Inorganica Chimica Acta, 114 (1986) L1–L3

Synthesis of *cis*-[Co(en)$_2$(MF$_6$)$_2$]MF$_6$ (M = As or Sb): Cobalt(III) Complexes Containing η^1-MF$_6^-$ Characterizable by ^{19}F NMR

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Received October 14, 1985

Recently, Hersh [1] has reported η^1-SbF$_6^-$ bound to a transition metal in (Me$_2$PhP)(CO)$_3$(NO)W(μ-F)-SbF$_5$. In this compound the SbF$_6^-$ was characterized in the solid state by X-ray analysis and in CD$_2$Cl$_2$ solution by the ^{19}F–^{31}P nuclear spin–spin coupling seen in the variable temperature ^{31}P NMR spectrum. The ^{19}F NMR spectrum was broad, and therefore, apparently, uninformative, the broadness being attributed to efficient quadrupolar coupling to ^{121}Sb and ^{123}Sb (I = 5/2 and 7/2, respectively).

Described here are the reactions of *trans*-[Co(en)$_2$-Cl$_2$]Cl (**1**) with AgMF$_6$ and MF$_5$ (M = As or Sb) in liquid SO$_2$ which lead to Co(III) species in which the presence of η^1-MF$_6^-$ is shown by sharp reduced temperature ^{19}F NMR spectra.

Experimental

Materials

AsF$_5$ (Ozark-Mahoning, Inc.) was used as received, and SbF$_5$ (Ozark-Mahoning) was purified by double distillation under dry N$_2$ in glass apparatus. SO$_2$ (Matheson, Anhydrous Grade) was dried by standing in the gas phase over Linde 3A Molecular Sieves for at least 12 h before use. Ag powder (99.999%) was from Alfa.

Literature syntheses were used for **1** [2] and AgAsF$_6$ [3], and AgSbF$_6$ was prepared from Ag powder and SbF$_5$ in liquid SO$_2$ in the manner described for other SbF$_6^-$ salts [4a].

Manipulations

A calibrated standard glass and Teflon vacuum line was used for transfers of AsF$_5$ and SO$_2$ and for vacuum-drying. All moisture-sensitive solids were handled in a glove box in which the dry N$_2$ atmosphere was maintained by circulation through traps cooled with liquid N$_2$; transfers of SbF$_5$ were made using an all-glass syringe.

Preparative reactions in liquid SO$_2$ were carried out at room temperature in sealed glass H-shaped reaction vessels, having the arms separated by a fine sinter, as described earlier [5]; *in situ* preparation of NMR samples was carried out similarly but in smaller vessels having an NMR tube attached via a fine glass frit [4b]. Samples for UV–Vis spectroscopy in liquid SO$_2$ were prepared in a sealed glass tube having a quartz cell of 1 cm pathlength attached by a sidearm.

Spectroscopy

CW 94.1 MHz ^{19}F NMR spectra were obtained using a Varian HA-100 spectrometer; C$_6$F$_6$ was used as an internal reference and data were converted to CF-Cl$_3$ as reference using δ(CFCl$_3$) = δ(C$_6$F$_6$) – 164.9 [6]. FT 25.2 MHz ^{13}C-{^{1}H} NMR spectra were measured using a Varian XL-100-15 spectrometer; as described previously [3], external dioxane/D$_2$O in the outer annulus of two concentric tubes was used as a reference/lock, and chemical shifts were converted to internal TMS as reference using δ_c (TMS in SO$_2$, int) = δ_c (dioxane in D$_2$O, ext) + 67.8. UV–Vis spectra were run on Coleman 124 or Beckman 24 recording spectrophotometers.

Analysis

Microanalyses were carried out by Alfred Bernhardt Mikroanalytisches Laboratorium. Chloride analyses were made using gravimetry [7].

Synthesis of Co(en)$_2$(SbF$_6$)$_3$ (2) and Co(en)$_2$-(AsF$_6$)$_3$ (3)

In a sealed glass H-tube (see above) **1** was stirred with just less than 3 equivalents* of AgMF$_6$ in liquid SO$_2$ at room temperature. The poorly-soluble **1** reacts over a period of *ca.* 90 min** to give AgCl together with, first, an SO$_2$-insoluble pink substance, then the SO$_2$-soluble purple product. The product-containing solution was separated by filtration from the insolubles which were washed several times with SO$_2$ to retrieve adhering product. By slow cooling of the opposite arm with liquid N$_2$ to remove the solvent, the product was obtained dry, then the arm containing it was separated by flame sealing. In the glove box, the product was transferred to a glass drying vessel to allow removal of final traces of SO$_2$ under vacuum. Both salts Co(en)$_2$(MF$_6$)$_3$ were obtained in near-quantitative yield as highly water-sensitive glassy purple solids. *Anal.* Calc. for C$_4$H$_{16}$As$_3$CoF$_{18}$N$_4$: C, 6.44; H, 2.16; As, 30.13. Found: C, 6.57; H, 2.23; As, 29.92%. *Anal.* Calc.

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*Co(en)$_2$(MF$_6$)$_3$ is formed using AgMF$_6$/**1** >3 but cannot be separated from the excess silver salt.

****1** undergoes no reaction with SO$_2$ alone in the same time period; there is an apparent slow conversion to the *cis*-compound on stirring in liquid SO$_2$ for many days.

0020-1693/86/$3.50

TABLE I. Fluorine-19 NMR Spectroscopic Data for some species Containing η^1-MF_6^- (M = As or Sb) and for $[(H_3N)_5CoF]^{2+}$

Species	Solvent	Temperature (°C)	δ_F in $-CoF_{br}-M(F_e)_4-F_t$ (ppm)[a]			J(F–F) in $-CoF_{br}-M(F_e)_4-F_t$ (Hz)		
			F_{br}	F_e	F_t	$F_{br}-F_e$	$F_{br}-F_t$	F_e-F_t
$(en)_2Co(SbF_6)_3$[b]	SO_2	−40	−308.3	−111.4	−131.8	77[c]	d	104[c]
$(en)_2Co(AsF_6)_3$[b]	SO_2	−40	−263.1	−52.0	−79.6	84[c]	d	126[c]
$Sb_2F_{11}^-$[e]	SO_2	−60	−89.4	−109.1	−131.2	59	d	102
$Sb_2F_{11}^-$[f]	SO_2ClF	−94	−93.4	−114.6	−136.4	60	d	101
$As_2F_{11}^-$[g]	SO_2ClF	−140	−21.1	−48.6	−85.0	51	d	127
$F_5SbFAsF_5^-$[h]	CH_2Cl_2	−96	−118	−118[i]	−138.9[i]	j	d	112[i]
			−118	−50.5[k]	−92.9[k]	47[k]	d	126[k]
$[(H_3N)_5CoF]^{2+}$[l]	HF	−60			~−380			

[a] Relative to external $CFCl_3$; shifts to higher frequency than the reference are taken as positive. [b] This work; see text. [c] Estimated error ±2 Hz. [d] Not observed. [e] Chemical shifts from ref. 11(a) are for the Cs^+ salt; coupling constants are from ref. 11b. [f] Ref. 11b; for the Bu_4N^+ salt. [g] Ref. 12. [h] Ref. 13. [i] F-on-Sb. [j] Could not be measured with certainty. [k] F-on-As. [l] Ref. 14.

for $C_4H_{16}CoF_{18}N_4Sb_3$: C, 5.41; H, 1.82; Sb, 41.21. Found: C, 5.54; H, 1.90; Sb, 40.92%.

Reaction of 1 with MF_5 (M = As or Sb) in SO_2

1 reacts with MF_5 (M = As or Sb) in SO_2 to give pink SO_2-insoluble products without sign of residual **1** when $2.5 \leqslant AsF_5/Co \leqslant 6.0$ or $2.0 \leqslant SbF_5/Co \leqslant 3.0$. Above the higher ratios the product mixtures are purple and completely SO_2 soluble*. The insoluble pink intermediate products appear to be mixtures: from $AsF_5/1$ = 3.25, *Anal.* Calc. for $Co(en)_2As_2Cl_{0.90}F_{12.10}$: Cl, 5.40. Found: Cl, 5.42%; from $SbF_5/1$ = 2.35, *Anal.* Calc. for $Co(en)_2Sb_2Cl_{2.1}F_{10.9}$: Cl, 10.59. Found: Cl, 10.53%.

Results and Discussion

In SO_2, **1** reacts with three mols of $AgMF_6$ (M = As or Sb) to give purple products of composition $Co(en)_2(MF_6)_3$. These compounds are based on octahedral Co(III) with *cis* en ligands as shown by (a) the observation of two ^{13}C NMR resonances (δ_C = 44.5, 49.3 ppm (both resonances broad) for both salts) [8]; (b) the position and intensity of the visible absorption band (λ_{max} 502 nm, ϵ_{max} *ca.* 70 M^{-1} cm^{-1} for both salts) [9]; and (c) the reaction of the compounds with H_2O to give predominantly *cis*-$[Co(en)_2(OH_2)(OH)]^{2+}$ (identified by UV–Vis). The last noted reaction is so rapid that handling of the compounds even in a good dry box is difficult, a contrast with the otherwise rather similar *cis*-$[Co(en)_2(O_3SCF_3)_2](O_3SCF_3)$ [10].

Details of the ^{19}F NMR spectra of the compounds $Co(en)_2(MF_6)_2$ in liquid SO_2 are included in Table I. At ambient probe temperature the ^{19}F NMR spectrum of **2** shows three broad resonances which sharpen at reduced temperature to a pattern of (from low to high shielding) a double–doublet and two quintets, relative intensities 4, 1 and 1. The double–doublet and one quintet occur in the F-on-Sb region (by comparison with the corresponding region in the ^{19}F NMR spectra of $Sb_2F_{11}^-$ and $AsSbF_{11}^-$ (see Table I)) while the second quintet is unusually highly shielded. Such high shielding has been reported previously for ^{19}F attached to low-spin d^6 centres [14, 15]. Of special note here, the highly shielded quintet occurs in the same general region as the ^{19}F NMR signal of $[(H_3N)_5CoF]^{2+}$ (see Table I). Clearly the chemical shifts and NMR pattern are consistent with the presence of the grouping** $Co^{III}-F_{br}-(Sb(F_e)_4)-F_t$, an assignment strengthened by the values of $J(F_e-F_t)$ and $J(F_{br}-F_t)$ which also resemble those found for F-on-Sb in $Sb_2F_{11}^-$ and $AsSbF_{11}^-$ (see Table I). Thus **2** must be *cis*-$[(en)_2Co\{(\mu\text{-}F)SbF_5\}_2](SbF_6)$. No ^{19}F NMR signal attributable to the uncoordinated octahedral SbF_6^- ion was found, but this signal is expected to be broad due to the quadrupolar properties of $^{121/123}Sb$. In addition, no evidence was found for ^2J(F–Co–F); apparently this is zero or near-zero.

The ^{19}F NMR spectral pattern found for **3** resembles that of **2**; at reduced temperature it is com-

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*At concentrations typically used (*ca.* 0.5 M) slow crystallization occurs on standing at room temperature.

**The subscripts, br, e, and t indicate bridging, equatorial and terminal fluorines, respectively.

prised of a double–doublet and quintet, relative intensities 4 and 1, in the F-on-As region (by comparison with same region in the spectra of $As_2F_{11}^-$ and $AsSbF_{11}^-$ (see Table I)), and a highly shielded quintet, relative intensity 1. Here the occurrence of the grouping $Co–F_{br}–(As(F_e)_4)–F_t$ is indicated; Again $J(F_e–F_t)$ and $J(F_{br}–F_t)$ resemble those found in simple models, $As_2F_{11}^-$ and $AsSbF_{11}^-$, and ^2J-(F–Co–F) must be near zero. Thus **3** is *cis*-$[(en)_2Co\{(\mu\text{-}F)AsF_5\}_2](AsF_6)$. Not unexpectedly no signal from the free octahedral AsF_6^- is seen; this can be attributed to the quadrupolar nature of ^{75}As ($I = 3/2$, 100% abundant).

If **1** is reacted with $AgMF_6$ in the ratio $2 \leqslant AgMF_6/Co < 3$ an SO_2-insoluble pink substance, mixed with AgCl, is formed along with soluble $Co(en)_2(MF_6)_3$. Extraction of isolated insoluble material with water gives predominantly *cis*-$[Co(en)_2Cl(OH_2)]^{2+}$ in solution (by UV–Vis) and shows that formation of AgCl is quantitative. The pink products may thus be formulated *cis*-$Co(en)_2Cl(MF_6)_2$. As these are not highly water-sensitive, unlike **2** and **3**, they probably do not contain coordinated MF_6^-; they may be halogen-bridged dimers or polymers.

There is a direct reaction between **1** and SO_2 solutions of MF_5 (M = As or Sb). Qualitatively the reaction sequence resembles that found with $AgMF_6$. Pink insoluble products are found when $2.5 \leqslant AsF_5/1 \leqslant 6.0$ or $2.0 \leqslant SbF_5/1 \leqslant 3.0$, though these appear to be mixtures (see 'Experimental'), probably because of the complexity of the halogen abstraction and exchange reactions of the pentafluorides (e.g. ref. 11c). Soluble purple products are formed when larger amounts of MF_5 are used, and in solutions of these, $Co–F–MF_4–F$ groupings are again detectable by ^{19}F NMR.

Acknowledgements

I am grateful to the Natural Sciences and Engineering Research Council of Canada for financial support, to John M. Decesare and Thomas Vockeroth, summer students in 1974 and 1975, respectively, for technical assistance, and to Prof. J. B. Stothers of this Department for measuring ^{13}C NMR spectra.

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