (5)$ Å^3
$Z = 4$
$D_x = 1.459$ Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 47 reflections
$\theta = 4.59–12.51°$
$\mu = 0.924$ mm^{-1}
$T = 293\ (2)$ K
Plate
0.35 × 0.15 × 0.15 mm
Colourless

Data collection

Siemens $P4$ diffractometer
ω scans
Absorption correction: ψ scan (Fait, 1991)
$T_{\min} = 0.746$, $T_{\max} = 0.871$
10 006 measured reflections
8271 independent reflections
3677 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.050$
$\theta_{\max} = 28°$
$h = -1 \rightarrow 20$
$k = -1 \rightarrow 16$
$l = -24 \rightarrow 24$
3 standard reflections every 97 reflections intensity decay: 7.9%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.067$
$wR(F^2) = 0.145$
$S = 1.016$
8271 reflections
443 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0765P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.020$
$\Delta\rho_{\max} = 0.508$ e Å^{-3}
$\Delta\rho_{\min} = -0.327$ e Å^{-3}
Extinction correction: *SHELX*97 (Sheldrick, 1997)
Extinction coefficient: 0.0014 (3)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Cd1—O41	2.543 (5)	S3—C21	1.645 (9)
Cd1—O51	2.535 (5)	S4—C31	1.669 (9)
Cd1—S1	2.5768 (19)	N41—O41	1.261 (7)
Cd1—S2	2.578 (2)	N41—O42	1.185 (8)
Cd1—S4	2.658 (2)	N41—O43	1.199 (8)
Cd1—S3	2.6828 (18)	N51—O51	1.271 (7)
S1—C1	1.695 (7)	N51—O52	1.207 (7)
S2—C11	1.703 (8)	N51—O53	1.214 (8)
O41—Cd1—S1	88.51 (13)	S4—Cd1—S3	83.38 (7)
O41—Cd1—S2	88.13 (13)	C1—S1—Cd1	115.1 (3)
O51—Cd1—S1	88.39 (13)	C11—S2—Cd1	115.3 (3)
O51—Cd1—S2	88.02 (13)	C21—S3—Cd1	113.4 (3)
O51—Cd1—O41	95.89 (18)	C31—S4—Cd1	114.4 (3)
S1—Cd1—S2	174.81 (6)	O41—N41—O42	119.9 (7)
S1—Cd1—S4	95.15 (7)	O41—N41—O43	117.8 (8)
S2—Cd1—S4	88.55 (8)	O42—N41—O43	122.2 (8)
O41—Cd1—S3	91.70 (13)	O51—N51—O52	118.5 (7)
O41—Cd1—S4	173.75 (14)	O51—N51—O53	118.6 (7)
O51—Cd1—S3	171.51 (14)	O52—N51—O53	122.9 (7)
O51—Cd1—S4	89.28 (14)	N41—O41—Cd1	137.4 (5)
S1—Cd1—S3	88.03 (6)	N51—O51—Cd1	134.1 (5)
S2—Cd1—S3	96.02 (6)		

Compound (II)

Crystal data

$[Ag_4(C_6H_{11}NS)_8](NO_3)_4$
$M_r = 1713.26$
Monoclinic
$P2_1/n$
$a = 14.3913\ (14)$ Å
$b = 11.0072\ (11)$ Å
$c = 22.163\ (2)$ Å
$\beta = 100.898\ (7)°$
$V = 3447.5\ (6)$ Å^3
$Z = 2$
$D_x = 1.650$ Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 40 reflections
$\theta = 4.59–11.98°$
$\mu = 1.423$ mm^{-1}
$T = 293\ (2)$ K
Plate
0.40 × 0.12 × 0.08 mm
Pale yellow

Data collection

Siemens $P4$ diffractometer
ω scans
Absorption correction: ψ scan (Fait, 1991)
$T_{\min} = 0.691$, $T_{\max} = 0.883$
7629 measured reflections
6071 independent reflections
3637 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.041$
$\theta_{\max} = 25°$
$h = -1 \rightarrow 17$
$k = -1 \rightarrow 13$
$l = -26 \rightarrow 26$
3 standard reflections every 97 reflections intensity decay: 9.52%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.056$
$wR(F^2) = 0.108$
$S = 1.010$
6070 reflections
389 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0545P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.009$
$\Delta\rho_{\max} = 0.94$ e Å^{-3}
$\Delta\rho_{\min} = -0.67$ e Å^{-3}
Extinction correction: *SHELX*97 (Sheldrick, 1997)
Extinction coefficient: 0.00028 (16)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Ag1—S1	2.4850 (19)	Ag2···Ag2$^{\rm i}$	3.2548 (11)
Ag1—S3	2.4878 (17)	S1—C1	1.682 (7)
Ag1—S4	2.6976 (18)	S2—C11	1.691 (7)
Ag2—S2	2.478 (2)	S3—C21	1.702 (7)
Ag2—S3	2.6660 (18)	S4—C31	1.710 (7)
Ag2—S4$^{\rm i}$	2.4608 (17)		
S1—Ag1—S3	138.14 (6)	C1—S1—Ag1	111.4 (3)
S1—Ag1—S4	107.48 (6)	C11—S2—Ag2	107.3 (3)
S3—Ag1—S4	103.24 (6)	C21—S3—Ag1	114.5 (2)
S2—Ag2—S3	94.02 (6)	C21—S3—Ag2	110.6 (2)
S4$^{\rm i}$—Ag2—S2	139.97 (7)	C31—S4—Ag1	99.9 (2)

S4^{i}—Ag2—S3	125.85 (6)	C31—S4—Ag2^{i}	108.8 (2)
S4^{i}—Ag2···Ag2^{i}	109.90 (5)	Ag1—S3—Ag2	122.82 (7)
S2—Ag2···Ag2^{i}	75.22 (5)	Ag2^{i}—S4—Ag1	94.77 (6)
S3—Ag2···Ag2^{i}	73.30 (4)		

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

For complex (I), a positional disorder was resolved for two Hthcl moieties; atoms C22, C23, C25, C26, C32, C33, C35 and C36 are disordered and were refined with fixed site-occupation factors of 0.5. In the last least-squares cycles, distances involving one or two disordered atoms were restrained to target values of 1.52 Å with an s.u. of 0.02 Å for C—C bonds (20 restraints), and 1.48 Å with an s.u. of 0.02 Å for N—C bonds (four restraints). In the case of complex (II), a minor positional disorder was encountered for an O atom of one of the nitrate ions; O41 is disordered and was refined with a fixed site-occupation factor of 0.5. Moreover, in the last cycles of refinement for (II), reflection $\bar{1}01$ was omitted because it presented a very large discrepancy between F_o^2 and F_c^2 (ΔF^2/s.u. = 25.8) due to a tube surge during the measurement of this reflection. Omitting this reflection reduced the wR_2 value for all data from 14.06 to 12.95%. For both compounds, H atoms were placed on idealized positions (N—H = 0.86 and C—H = 0.97 Å) with an isotropic displacement parameter $1.2U_{eq}$ of the bonded atom.

For both compounds, data collection: *XSCANS* (Fait, 1991); cell refinement: *XSCANS*; data reduction: *XSCANS*. Program(s) used to solve structures: *SIR*92 (Altomare *et al.*, 1992) for (I); *SHELXTL-Plus* (Sheldrick, 1995) for (II). For both compounds, program(s) used to refine structures: *SHELX*97 (Sheldrick, 1997); molecular graphics: *SHELXTL-Plus*; software used to prepare material for publication: *SHELX*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1179). Services for accessing these data are described at the back of the journal.

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Bis[(2-chloroethyl)diisopropylammonium] tetrachlorocobaltate(II)

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Abstract

The crystal structure of the title compound, $(C_8H_{19}ClN)_2[CoCl_4]$, has been determined at 203 K. It is built up from alternating layers of organic cations and inorganic $[CoCl_4]^{2-}$ anions. The asymmetric unit consists of two cations with different conformations, one cation being disordered. The structure exhibits both N—H···Cl and C—H···Cl hydrogen bonds.

Comment

Mixed organic–inorganic salts with the general formula $[R_nNH_{4-n}]_2[MX_4]$ (where R is an alkyl group, M is a divalent metal ion, X is Cl^-, Br^- or I^-, and n = 1, 2, 3, 4) have been widely investigated due to their structural diversity, ferroelectric and ferroelastic properties, and the presence of different phase transitions, including incommensurate ones. These structures are built up from discrete organic cations and inorganic anions and are often dominated by the presence of disordered organic cations (Bloomqvist & Willett, 1981; Hasebe *et al.*, 1990*a*,*b*; Madariaga *et al.*, 1987; Mahoui *et al.*, 1996*a*,*b*; Nishihata *et al.*, 1993; Willett, 1991; Zaleski, 1997). This behaviour is more pronounced in the absence of hydrogen bonds linking the organic and inorganic species. Indeed, the compounds with more alkyl groups on the N atom or with a long-chain alkyl group exhibit disorder in both the organic and inorganic species (Mahoui *et al.*, 1996*a*,*b*; Madariaga *et al.*, 1987). The presence of hydrogen bonds results in directional cation–anion interactions within the layers and adoption

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