Inorganica Chimica Acta, 149 (1988) 63–67

Halide Abstraction Reactions of Sb(V) Chloride: Synthesis and Characterisation of Hexachloroantimonate Salts of M(II) M = Zn, Mg; M(III) M = Cr; and M(IV) M = Ti, Sn and Related $Cp_2M(IV)$ M = Ti, Zr and Hf

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(Received December 28, 1987)

Abstract

Reactions of $SbCl_5$ with various covalent metal halides in MeCN have been studied as a convenient and direct route to metal hexachloroantimonate salts via Sb(V) halide abstraction. The isolation and characterization (Ir, Vis–UV, ^1H NMR spectroscopic and microanalytical) of the complexes $[Zn(MeCN)_6][SbCl_6]_2$, $[CrCl_2(MeCN)_4][SbCl_6]$, $[SnCl_3(MeCN)_3][SbCl_6]$, $[TiCl_2(MeCN)_4][SbCl_6]_2$, $[Cp_2M(Cl)(MeCN)_x][SbCl_6]$ M = Ti, $x = 1$; M = Zr, Hf, $x = 2$, and $[Cp_2M(MeCN)_y][SbCl_6]_2$ M = Ti, $y = 2$; M = Zr, Hf, $y = 3$, is described. The reaction of $MgCl_2$ with $SbCl_5$ was carried out in EtOAc as solvent and gave $[Mg(EtOAc)_6][SbCl_6]_2$. ^{121}Sb NMR, IR and UV spectroscopic measurements provide positive identification of the $SbCl_6^-$ anion.

Introduction

One of the characteristic properties of both Sb(III) and Sb(V) is an ability to accept halide ions with consequent salt formation

$$RX + SbX_n \longrightarrow [R][SbX_{n+1}]$$

For the chlorides in particular the range of complex anions is extensive e.g. $SbCl_4^-$, $SbCl_5^{2-}$, $SbCl_6^{3-}$, $Sb_2Cl_8^{2-}$, $Sb_2Cl_9^{3-}$, $Sb_4Cl_{16}^{4-}$, $SbCl_6^-$ and normally feature R = tetraethylammonium, pyridinium or related organic groups [1]. Our interest in this particular facet of antimony chemistry lies in the development of non-redox halide abstraction from covalent metal halides as a direct route to reactive cationic metal species. In preliminary communications we have described the formation and structures of $[TiCl_3(MeCN)_3][SbCl_6]$ [2] and $[Mg(MeCN)_6][Sb_2Cl_8]$ [3] as obtained from the $TiCl_4/SbCl_5$ and $MgCl_2/SbCl_3$ systems respectively in acetonitrile solution.

The results of further studies involving halide transfer reactions of Sb(V) chloride with a variety of anhydrous metal chlorides are presented in this paper.

Experimental

All operations were carried out under a N_2 atmosphere using a conventional 'dry box' and, in some instances, a Schlenk system. The anhydrous metal chlorides and $SbCl_5$ were obtained commercially and used directly as supplied. The $SbCl_5$ was stored over molecular sieves. Purification of MeCN followed the treatment recommended by Walter and Ramaley [4]. All other solvents were stored over CaH_2 and distilled *in vacuo* prior to use.

IR spectra were recorded as mulls located between CsI plates using a Perkin-Elmer 580 B spectrometer. ^{121}Sb NMR spectra (95.72 MHz) were recorded on a Bruker WH 400 spectrometer and ^1H NMR spectra (220 MHz) were recorded on a Perkin-Elmer R34 spectrometer with samples in sealed tubes. For details of ^1H and ^{121}Sb chemical shift measurements see footnote to Table I. Vis–UV spectroscopic measurements were made with a Shimadzu UV35 spectrophotometer using MeCN solutions sealed in quartz cells with a light path of 1 cm. Elemental analyses were performed by Butterworth Laboratories Ltd., Teddington TW11 8LG, Middlesex, U.K. Chloride was estimated by the Volhard titration method.

Preparation of Complexes

The standard procedure involved direct addition under a N_2 atmosphere of the stoichiometric amount of $SbCl_5$ in MeCN solution to the appropriate anhydrous metal chloride dissolved in excess MeCN. Purification of the product was by straightforward recrystallisation from a concentrated MeCN solution. As typical examples:

$[Cp_2Hf(MeCN)_3][SbCl_6]_2$

$SbCl_5$ (0.96 g, 3.2 mmol) in MeCN (20 cm^3) was added dropwise to a chilled (0 °C) and stirred solution of Cp_2HfCl_2 (0.55 g, 1.5 mmol) in MeCN (50 cm^3). The resulting yellow solution was allowed to warm to room temperature and stirred for a further 6 h. Removal of solvent *in vacuo* leaves an off-white solid which was washed with benzene

0020-1693/88/\$3.50

TABLE I. Microanalytical and Principal Spectroscopic (^{1}H and ^{121}Sb NMR, IR, Electronic) Data for Antimonate(V) Salts

Compound	Colour	Melting point (°C)	Analyses: found (calc.) (%)				^{121}Sb NMR^a		^{1}H NMR^b		Electronic^c	Infrared^d (cm^{-1})	
			C	H	N	Cl	δ(ppm)	$W_{1/2}$ (Hz)	$\delta_{C_5H_5}$	δ_{CH_3}	λ_{max} (cm^{-1})	ν(M – Cl) [450–200]	ν(CN)
$[Zn(CH_3CN)_6][SbCl_6]_2$ (I)	white	193–195	13.8 (14.7)	1.9 (1.9)	8.0 (8.6)	43.0 (43.4)	−0.28	182			37037	396m 346vs br 287w	2320 2294
$[Mg(EtOAc)_6][SbCl_6]_2$ (II)	white	114–115	23.3 (23.6)	3.9 (4.0)		34.5 (34.8)	−2.15	840			36980	398m 344vs br 305sh 280(sh)	ν(C=O) ester 1748vw 1715sh 1680vs br 1650sh
$[CrCl_2(CH_3CN)_4][SbCl_6]$ (III)	dark green	74–76	15.2 (15.5)	2.3 (2.0)	8.6 (9.0)	45.2 (45.6)	7.10	210			16234 22321 37037	435s 345vs, br 424w 305s 382s 265w br	2330 2300
$[SnCl_3(CH_3CN)_3][SbCl_6]$ (IV)	cream	74–76	11.8 (10.6)	1.7 (1.3)	6.2 (6.2)	46.7 (46.7)	−0.41	168			37037	410(sh) 373s 342vs br 310m 265w	2322 2295
$[TiCl_2(CH_3CN)_4][SbCl_6]_2$ (V)	yellow	88–90	10.4 (10.8) [Ti: obs. 4.8%, calc. 5.0%]	1.5 (1.3)	5.8 (5.9)	51.8 (52.1)	−0.48	177			37453	432vs 352sh 412w 344vs br 375sh	2320 2292
$[(C_5H_5)_2Ti(Cl)(CH_3CN)][SbCl_6]$ (VI)	olive green	158–159	24.6 (24.4)	2.3 (2.2)	2.3 (2.4)		−0.45	201	6.86	1.95		418m 380w 344vs br 305m 265m	2318 2290
$[(C_5H_5)_2Ti(CH_3CN)_2][SbCl_6]_2$ (VII)	mauve	174–176	17.2 (18.0)	1.9 (1.7)	3.1 (3.0)		−0.38	306	6.95	1.95		420w 410w 347vs br 280m	2320* 2290* *each sharp band shows evidence of doublet profile
$[(C_5H_5)_2Zr(Cl)(CH_3CN)_2][SbCl_6]$ (VIII)	white	130–132	20.8 (24.9)	2.5 (2.4)	4.4 (4.2)		−0.45	230	6.58	1.95		422w 402w 345vs br 290w 235w	2320 2291

$[(C_5H_5)_2Zr(CH_3CN)_3][SbCl_6]_2$ (IX)	cream	132–134	21.0 (18.9)	2.3 (1.9)	4.2 (4.1)		−0.38	220	6.58	1.95	421w 400w 347vs br 290w 260w 235w	2321 2291
$[(C_5H_5)_2Hf(Cl)(CH_3CN)_2][SbCl_6]$ (X)	cream		21.8 (22.0)	2.3 (2.1)	3.8 (3.7)	32.8 (32.7)	−0.38	301	6.45	1.95	425vw 345vs br	2321 2297
$[(C_5H_5)_2Hf(CH_3CN)_3][SbCl_6]_2$ (XI)	cream		16.9 (17.4)	1.9 (1.7)	3.9 (3.8)	37.1 (38.6)	−0.17	290	6.41	1.95	430vw 348vs br	2322 2296

[a] δ(ppm) for MeCN solutions (*ca.* 10^{-2} M) doped with 10% (by volume) of CD_3CN with $[Et_4N][SbCl_6]$ [$\delta 0$, $W_{1/2}$ 190 Hz) as external reference. A negative δ value indicates an upfield chemical shift with respect to $SbCl_6^-$. [b] δ(ppm) for CD_3CN solutions with tetramethylsilane as internal reference. [c] CH_3CN solutions. [d] ν(cm^{-1}) for nujol mull.

(5 X 50 cm^3) and then n-hexane (2 X 50 cm^3) and pumped dry for 1 h. (Yield 1.18 g 74%.) The product **XI** was recrystallised from a concentrated MeCN solution following layering with diethylether to provide minute white needle crystals.

$[Mg(EtOAc)_6][SbCl_6]_2$

A solution of $MgCl_2$ (1.02 g, 10.7 mmol) in EtOAc (50 cm^3) was obtained by direct Soxhlet extraction. This solution was chilled (0 °C) and to it was added dropwise a solution of $SbCl_5$ (6.28 g, 21.0 mmol) in EtOAc (25 cm^3). The resulting solution was allowed to warm to room temperature and then stirred for 3 h. Removal of solvent *in vacuo* provided a white solid which was washed with n-hexane (3 X 50 cm^3) and pumped dry for 1 h. (Yield 7.31 g, 56%). The product **II** was recrystallised from EtOAc/CH_2Cl_2 as colourless needle crystals.

Results and Discussion

General Comments

Table I lists the series of complexes obtained in this study following the direct addition of $SbCl_5$ to the appropriate metal chloride dissolved in acetonitrile. The resulting products were washed thoroughly with benzene and n-hexane and recrystallised from concentrated acetonitrile solutions via layering with diethylether. The majority gave well-defined melting points. All are extremely sensitive to air-moisture hydrolysis but can be safely handled in a conventional N_2 box.

Formulation of these adducts as monocationic or dicationic antimonate salts is based on ^{121}Sb NMR and UV spectroscopic identification of $SbCl_6^-$ and accompanying microanalytical, and electronic, IR and ^{1}H NMR spectroscopic data. The ^{121}Sb NMR spectra show a clearly resolved singlet in each case; these lie within the range δ −2.15 to +7.10 ppm with linewidths essentially the same as in the reference $[Et_4N][SbCl_6]$ $\delta = 0$, $W_{1/2}$, 190 Hz. The relatively narrow linewidths observed, *cf.* $SbCl_5$ neat solution δ 428.68 ppm; $W_{1/2}$, 7000 Hz*, reflect the favourable rate of quadrupole relaxation of the ^{121}Sb nucleus under the high symmetry (O_h) imposition of six chlorine atoms [6]. Further confirmation of $SbCl_6^-$ formation comes from the ultraviolet spectra of acetonitrile solutions where the presence of a charge transfer band at λ_{max} *ca.* 36 765 cm^{-1} is diagnostic of $SbCl_6^-$ species in solution [7] (see Table I).

Excepting **II** the IR spectra show a sharp doublet profile in the 2350–2250 cm^{-1} region throughout the series consistent with coordinated acetonitrile.

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*Kidd and Matthews [5] report values of δ 509 ± 20, $W_{1/2}$, 8000 Hz at an operating frequency of 14.4 MHz.

With ν(CN) bands at *ca.* 2320 and 2290 cm^{-1} as compared with those at 2287 and 2251 cm^{-1} for the free ligand, there is clear evidence of the predicted strong ligand binding to these cationic metal species. For the Mg(II) complex (**II**) an intense band at 1680 cm^{-1} indicates coordination of EtOAc as ligand to the metal centre via the carbonyl oxygen of the ester group: free EtOAc has a prominent ν(C=O) band at 1743 cm^{-1} [8]. In the far IR region (450–200 cm^{-1}) the presence of a broad intense band at *ca.* 345 cm^{-1} is a common feature, *cf.* the exceptionally strong ν(SbCl) 346 cm^{-1} [F_{1u} bending mode (ν_3)] observed for [K][$SbCl_6$] [9]. However, for those complexes where a metal–chlorine bond has been retained e.g. **III–VI**, **VIII** and **X** this dominant band is likely to include a pertinent ν(M–Cl) stretching mode component [8].

Comments on Specific Compounds

$Cp_2M(IV)$ complexes

Current interest in cationic Group IVA metal species of the types $[Cp_2M(X)L_x]^+$, X = R or halogen, and $[Cp_2ML_y]^{2+}$, L = THF or MeCN, is focussed on their extreme reactivity as a reflection of the residual +ve charge(s) at the metal centre [10]. Synthetic approaches have included halide removal from Cp_2MX_2 using a silver salt (BPh_4^-, PF_6^-) [11] or alkyl abstraction from Cp_2MR_2 again via reaction with a silver salt [12] or hydrofluoroboric acid diethylether [13].

Our present studies confirm halide abstraction by Sb(V) is an effective variant route: reactions are rapid and direct and there are no complications from side-products. The six compounds **VI–XI** make up the complete series $[Cp_2M(Cl)(MeCN)_x][SbCl_6]$ and $[Cp_2M(MeCN)_y][SbCl_6]_2$ for M = Ti, Zr, Hf. Neither of the hafnium cation species has been described previously but there are reports for $[Cp_2Ti(Cl)(MeCN)][FeCl_4]$ [14], $[Cp_2Ti(MeCN)_2][PF_6]_2$ [15], $[Cp_2Ti(C_8H_4N_2)_2][SbCl_6]_2$ ($C_8H_4N_2$ = phthalonitrile), $[Cp_2Ti(Cl)(C_3H_2N_2)_2]_2[SnCl_6]$ ($C_3H_2N_2$ = malonitrile) [16], $[Cp_2Zr(MeCN)_3][BPh_4]_2$ and its 4,4′-dimethylbipyridine and trimethylphosphine derivatives [11]; other related $Cp_2M(IV)$ species include chloro-cationic: $[Cp_2Zr(Cl)(OPPh_3)][ClO_4]$, $[(Cp_2ZrCl)_2(\mu\text{-bipyridine})][ClO_4]_2$ and $[(Cp_2ZrCl)]_2[BF_4]_2$ [17]; dicationic $[Cp_2Zr(H_2O)_3][CF_3SO_3]_2 \cdot THF$ [18], $[Cp_2Ti(H_2O)_2][ClO_4]_2$ [19] and $[Cp_2Ti(L\text{-}L)][CF_3SO_3]_2$ (L-L = bipyr or phen) [20]. Many of the characteristics of these species have been described previously. The essential points of difference between the chloro- and non-chloro-cationic antimonate salts presented here can be summarised as follows:

(a) Coordination geometry. For $[Cp_2M(Cl)(MeCN)_x]^+$ $x = 1$ for Ti; $x = 2$ for Zr and Hf, and for $[Cp_2M(MeCN)_y]^{2+}$ $y = 2$ for Ti, $y = 3$ for Zr and Hf. The change in coordination between Ti species (*CN* = 4) and Zr/Hf species (*CN* = 5), regarding the cyclopentadienyl groups as unidentate ligands, is seen as a direct reflection of the size difference between these metal ions and denotes the former as 16-electron and the latter as 18-electron species respectively.

(b) Ligand binding. There is no apparent difference in CH_3CN attachment to either monocationic or dicationic metal species as reflected in the repetitive similarity of ν(CN) band shifts (mull), see Table I. In the case of the Cp_2Ti^{2+} complex (**VII**) however there is a discernible doublet profile to each of the sharp ν(CN) singlets at 2320, 2290 cm^{-1} which is real and which presumably results from some site irregularity concerning the ligand environment. Why this is seemingly specific to this one complex is unclear. Bands for coordinated CH_3CN in $[Cp_2Ti(MeCN)_2][PF_6]_2$ are reported at 2325 and 2288 cm^{-1} [15]. For the Cp_2Zr^{2+} complex (**IX**) (ν(CN) 2321, 2291 cm^{-1}) the pronounced high energy shift of these bands compared with those reported for the tetraphenylborate counterpart $[Cp_2Zr(MeCN)_3][BPh_4]_2$ (ν(CN) 2295, 2270 cm^{-1} [11]) is attributed to an anionic perturbation $SbCl_6^- > BPh_4^-$. The room temperature ^{1}H NMR spectra for MeCN-d^3 solutions show a similar pattern of two singlets: the one at δ 1.95 for the MeCN resonance and the other at *ca.* δ 6.4–6.9 for the C_5H_5 resonance.

$[CrCl_2(MeCN)_4][SbCl_6]$

The cation is assigned a *trans*-octahedral geometry based on the electronic spectrum which shows broad bands (with evidence of doublet structure) at 16234 cm^{-1} $^4A_{2g} \rightarrow {}^4T_{2g}$ (O_h) [$^4B_{1g} \rightarrow$ (^4E_g, $^4B_{2g}$)(D_{4h})] and 22321 cm^{-1} $^4A_{2g} \rightarrow {}^4T_{1g}$(F)($O_h$)-[$^4B_{1g} \rightarrow$ (^4E_g, $^4A_{2g}$)(D_{4h})] similar to those observed for *trans* $[CrCl_2(H_2O)_4]^+$ with its pronounced tetragonal (D_{4h}) distortion [21]. The third band expected at *ca.* 36000 cm^{-1} $^4A_{2g} \rightarrow {}^4T_{1g}$(P)($O_h$)[$^4B_{1g} \rightarrow$ (^4E_g, $^4A_{2g}$)(D_{4h})] is masked by the intense charge transfer band arising from the $SbCl_6^-$ anion.

M(II) Complexes (M = Mg, Zn)

For the Mg(II) and Zn(II) complexes where the dications $[Mg(EtOAc)_6]^{2+}$ and $[Zn(MeCN)_6]^{2+}$ are formed, the double halide abstraction emphasises the powerful Lewis acid acceptor behaviour of Sb(V). The use of EtOAc as solvent in the case of Mg(II) does not affect salt formation. If, as seems likely, the role of solvent in these reactions is simply to ensure coordinative saturation of the metal cation following halide transfer, then the choice is open e.g. THF, Et_2O, DMSO, etc. By way of contrast, with $SbCl_3$ as reference Lewis acid in the reaction systems $\mathrm{MCl_2/SbCl_3/MeCN}$ (M = Mg, Zn), whereas halide transfer does occur in the case of magnesium to give $\mathrm{[Mg(MeCN)_6][SbCl_4]_2}$ [3] there is no reaction at all in the case of zinc. Reactants are recovered unchanged. This would suggest that halide abstraction by Sb(III) is favoured only when the antimony is placed in conjunction with an electropositive metal. Indeed the product obtained from the reaction system $\mathrm{SbCl_3/GaCl_3/SO_{2(liq)}}$ has the salt formulation $\mathrm{[SbCl_2][GaCl_4]}$ commensurate with (formal) halide ion donacity Sb(III) → Ga(III). An X-ray crystal structure determination shows $\mathrm{SbCl_2^+}$ cations and $\mathrm{GaCl_4^-}$ anions with strong interionic halogen bridging (Sb–Cl-----Ga) resulting in a pronounced zig-zag chain arrangement [22]. The 'duality' of Zn(II) in respect of the direction of halide transfer (donor $\sim$ acceptor) is amply demonstrated in the reaction systems $\mathrm{MCl_3/ZnCl_2/THF}$, M = Ti [23], V [24] where the zinc behaves as the favoured halide abstractor to give *trans* $\mathrm{[MCl_2(THF)_4][ZnCl_3(THF)]}$.

M(IV) complexes (M = Ti, Sn)

Having established the formation of the monocationic complex *fac*-$\mathrm{[TiCl_3(MeCN)_3][SbCl_6]}$ from the $\mathrm{TiCl_4/SbCl_5/MeCN}$ reaction system [2] we now find that a second halide abstraction can be effected to provide the novel Ti(IV) $\mathrm{d^0}$ dicationic species $\mathrm{[TiCl_2(MeCN)_4][SbCl_6]_2}$ (**V**). This appears to be the limit of halide removal from $\mathrm{TiCl_4}$ however, since no matter the excess of $\mathrm{SbCl_5}$ used, complex **V** is always the end product. Although a *cis* $\sim$ *trans* octahedral structure differentiation for this dication, based on the number and location of ν(TiCl) stretching modes, is baulked by the intense ν(SbCl) 344 cm^{-1} band, the latter is favoured intuitively pending an X-ray structure determination. Preliminary observations indicate that this is an extremely reactive titanium species both for ligand exchange and chloride replacement reactions*. A single halide abstraction from Sn(IV)chloride provides the monocationic complex $\mathrm{[SnCl_3(MeCN)_3][SnCl_6]}$ (**IV**) which by analogy with its Ti(IV) counterpart is likely to be the *fac*-isomer*.

Acknowledgement

We thank Dr Aidan Harrison for carrying out the ^{121}Sb NMR measurements and the SERC for financial assistance with studentships (to P.P.K.C., P.N.B. and H.C.).

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*The derivative chemistry of this (and related) cationic M(IV) species will be described in a separate report.