Halide abstraction as a route to cationic molybdenum(IV) compounds: crystal and molecular structure of [CpMoCl(MeCN)$_4$][SbCl$_6$]$_2$ · MeCN

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Abstract

Treatment of CpMoCl$_3$(MeCN)$_2$ with SbCl$_5$ in acetonitrile solution provides the solvated cationic series [CpMoCl$_2$(MeCN)$_3$]$^+$, [CpMoCl(MeCN)$_4$]$^{2+}$ and [CpMo(MeCN)$_6$]$^{3+}$ as hexachloroantimon(V)ate salts following sequential halide abstraction. Characterization follows from microanalytical and spectroscopic (IR, and ^{1}H NMR) data and, in the case of [CpMoCl(MeCN)$_4$][SbCl$_6$]$_2$ · MeCN, by X-ray crystallographic studies. The structure is disordered but individual cations contain a six coordinated pseudo-octahedral metal geometry in which the cyclopentadienyl ligand (regarded as unidentate) and the chlorine atom occupy axial positions with an equatorial array of four acetonitrile ligands.

Keywords: Cyclopentadienyl; Cationic; Halide abstraction; Molybdenum(IV); Crystal structure

1. Introduction

Removal of chloride ion(s) from covalent metal chlorides using antimony(V) chloride in acetonitrile as abstractor has proved a convenient route to some challenging cationic species of the early transition metal series, e.g. *fac*-[TiCl$_3$(MeCN)$_3$]$^+$ [1], [CpTi(MeCN)$_5$]$^{3+}$ [2] and [CpHf(MeCN)$_6$]$^{3+}$ [3] as representatives from Group 4, and [CpNbCl(MeCN)$_4$]$^{3+}$ and [CpNb(MeCN)$_6$]$^{4+}$ from Group 5 [4]. As a demonstration that the same facility extends to the Group 6 elements we now report the formation and characterization of several cationic Mo(IV) compounds as derived by halide abstraction from CpMoCl$_3$(MeCN)$_2$.

2. Experimental details

All reactions were carried out using a conventional Schlenk system with either argon or oxygen-free dinitrogen as the inert atmosphere. Solvents were stored over CaH$_2$ and subsequently P$_4$O$_{10}$ and then freshly distilled under a dinitrogen atmosphere prior to use. CpSn^{n}Bu$_3$ was prepared as detailed in the literature [5], MoCl$_5$ and SbCl$_5$ were used as supplied commercially.

The IR spectra were recorded as mulls (Nujol) between CsI plates using a Perkin–Elmer 580B spectrometer and ^{1}H NMR spectra (220 MHz) on a Perkin–Elmer R34 spectrometer with samples in sealed tubes. Microanalyses were performed using the Leeman Laboratories Inc., PS 1000 sequential inductively coupled plasma (ICP) spectrometer and CE 440 elemental analyser (CHN) facilities of the Department of Chemistry, University of Warwick.

3. Preparation of compounds

3.1. MoCl$_4$(MeCN)$_2$

MoCl$_5$ (24.83 g, 90.87 mmol) was placed in a rigorously pre-dried thimble and extracted with hot acetonitrile in a Soxhlet apparatus under an atmosphere of dinitrogen. The initial exothermic reaction provided a light-brown solution which assumed a very-dark-brown colour over a period of 3 h. On cooling this solution to room temperature a mass of green needle crystals deposited (23.02 g (79.2%)). The insoluble brown–black residue remaining in the thimble was not investigated further.

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3.2. CpMoCl₃(MeCN)₂

A solution of CpSn^{n}Bu₃ (2.14 g, 6.03 mmol) in toluene (20 cm³) was added dropwise to a chilled (0°C) and stirred solution of MoCl₄(MeCN)₂ (1.92 g, 6.01 mmol) in toluene (30 cm³) maintained under an argon atmosphere. The resulting dark-purple solution was stirred at room temperature for 6 h to provide a deep-purple precipitate. The mother liquor was concentrated to one third volume and yet more purple solid deposited. The combined purple solids were washed with dichloromethane (3 × 20 cm³) and hexane (2 × 20 cm³) and recrystallization from boiling acetonitrile-activated charcoal provided the title compound as a chunky semicrystalline purple solid (1.73 g (82.4%)).

3.3. [CpMoCl₂(MeCN)₃][SbCl₆]

A solution of SbCl₅ (0.22 g, 0.73 mmol) in acetonitrile (25 cm³) was added dropwise to a chilled (0°C) and stirred solution of CpMoCl₃(MeCN)₂ (0.25 g, 0.72 mmol) in acetonitrile (50 cm³) under an atmosphere of argon. On warming to room temperature a deep-orange solution developed which was stirred for 3 h. Removal of solvent in vacuo gave a red solid which was washed with dichloromethane (3 × 20 cm³) and then hexane (3 × 20 cm³). An attempted recrystallization from acetonitrile provided the title compound as a feathery red solid (0.31 g (63.7%)).

3.4. [CpMoCl(MeCN)₄][SbCl₆]₂

Slow addition of SbCl₅ (0.18 g, 0.61 mmol) in acetonitrile (20 cm³) to [CpMoCl₂(MeCN)₃][SbCl₆] (0.42 g, 0.62 mmol) in acetonitrile (50 cm³) provided a deep-red solution which was warmed (50°C) for several hours under a blanket of argon. Removal of solvent in vacuo gave a deep-red solid which was washed with hexane (4 × 20 cm³) and then pumped dry in vacuo for several hours at room temperature (0.42 g (66.1%)). Recrystallization from acetonitrile : dichloromethane (50 : 50) provided crimson block crystals of the title compound as the monosolvate (MeCN).

3.5. [CpMo(MeCN)₆][SbCl₆]₃

Direct addition of SbCl₅ (1.72 g, 5.76 mmol) in acetonitrile (20 cm³) to CpMoCl₃(MeCN)₂ (0.34 g, 0.96 mmol) in acetonitrile (30 cm³) under an argon atmosphere produced a deep-green solution which was stirred and warmed (50°C) for 24 h. Removal of solvent yielded a green solid which was washed with hexane (2 × 20 cm³) and pumped dry in vacuo for several hours. An attempted recrystallization from acetonitrile : dichloromethane (50 : 50) in the presence of

Table 1
Crystal data and structure refinement for 1

Formula	[CpMoCl(MeCN)₄][SbCl₄]₂ · MeCN
Empirical formula	C₁₅H₂₀Cl₁₃MoN₅Sb₂
Formula weight	1070.65
Temperature (K)	293(2)
Wavelength (Å)	0.71070
Crystal system	Orthorhombic
Space group	Pmn2₁
Unit cell dimensions	
a (Å)	15.382(8)
b (Å)	7.532(7)
c (Å)	15.681(9)
Volume (Å³)	1816.8
Z	2
Density (calculated) (Mg m⁻³)	1.957
Absorption coefficient (mm⁻¹)	2.789
F(000)	1020
Crystal size (mm)	0.2×0.2×0.2
θ range for data collection (°)	3.28–24.91
Index ranges	−18 ⩽ h ⩽ 18, 0 ⩽ k ⩽ 8, −18 ⩽ l ⩽ 18
Number reflections collected	5226
Number of independent reflections	3075 (R(int) = 0.0549)
Refinement method	Full-matrix least-squares on F²
Number of data	3075
Number of parameters	163
Goodness of fit on F²	0.475
Final R indices	
(I > 2σ(I); 2359 reflect.)	
R₁	0.0742
wR₂	0.2175
R indices (all data)	
R₁	0.0927
wR₂	0.2759
Largest difference peak and hole	
(electrons Å⁻³)	1.540 and − 1.094

SbCl₅ (0.5 cm³) provided the title compound as a microcrystalline green solid (0.65 g (48.1%)).

3.6. X-ray crystallography

One of the crimson block crystals of [CpMoCl-(MeCN)₄][SbCl₆]₂ · MeCN was carefully selected and sealed in a Lindemann tube under an atmosphere of argon.

Crystal data are given in Table 1, together with refinement details. Data were collected with Mo Kα radiation using the MAR research image plate system. The crystal was positioned at 75 mm from the image plate. 95 frames were measured at 2° intervals with a counting time of 2 min. Data analysis was carried out with the XDS program [6]. The structure was solved using direct methods with the SHELX86 program [7]. No absorption correction was applied. The cation has crys-

Table 2

Atomic coordinates and equivalent isotropic displacement parameters for **1**, where U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor

Mo(1)	0	701(2)	0	37(1)
Cl(1)	0	−2446(6)	−17(8)	61(1)
Sb(1)	7501(1)	5005(2)	2502(3)	56(1)
Cl(2)	8378(8)	6612(13)	1566(8)	124(4)
Cl(3)	6631(7)	3337(12)	3387(7)	102(3)
Cl(4)	6310(8)	6686(23)	2138(10)	160(6)
Cl(5)	7220(10)	3058(20)	1361(9)	175(7)
Cl(6)	8706(10)	3173(21)	2815(10)	187(8)
Cl(7)	7883(12)	6713(30)	3655(11)	177(7)
N(100)	1352(9)	105(17)	84(14)	53(4)
C(101)	2014(10)	−346(24)	−125(12)	44(4)
C(102)	2975(10)	−1009(40)	−71(28)	95(10)
N(200)	0	146(31)	1388(22)	49(7)
C(201)	0	−228(49)	2050(18)	48(7)
C(202)	0	−1102(88)	2855(30)	94(19)
N(300)	0	141(43)	−1258(15)	73(10)
C(301)	0	−370(52)	−1926(35)	88(15)
C(302)	0	−806(89)	−2918(34)	114(20)
C(11) [a]	301(13)	3260(40)	725(16)	49(3)
C(12) [a]	−590(11)	3167(29)	494(17)	49(3)
C(13) [a]	−645(9)	3268(38)	−409(17)	49(3)
C(14) [a]	212(13)	3424(39)	−735(16)	49(3)
C(15) [a]	797(7)	3419(30)	−35(20)	49(3)
N(400)	0	−859(51)	4830(32)	114(14)
C(401) [a]	0	−2844(72)	4975(72)	67(12)
C(402) [a]	0	−4998(62)	5124(42)	61(14)
C(403) [a]	0	845(102)	4909(109)	96(26)
C(404) [a]	0	2497(172)	5445(84)	120(35)

[a] 50% occupancy.

tallographic mirror symmetry, although the cyclopentadienyl ring is disordered. We refined one ring with 50% occupancy with a constrained pentagonal shape. The solvent is disordered, two molecules with half-occupancy sharing a nitrogen atom. All ordered non-hydrogen atoms were refined with anisotropic thermal parameters. The disordered carbon atoms were refined with a common isotropic thermal parameter. Hydrogen atoms were included in geometric positions though the hydrogen atoms on the solvent could not be located. The structure was then refined on F^2 using SHELXL93 [8]. All calculations were carried out on a Silicon Graphics R4000 Workstation at the University of Reading.

The final atomic coordinates are listed in Table 2 and selected bond lengths and angles are given in Table 3. Tables of hydrogen atom coordinates and anisotropic displacement parameters and a complete list of bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.
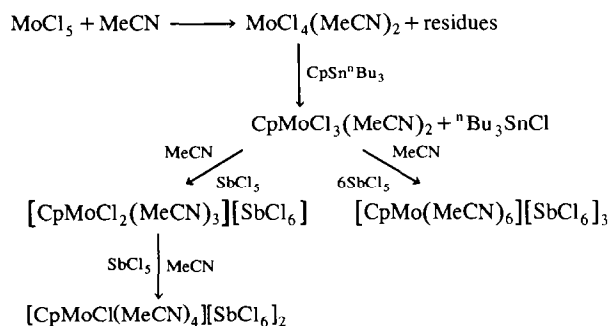
4. Results and discussion

Our approach to the formation of cationic molybdenum(IV) complexes has involved the sequential removal

Table 3

Selected bond lengths (Å) and angles (°) for **1**

Cation dimensions	
Bond lengths	
Mo(1)–N(100)	2.132(14)
Mo(1)–N(200)	2.22(3)
Mo(1)–N(300)	2.02(2)
Mo(1)–C(12)	2.21(2)
Mo(1)–C(11)	2.29(3)
Mo(1)–C(13)	2.27(3)
Mo(1)–C(14)	2.37(3)
Mo(1)–C(15)	2.39(2)
Mo(1)–Cl(1)	2.370(5)
Bond angles	
N(300)–Mo(1)–N(100)	90.9(6)
N(100) [a] –Mo(1)–N(100)	154.6(8)
N(300)–Mo(1)–N(200)	157.1(8)
N(100) [a] –Mo(1)–N(200)	84.2(6)
N(100)–Mo(1)–N(200)	84.3(6)
N(300)–Mo(1)–Cl(1)	77.3(10)
N(100)–Mo(1)–Cl(1)	77.9(3)
N(200)–Mo(1)–Cl(1)	79.8(7)
Bond lengths	
N(100)–C(101)	1.12(2)
C(101)–C(102)	1.56(2)
N(200)–C(201)	1.07(4)
C(201)–C(202)	1.42(4)
N(300)–C(301)	1.12(6)
C(301)–C(302)	1.59(7)
Bond angles	
C(101)–N(100)–Mo(1)	159(2)
N(100)–C(101)–C(102)	160(3)
C(201)–N(200)–Mo(1)	176(3)
N(200)–C(201)–C(202)	168(5)
C(301)–N(300)–Mo(1)	172(3)
N(300)–C(301)–C(302)	172(5)
Anion dimensions	
Bond lengths	
Sb(1)–Cl(4)	2.298(14)
Sb(1)–Cl(3)	2.301(9)
Sb(1)–Cl(2)	2.332(9)
Sb(1)–Cl(7)	2.30(2)
Sb(1)–Cl(5)	2.352(10)
Sb(1)–Cl(6)	2.364(10)
Bond angles	
Cl(4)–Sb(1)–Cl(3)	89.3(4)
Cl(4)–Sb(1)–Cl(2)	91.1(5)
Cl(3)–Sb(1)–Cl(2)	177.9(5)
Cl(4)–Sb(1)–Cl(7)	95.2(7)
Cl(3)–Sb(1)–Cl(7)	88.8(6)
Cl(2)–Sb(1)–Cl(7)	93.2(6)
Cl(4)–Sb(1)–Cl(5)	90.5(8)
Cl(3)–Sb(1)–Cl(5)	90.7(4)
Cl(2)–Sb(1)–Cl(5)	87.2(4)
Cl(7)–Sb(1)–Cl(5)	174.3(10)
Cl(4)–Sb(1)–Cl(6)	177.0(8)
Cl(3)–Sb(1)–Cl(6)	90.7(5)
Cl(2)–Sb(1)–Cl(6)	88.8(5)
Cl(7)–Sb(1)–Cl(6)	87.8(8)
Cl(5)–Sb(1)–Cl(6)	86.5(6)

[a] Symmetry transformations used to generate equivalent atoms: − x, y, z.

$MoCl_5 + MeCN \longrightarrow MoCl_4(MeCN)_2 + \text{residues}$

$\downarrow CpSn^nBu_3$

$CpMoCl_3(MeCN)_2 + {}^nBu_3SnCl$

MeCN ↙   ↘ MeCN

SbCl$_5$ 6SbCl$_5$

$[CpMoCl_2(MeCN)_3][SbCl_6]$ $[CpMo(MeCN)_6][SbCl_6]_3$

SbCl$_5$ | MeCN

$[CpMoCl(MeCN)_4][SbCl_6]_2$

Scheme 1.

of chloride ions from $CpMoCl_3(MeCN)_2$ using $SbCl_5$ as the halide abstractor. A summary of the reactions investigated is given in Scheme 1.

At the outset the Soxhlet treatment of molybdenum (V) chloride with acetonitrile provided the green molybdenum(IV) bis adduct $MoCl_4(MeCN)_2$ following in-situ reduction. The analytical and spectroscopic data used for characterization of this bis adduct are listed in Table 4 together with the corresponding data which serve to identify the trio of molybdenum(IV) cations isolated in this study. This spectroscopic evidence is not further discussed except where there is some point of clarification to be made. Reduction of molybdenum(V) chloride is facile particularly in the presence of nitrogen-containing ligands such as pyridine, 2,2'-bipyridyl and alkyl cyanides [9]; in this study, extraction with acetonitrile was quite effective with a 79% yield of the tetrachloride but identification of the (redox) oxidized species was not pursued. Introduction of the cyclopentadienyl ring for the formation of $[CpMoCl_3]$ was effected by direct treatment of the tetrachloride with $CpSn^nBu_3$; the high

yield (82%) of the bis-solvate $CpMoCl_3(MeCN)_2$ (82%) attests to the suitability of $^nBu_3Sn$ as an effective leaving group [10]. Evidence for the presence in solution of the three geometrical isomers possible for this compound derives from the ^1H NMR spectrum where three distinct signals for ring protons are observed, namely $\delta = 7.23, 7.19$ and 7.15 ppm.

The green $CpMoCl_3(MeCN)_2$ is a convenient precursor for cationic monocyclopentadienyl Mo(IV) species following halide abstraction using antimony(V)chloride. Direct addition with 1 : 1 stoichiometry results in single halide removal to provide the red hexachloroantimonate(V) salt, $[CpMoCl_2(MeCN)_3][SbCl_6]$. Using a 1 : 2 stoichiometry promotes the removal of two chloride ions with formation of the crimson dicationic species $[CpMoCl(MeCN)_4][SbCl_6]_2$. Total halide abstraction can only be realized in the presence of an excess of $SbCl_5$, i.e. a 1 : 6 mol ratio was used to obtain
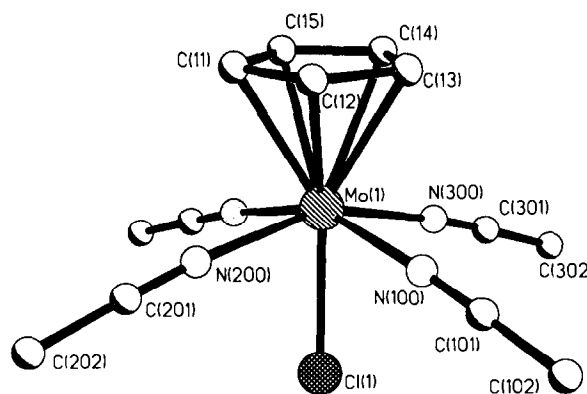

Fig. 1. A perspective view of the $[CpMoCl(MeCN)_4]^{2+}$ cation showing the numbering scheme employed.

Table 4
Microanalytical and principal spectroscopic data

Compound	Colour	Microanalysis, observed; calculated (%)				IR, ν (cm^{-1})			^1H NMR [b], δ (ppm)		
		C	H	N	Cl	ν(CN)	ν(MCl)	ν(SbCl)	η^5-C$_5$H$_5$	η^5C$_5$H$_5$	MeCN
MoCl$_4$(MeCN)$_2$	Green	14.88; 15.02	1.76; 1.89	8.40; 8.76	43.96; 44.34	2320, 2291	415(sh), 370(br), 345(br)				2.07
CpMoCl$_3$(MeCN)$_2$	Purple	30.22; 30.93	3.02; 3.17	7.91; 8.02	30.14; 30.43	2321, 2282	365(sh), 340(br)		3104, 1415, 1020, 871	7.23, 7.19, 7.15	2.36
[CpMoCl$_2$(MeCN)$_3$][SbCl$_6$]	Red	18.97; 19.17	1.99; 2.05	5.97; 6.10	40.87; 41.15	2314, 2289	260(br)	345(vs)	3128, 1408, 1028, 867	6.20	2.51, 2.24
[CpMoCl(MeCN)$_4$][SbCl$_6$]$_2$	Crimson	15.02; 15.17	1.37; 1.66	5.11; 5.44	44.26; 44.76	2316, 2286	235(br)	346(vs)	3109, 1422, 1026, 863	6.22	2.25, 2.64
[CpMo(MeCN)$_6$][SbCl$_6$]$_3$	Green	12.96; 13.15	1.28; 1.47	4.96; 5.11	46.08; 46.59	2320, 2290		346(vs)	3128, 1411, 1025, 869	6.37, 6.21	2.26, 2.61, 2.78

[a] For Nujol mulls
[b] For CDCl$_3$ solutions referenced to CH solvent at 7.26 ppm.

the green salt [CpMo(MeCN)$_6$][SbCl$_6$]$_3$. The IR spectra of these cationic species show a common profile which includes four bands characteristic of the cyclopentadienyl ligand, ν(CH) $\approx$ 3100 cm^{-1}, ν(CC) $\approx$ 1435 cm^{-1}, δ(CH) $\approx$ 1020 cm^{-1} and δ(CH) $\approx$ 870 cm^{-1}, an intense broad band ν(SbCl) $\approx$ 345 cm^{-1} indicative of the anion and two sharp bands at about 2320 and 2290 cm^{-1} due to coordinated acetonitrile ligands. As a general observation, high energy shifts of about 30–40 cm^{-1} with respect to the free nitrile (2287 and 2251 cm^{-1}) are typical for such solvated cationic species, e.g. [Cp$_2$Ti(MeCN)$_2$][PF$_6$]$_2$ [11] (2325 and 2288 cm^{-1}) and [Cp$_2$Zr(MeCN)$_3$][BPh$_4$]$_2$ [12] (2295 and 2270 cm^{-1}).

5. Crystallographic studies

An X-ray structure determination of [CpMoCl-(MeCN)$_4$][SbCl$_6$]$_2$ · MeCN was carried out as a means of establishing the ionic character for the series. The structure consists of discrete [CpMoCl(MeCN)$_4$]$^{2+}$ cations, two independent SbCl$_6^-$ anions and one MeCN (solvent) molecule all with imposed C$_2$ symmetry. A picture of the 2 + cation is shown in Fig. 1 with the atom-numbering scheme. The geometry of the molybdenum atom can be regarded as six-coordinated pseudo-octahedral with the cyclopentadienyl ligand (regarded as unidentate) mutually *trans* to the chlorine atom. The cyclopentadienyl ring is symmetrically bonded (η^5) to the central metal: Mo–C$_{ring}$, 2.21(2)–2.39(2) Å. The ring centroid–Mo distance (1.98 Å) is comparable with those noted for other cationic species, e.g. 2.032(5) Å for [CpMoCl(NO)(MeCN)$_2$][BF$_4$] [13] and 1.98(2) Å for [CpMoI$_2$(PMe$_3$)$_2$] [14] but is conspicuously shorter than that observed for neutral complexes, e.g. 2.30 Å for CpMoCl$_3$(dmpe) [15] and 2.32 Å for CpMoCl$_3$(dppe) [16]. The four bonded acetonitrile molecules lie in an equatorial plane (maximum deviation of any one of the donor nitrogen atoms, 0.01 Å) with Mo–N bond distances of 2.02(2), 2.13(1) and 2.22(3) Å and *cis* N–Mo–N bond angles of 84.2(6), 84.3(6) and 90.9(6)°. It emerges that the metal lies above this N$_4$ plane, 0.43 Å in the direction of the ring, leaving the four Cl$_{ax}$–Mo–N$_{eq}$ bond angles of 77.3(10), 77.9(3) and 79.8(7)° much less than the 90° ideal. Deformational bending of equatorial ligands away from the cyclopentadienyl ring appears to be a characteristic feature for such cationic species, presumably to minimize unfavourable interactions with the aromatic ring, e.g. for [CpNbCl-(MeCN)$_4$]$^{3+}$, Cl$_{ax}$–Nb–N$_{eq}$, 73.5(9)–80.7(8)° [4]; for [CpHf(MeCN)$_6$]$^{3+}$, N$_{ax}$–Hf–N$_{eq}$, 74.1(7)–80.5(7)° [3]; for [CpTi(MeCN)$_5$]$^{3+}$, N$_{ax}$–Ti–N$_{eq}$, 76.7(4)–77.8(4)° [2]. The Mo–Cl bond distance of 2.370(5) Å is comparable with those in similar cationic monocyclopentadi-

enyl–Mo(IV) species, e.g. for [CpMoCl$_2$(PMe$_3$)$_2$][PF$_6$] 2.374(3) and 2.369(3) Å [17]. When viewed against related neutral Mo(IV) compounds (e.g. CpMoCl$_3$(dmpe), 2.487(1)–2.500(1) Å [15]; CpMoCl$_3$ [P(OCH$_2$)$_3$CEt]$_2$, 2.43(1)–2.50(1) Å [18]), there is a marked decrease of about 0.1 Å, presumably as a reflection of the positive charge associated with the metal which leads to a reduction in the effective metal radius and, in turn, a concomitant increase in the metal–chlorine bond strength ($\sigma + \pi$). The SbCl$_6^-$ anions show no significant structural variation from regular octahedral geometry with Sb–Cl bond distances in the range 2.298(14)–2.364(10) Å and *cis* Cl–Sb–Cl bond angles in the range 86.5(6)–95.2(7)°.

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