S4 ¹ —Ag2—S3	125.85 (6)	C31—S4—Ag2'	108.8 (2)
S4'—Ag2···Ag2'	109.90 (5)	Ag1—S3—Ag2	122.82 (7)
S2—Ag2···Ag2 ⁱ	75.22 (5)	Ag2'—S4—Ag1	94.77 (6)
S3—Ag2···Ag2'	73.30 (4)		
a			

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 siteoccupation 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 101 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 $1.2U_{cq}$ of the bonded atom.

For both compounds, data collection: XSCANS (Fait, 1991); cell refinement: XSCANS; data reduction: XSCANS. Program(s) used to solve structures: SIR92 (Altomare *et al.*, 1992) for (I); SHELXTL-Plus (Sheldrick, 1995) for (II). For both compounds, program(s) used to refine structures: SHELX97 (Sheldrick, 1997); molecular graphics: SHELXTL-Plus; software used to prepare material for publication: SHELX97.

SB is grateful to UNAM for financial support and USAI for diffractometer time. The authors acknowledge DGAPA (project No. IN501897).

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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Acta Cryst. (1999). C55, 1631-1634

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

AMIR H. MAHMOUDKHANI^a* AND VRATISLAV LANGER^b

^aDepartment of Inorganic Chemistry, Göteborg University, SE-41296 Göteborg, Sweden, and ^bDepartment of Environmental Inorganic Chemistry, Chalmers University of Technology, SE-41296 Göteborg, Sweden. E-mail: amir@inoc.chalmers.se

(Received 26 February 1999; accepted 27 May 1999)

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— $H \cdots Cl$ and C— $H \cdots Cl$ hydrogen bonds.

Comment

Mixed organic-inorganic salts with the general formula $[R_n NH_{4-n}]_2[MX_4]$ (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., 1990a,b; Madariaga et al., 1987; Mahoui et al., 1996a,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., 1996a,b; Madariaga et al., 1987). The presence of hydrogen bonds results in directional cation-anion interactions within the layers and adoption of a well behaved three-dimensional structure. The structural phase transitions for these compounds have been attributed to the order-disorder transition of the alkylammonium group (Mahoui *et al.*, 1996*a*; Ning *et al.*, 1992) and/or changing of the hydrogen-bond network (Ning *et al.*, 1992; Williams *et al.*, 1992*a*).

Hydrogen bonding plays an important role in the crystal engineering of organic and organometallic solids (Desiraju, 1989; Braga et al., 1998). The N—H $\cdots X$ and C—H···X (X = Cl or Br) hydrogen-bonding ability of MX_4^{2-} anions has been described previously (Feist *et al.*, 1995; Hitchcock *et al.*, 1993; Mahmoudkhani & Langer, 1999a; Waśkowska, 1994), and is important for stabilization of the crystal structure, though the medium-strong N— $H \cdots X$ hydrogen bonds (Gilli, 1995) have a more significant contribution than the $C = H \cdots X$ bonds. This can be seen in the structure of $[(CH_3)_3NH_2]_2[CuCl_4]$, with more hydrogen bonds and no disorder, while the structure of [(CH₃)₃NH]₂[ZnCl₄] with less hydrogen bonds suffers from disorder (Williams et al., 1992b). Recently, we have shown that the hydrogen-bonding network in the crystal structure of [(CH₃)₂NH₂]₂[CoCl₄] remains unchanged and thereby the structure behaves well even at temperatures up to 366 K (Mahmoudkhani & Langer, 1999a). It is of interest to investigate the effect of hydrogen bonding on the structure and properties of these compounds with respect to the size and nature of the alkyl groups on the N atom.

Bis[(2-chloroethyl)diisopropylammonium] tetrachlorocobaltate(II), CEDPA-Co, crystallizes in the monoclinic space group $P2_1/n$. The structure determination at room



temperature results in a unit cell with a = 8.1263(1), b = 26.1325(4), c = 12.1909(1) Å and $\beta = 93.918(1)^{\circ}$ [8192 reflections with $I > 10\sigma(I)$]. Nevertheless, the high atomic displacement parameters (ADPs) of one of the organic cations hampered the structure refinement process. Cooling to 173 K failed as the crystals cracked. A more satisfactory result was obtained at 203 K. Disorder persists even at low temperature and this is reflected in high ADPs for substituents on the N1 atom. One isopropyl group was disordered over two positions with site occupancies of 0.64(1) and 0.36(1), and the other isopropyl group had an artificially short C13—C14 bond of 1.410(6) Å. The $[CoCl_4]^{2-}$ anion behaves normally as a tetrahedron, while the ammonium cations exhibit different conformations. The dihedral angle Cl1—Cl1—Cl2—N1 is $-162.8 (2)^{\circ}$, which corresponds to a *trans* conformation similar to that found for (2-chloroethyl)diisopropylammonium chloride (Mahmoudkhani & Langer, 1999b), while the dihedral angle Cl2—C21—C22—N2 is $-78.7 (3)^{\circ}$ and presents a *gauche* conformation for the corresponding N and Cl atoms. The conformations of the isopropyl groups on the N1 and N2 atoms (with relevance for the corresponding H—N—C—H dihedral angles) are *gauche-gauche* and *gauche-trans*, respectively. The hydrogen-bonding scheme is shown in Fig. 2. Although all the Cl atoms



Fig. 1. The molecular structure of CEDPA-Co. Displacement ellipsoids are shown at the 50% probability level and H atoms have been omitted for clarity. The disordered isopropyl group is shown with dotted ellipsoids. The C17 and C7 atoms have almost the same coordinates.



Fig. 2. The hydrogen-bonding scheme for a $[CoCl_4]^{2-}$ anion. The H atoms are represented with thin lines.

of the $[CoCl_4]^{2-}$ anion are involved in hydrogen bonds either of the N—H···Cl or C—H···Cl type (Table 2), there are less hydrogen-bond contacts compared with the structure of $[(CH_3)_2NH_2]_2[CoCl_4]$ (Mahmoudkhani & Langer, 1999*a*). The structure of CEPDA–Co consists of organic–inorganic layers which are perpendicular to the *b* axis. Each layer of $[CoCl_4]^{2-}$ anions is 'sandwiched' between ordered and disordered organic layers. Similar behaviour has been reported by Bloomqvist & Willett (1981) for $[Et_2NH_2]_2[ZnCl_4]\cdot xH_2O$.

Experimental

The title compound was prepared by the reaction of (2-chloroethyl)diisopropylammonium chloride with CoCl₂·6H₂O in ethanol at 323 K. The solvent was removed by azeotropic distillation with toluene. Crystals suitable for X-ray diffraction analysis were obtained by slow evaporation from a solution in acetone–ethyl acetate when allowed to stand over silica gel in a desiccator. The crystal chosen was stable enough for data collection under normal conditions.

Crystal data

$(C_8H_{19}ClN)_2[CoCl_4]$	Mo $K\alpha$ radiation
$M_r = 530.11$	$\lambda = 0.71073 \text{ Å}$
Monoclinic	Cell parameters from 6564
$P2_{1}/n$	reflections
a = 8.0257(1) Å	$\theta = 1 - 32^{\circ}$
b = 25.8793(3) Å	$\mu = 1.328 \text{ mm}^{-1}$
c = 12.1196(1) Å	T = 203 (2) K
$\beta = 94.7901(2)^{\circ}$	Thin plate
$V = 2508.44(5) \text{ Å}^3$	$0.50 \times 0.40 \times 0.01$ mm
Z = 4	Blue
$D_x = 1.404 \text{ Mg m}^{-3}$	
D_m not measured	

Data collection

Siemens SMART CCD	460
diffractometer	I
ω scans	Rint
Absorption correction:	$ heta_{ m max}$
multi-scan (SADABS;	h =
Sheldrick, 1996; Blessing,	<i>k</i> =
1995)	<i>l</i> =
$T_{\rm min} = 0.557, T_{\rm max} = 0.987$	Inte
29 643 measured reflections	
6231 independent reflections	

Refinement

Refinement on F^2 $R[F^2 > 2\sigma(F^2)] = 0.045$ $wR(F^2) = 0.111$ S = 1.0216231 reflections 256 parameters H atoms: see below $w = 1/[\sigma^2(F_o^2) + (0.0413P)^2 + 3.3222P]$ where $P = (F_o^2 + 2F_c^2)/3$ 4601 reflections with $I > 2\sigma(I)$ $R_{int} = 0.051$ $\theta_{max} = 28.3^{\circ}$ $h = -10 \rightarrow 10$ $k = -34 \rightarrow 34$ $l = -16 \rightarrow 16$ Intensity decay: none

 $(\Delta/\sigma)_{max} = 0.002$ $\Delta\rho_{max} = 1.062 \text{ e } \text{\AA}^{-3}$ $\Delta\rho_{min} = -0.770 \text{ e } \text{\AA}^{-3}$ Extinction correction: none Scattering factors from International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Co1Cl4	2.2688 (8)	Co1Cl5	2.2881 (8)
Co1Cl3	2.2689 (8)	Co1Cl6	2.2886 (8)
Cl4—Co1—Cl3	112.96 (3)	Cl4Co1Cl6	107.66 (3)
Cl4—Co1—Cl5	109.28 (3)	Cl3Co1Cl6	107.49 (3)
Cl3—Co1—Cl5	112.38 (4)	Cl5Co1Cl6	106.76 (3)
Cl1-Cl1-Cl2-Nl Cl2-C21-C22-N2 H2-N2-C23-H23 H2-N2-C26-H26	-162.8 (2) -78.7 (3) 56.1 169.6	HINICI3HI3 HINICI6HI6 HINIC6H6	72.9 97.4 -62.8

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

D — $H \cdots A$	<i>D-</i> —H	H···A	$D \cdot \cdot \cdot A$	$D = H \cdot \cdot \cdot A$
N1—H1···Cl6	0.92	2.45	3.222 (2)	142
N2—H2· · ·C15'	0.92	2.37	3.253 (2)	160
C21H21A····Cl4 ⁿ	0.98	2.70	3.656 (4)	165
$C12-H12B\cdots C13^{n}$	0.98	2.87	3.648 (3)	136
C14H14C····Cl6	0.97	2.87	3.633 (4)	137
Symmetry codes: (i)	$x - \frac{1}{2}, \frac{1}{2} - y$	$z_{1}, \frac{1}{2} + z_{2};$ (ii).	x = 1, y, z.	

The disordered parts of the cations were restrained to have the same geometry. The H atoms on the N atoms were refined isotropically using an appropriate riding model, whereas the other H atoms were constrained to idealized geometries and assigned isotropic displacement parameters 1.5 times (for CH₃ groups) or 1.2 times (for CH₂ and CH groups) the U_{iso} value of their respective pivot atom.

Data collection: *SMART* (Siemens, 1995). Cell refinement: *SAINT* (Siemens, 1995). Data reduction: *SAINT* and *SAD-ABS* (Sheldrick, 1996). Program(s) used to solve structure: *SHELXTL* (Bruker, 1997). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1065). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). C55, 1634-1636

Bis(μ -acetato){ μ -2,6-bis[(2-hydroxybenzyl)-(2-pyridylmethyl)aminomethyl]-4-methylphenolato}diindium(III) nitrate dihydrate

Adailton J. Bortoluzzi,^a Ademir Neves,^a Ivo Vencato,^a Cesar Zucco^a and Manfredo Hörner^b

^aDepartamento de Química-UFSC, 88040-900 Florianópolis, SC, Brazil, and ^bDepartamento de Química-UFSM, 88040-900 Santa Maria, RS, Brazil. E-mail: adajb@alpha2.qmc. ufsc.br

(Received 30 March 1999; accepted 18 June 1999)

Abstract

In the title compound, $[In_2(C_{35}H_{33}N_4O_3)(C_2H_3O_2)_2]$ -NO₃·2H₂O, a new binuclear In¹¹¹ complex, the metal centers are linked by one phenolate and two acetate bridging groups. The In¹¹¹ ions are in a distorted octahedral environment and they are related by imposed crystallographic C_2 symmetry.

Comment

¹¹¹In and ¹¹³In are useful radionuclides for some diagnostic imaging procedures in nuclear medicine (Remy *et al.*, 1995; Jamar *et al.*, 1995). These isotopes are appropriate γ -emitters for imaging using techniques such as single-photon emission computed tomography.

Special conditions in the physiological environment (e.g. pH), and the high affinity between serum proteins in human blood (e.g. transferrin) and trivalent metal ions requires the development of indium complexes with high stability for radiopharmaceutical applications. They must be thermodynamically stable to avoid hydrolysis processes in the organism, as well as being kinetically

inert to prevent demetalation by transferrin (Jurisson et al., 1993).

A number of complexes with linear and tripodal polydentate amine-phenol ligands have been reported previously (Wong, Liu, Lügger *et al.*, 1995; Wong, Liu, Rettig & Orvig, 1995; Liu *et al.*, 1993). These ligands have been considered as effective chelating agents capable of producing highly stable mononuclear complexes with group 13 metal ions.

We report here for the first time the homodinuclear complex $[In_2(BBPMP)(OAc)_2]NO_3\cdot 2H_2O$, (I), with an N₄O₃-donor dinucleating ligand which contains phenolate and pyridyl pendant arms {H₃BBPMP is 2,6bis[(2-hydroxybenzyl)(2-pyridylmethyl)aminomethyl]-4-methylphenol and OAc is acetate}. H₃BBPMP is a symmetric and non-linear amine-phenol ligand. It has a molecular structure suitable for the formation of binuclear phenolate-bridged complexes (Neves *et al.*, 1993, 1996; de Brito *et al.*, 1997). In this work, we have used the H₃BBPMP ligand to synthesize the first example of a binuclear indium complex with two bridging acetate groups.



The $[In_2(BBPMP)(OAc)_2]^+$ cation has C_2 symmetry, with atoms O10, C11, C14 and C17 of the BBPMP³⁻ ligand lying on the crystallographic twofold axis (Fig. 1). Each In^{III} ion is coordinated by one O (phenolate) and two N (amine and pyridyl) atoms of the main ligand in the external face, while three O atoms of one phenolate and two carboxylate bridging groups in the internal face complete the coordination sphere. The O atom of the terminal phenolate arm is coordinated in a trans position to the phenolate bridging group. A similar arrangement of the BBPMP³⁻ ligand around a metal ion was also observed in the [Fe₂- $(BBPMP)(OAc)_2$ ClO₄·H₂O (Neves et al., 1993), NH₄- $[Fe_2(BBPMP)(SO_4)_2]$ (de Brito et al., 1997) and $[Fe_2 (BBPMP){O_2P(OPh)_2}_2]ClO_4 \cdot H_2O$ (Krebs et al., 1994) complexes. As in the iron complexes, the greatest distortion in the coordination sphere of the metal is the acute N_{amine} —In— $N_{pyridyl}$ angle of 75.7 (1)°, imposed by formation of the five-membered chelate ring. The M-O-M angle varies according to the rigidity of the bridging groups. In the complexes [In₂(BBPMP)(OAc)₂]NO₃-- $2H_2O$ and $[Fe_2(BBPMP)(OAc)_2]ClO_4 \cdot H_2O$, which are