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THE SYNTHESIS AND PROPERTIES OF DICHLOROHEPTAFLUOROPROPYLTRIPYRIDINECHROMIUM(III) AND SOME RELATED COMPOUNDS

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Summary

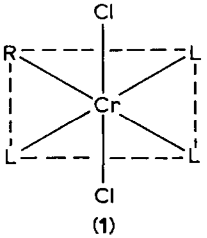
The reaction between C_3F_7I and $CrCl_2(CH_3CN)_2$ in the presence of pyridine allows the isolation of $C_3F_7CrCl_2py_3$ together with a $CrICl_2$-pyridine complex. Similar complexes can be prepared using 2,2′-bipyridyl, 2,2′,2″-terpyridyl and 1,10-phenanthroline. The latter complexes are resistant to hydrolysis whereas $C_3F_7CrCl_2py_2$ is rapidly hydrolysed to a pentafluoroalkyl aquo species.

Introduction

Perfluoroalkyl iodides such as CF_3I, C_2F_5I and C_3F_7I have been shown to react with $CrCl_2(CH_3CN)_2$ in acetonitrile to give perfluoroalkylchromium(III) intermediates [1] which can undergo subsequent reactions with acid–base chelate ligands such as salicylaldimines [1] or dithiocarbamates [2] to give R_FCr^{III}(chel)py derivatives.

The intermediate perfluoroalkylchromium(III) species could not be readily separated from the accompanying chromium halide complexes formed in the reaction but were suggested to be the dichloroperfluoroalkylchromium(III) species, $R_FCrCl_2(CH_3CN)_3$.

A small number of such organo-dichlorochromium(III) compounds are known of formulae $RCrCl_2L_3$ where R = alkyl [3], phenyl [4], *p*-tolyl [5], benzyl or chloroben-



(1)

zyl [6], and L is tetrahydrofuran or pyridine. The structure of *p*-tolyl-$CrCl_2(THF)_3$ [7] has the meridional form (**1**) with the R group having a tetrahydrofuran molecule in the *trans* position.

This paper reports the successful isolation of a representative dichloro-perfluoroalkyl chromium(III) complex as the tripyridinate, $C_3F_7CrCl_2py_3$ together with related organo-dihalo compounds containing the chelate ligands 2,2′-bipyridyl (bpy), 1,10-phenanthroline (phen) and 2,2′2″-terpyridyl (trpy).

Experimental

The preparation of $CrCl_2(CH_3CN)_2$ has been described [1]. Infrared spectra were recorded on Perkin–Elmer 180 or 521 spectrometers using Nujol mulls and visible spectra on a Unicam SP800A spectrometer. Magnetic measurements were made by the Gouy method.

Dichloroheptafluoropropyltripyridinechromium(III) ($C_3F_7CrCl_2py_3$)

Diacetonitrilechromium(II) chloride (1.0 g, 5 mmol) was suspended in an ethanol/10%-benzene mixture (80 ml) at 0°C under a nitrogen atmosphere and excess C_3F_7I (3.0 g, 10 mmol) added. On stirring for 1 h the solid material gradually dissolved and the solution turned green-brown. On addition of excess dry pyridine, a green precipitate of a mixed iodo-chloro-chromium pyridinate was formed. Further hexane was added dropwise to the mixture at 0°C until no more precipitate could be seen to form. The solution was then filtered and further hexane (usually at least 50 ml) added until the solution again became turbid. The mixture was kept at 0°C for several days for crystallization of the complex to be completed. Recrystallization from benzene/hexane gave brown crystals. (Yields varied between 20–30% of purified organometallic complex based on $CrCl_2(CH_3CN)_2$.) (Found: C, 40.8; H, 2.8; N, 7.9; F, 25.1. $C_{18}H_{15}Cl_2CrF_7N_3$ calcd.: C, 40.5; H, 3.0; N, 7.4; F, 24.8%.) IR: 1608m, 1490w, 1448s, 1319m, 1228s, 1204sh, 1183s, 1155s, 1073s, 1037m, 1015m, 996w, 982m, 802m, 765s, 720m, 699s cm^{-1}.

The iodo,chloro complex precipitated first in the reaction was found by microanalysis to have an I/Cl ratio of 1/2 and represented a yield of 45% calculated as $CrICl_2py_3$. The overall analysis of the dry but unrecrystallized complex indicated a pyridine content between $CrICl_2py_3$ and $CrICl_2py_4$. No further purification of the product was attempted. (Found: Cl, 12.8; I, 22.9; N, 9.0. $C_{15}H_{15}Cl_2CrIN_3$ calcd.: Cl, 14.5; I, 26.1, N, 8.6%. $C_{20}H_{20}Cl_2CrIN_4$ calcd.: Cl, 12.5; I, 22.4; N, 9.89%.) IR: 1595m, 1439s, 1214m, 1063m, 1041m, 1010w, 760m, 756sh, 692s, 690sh, 679m cm^{-1}.

A sample of $C_3F_7CrCl_2py_3$ kept in contact with moist air for several months became red-brown in colour. It was subsequently kept at 70°C in vacuo over P_2O_5 for 12 h. Analysis indicated loss of one pyridine and retention of 2 mol of water. (Found: C, 31.5; H, 2.7; N, 5.7. $C_{13}H_{10}Cl_2CrF_7(2H_2O)$ calcd.: C, 32.1; H, 2.9; N, 5.8%.) IR: identical to $C_3F_7CrCl_2py_3$ except for broad band in 3200–3000 cm^{-1} region, extra medium band at 1630 and a weak band at 890 cm^{-1}.

$C_3F_7CrCl_2(bpy)_2$

A mixture of acetonitrile (70 ml) and ethanol (12 ml) was deaerated by a stream of nitrogen and $CrCl_2(CH_3CN)_2$ (1.53 g, 7.5 mmol) added to form a suspension. The mixture was cooled to 0°C maintaining a constant atmosphere of nitrogen and

C_3F_7I (1 ml) added. As the mixture was stirred and allowed to reach room temperature, its colour slowly changed to brown-green. The 2,2'-bipyridyl (2.34 g, 15 mmol) was then added to the solution which was stirred for a further 2 h, during which time a yellow-brown solid precipitated. This was filtered and the filtrate allowed to slowly evaporate to yield the complex as an orange solid. Recrystallization from 5% water/ethanol gave the desired compound as orange crystals of the hydrated complex. (Found: C, 42.3; H, 3.3; N, 8.6. $C_{23}H_{16}Cl_2CrF_7N_2(2.5H_2O)$ calcd.: C, 42.5; H, 3.3, N, 8.5%.) IR: 3330w br, 1643m br, 1614s, 1604s, 1543m, 1450vs, 1327s, 1249m, 1222s, 1192s, 1182sh, 1169m, 1157s, 1089s, 1048s, 1031s, 1021m, 990s, 808m, 776s, 737s, 725s cm^{-1}. The initial iodo,chloro complex analysed quite well for $CrICl_2(bpy)_2$. (Found: C, 42.2; H, 2.9; Cl, 12.8; I, 22.9. $C_{20}H_{16}Cl_2IN_4Cr$ calcd.: C, 42.7; H, 2.9; Cl, 12.6; I, 22.6%.)

$[C_3F_7CrCl(bpy)_2][PF_6]$

$C_3F_7CrCl_2(bpy)_2$ was dissolved in 50% water/ethanol and aqueous KPF_6 added. An immediate orange precipitate formed which was filtered and washed several times with water and dried over P_2O_5. (Found: C, 38.3; H, 2.5. $C_{23}H_{16}ClCrF_{13}N_4$ calcd.: C, 38.7; H, 2.2%.) IR: 1610m, 1602s, 1500m, 1473s, 1448vs, 1323s, 1244m, 1210s, 1186s, 1168s, 1112m, 1084s, 1036m sh, 1030s, 1020m sh, 975m, 963m, 904m, 836vsbr, 804m, 770s, 733s, 720m cm^{-1}.

$C_3F_7CrCl_2bpy$

$C_3F_7CrCl_2py_3$ (0.3 g, 0.6 mmol) was dissolved in benzene (50 ml), 2,2'-bipyridyl (0.19 g, 1.2 mmol) was added and the solution refluxed for 1 h. The resulting brown crystalline precipitate was filtered and washed with benzene (yield 90%). (Found: C, 34.2; H, 2.8; N, 6.5. $C_{13}H_8Cl_2CrF_7N_2$ calcd.: C, 34.8; H, 1.79; N, 6.25%.) IR: 1605m, 1446s, 1326m, 1215s, 1188s, 1178s, 1167sh, 1148s, 1081m, 1048m, 1002m, 803w, 774s, 739w, 722m, 706s cm^{-1}.

$C_3F_7CrCl_2(phen)_2$

Similar conditions were used as for the preparation of the bis-bpy complex. The orange product was recrystallized from acetone (undried). The crystals contained both acetone and water of crystallization. (Found: C, 49.8; H, 3.3; N, 7.6. $C_{30}H_{24}Cl_2CrF_7N_4O_2$ calcd.: C, 49.5; H, 3.3; N, 7.7%). IR: 1709s, 1631w, 1603w, 1580w, 1517m, 1424vs, 1365m, 1324m, 1226s, 1214s, 1188s, 1153m, 1085m, 1050m, 876w, 865m, 848m, 802w, 795w, 786w, 721vs cm^{-1}.

The mixed halide complex was isolated as a monohydrate. (Found: C, 44.3; H, 2.9; Cl, 11.3; I, 20.2. $C_{24}H_{16}Cl_2CrIN_4(H_2O)$ calcd.: C, 44.6; H, 3.1; Cl, 11.0; I, 19.6%.)

$C_3F_7CrCl_2terpy$

Reaction conditions were as for the bpy synthesis with the reaction mixture stirred for 3 h. The solvent was then removed and the residue extracted with acetone. The insoluble green iodo,chloro complex was filtered and red crystals of the perfluoroalkyl derivative obtained from the filtrate on evaporation and cooling. (Found: C, 41.2; H, 2.4; F, 25.1; N, 7.9. $C_{18}H_{11}Cl_2CrF_7N_3$ calcd.: C, 41.2; H, 2.1; F, 25.3; N, 8.0%.) IR: 1602m, 1449vs, 1330s, 1236m, 1206m, 1184s, 1168s, 1150m, 1079m, 1034m, 1023m, 961m, 801s, 775s, 785w, 708s cm^{-1}.

Results and discussion

The products formed when R_FI react with $CrCl_2(CH_3CN)_2$ in CH_3CN solution are quite soluble in that medium and make separation of the products difficult and time consuming. $CrCl_2py_2$ does not react with R_FI so that such an alternative route to a pyridine substituted complex is not available [3]. However, the addition of pyridine to the reaction mixture of C_3F_7I with $CrCl_2(CH_3CN)_2$ in acetonitrile with benzene added to help reduce solubility has allowed the reaction products $ICrCl_2(py)_n$ and $C_3F_7CrCl_2py_3$ to be separated. Similar reactions have led to the isolation of the related compounds $C_3F_7CrCl_2(bpy)_2$, $C_3F_7CrCl_2(phen)_2$ and $C_3F_7CrCl_2trpy$ together with the accompanying iodo,dichloro species $CrICl_2(chel)_2$ (chel = bpy, phen) and $CrICl_2trpy$. The methods of isolation did not enable quantitative yields of compounds to be measured, but the halide complexes were recovered in > 40% yields based on $CrCl_2(CH_3CN)_2$ used whereas the various organometallics were isolated in lower yields.

The halide complex obtained from the reaction involving pyridine had a I/Cl ratio of 1/2 but its analytical composition indicated a pyridine content between 3 and 4 mol, suggesting a mixture of $CrICl_2py_3$ and $CrICl_2py_4$. The bpy and phen complexes both perfluoroalkyl and iodide-containing behaved as 1/1 electrolytes in water, viz. $[C_3F_7CrCl(bpy)_2]Cl$.

These preparative studies support the view [1,2] that R_FI can react like an alkyl halide with an appropriate chromium(II) compound [8] i.e. in a two stage process involving an initial halogen abstraction followed by release of a free radical which reacts with a further mol of chromium(II).

$$R_FI + Cr^{II} \rightarrow Cr^{III} - I + R_F\cdot$$

$$R_F\cdot + Cr^{II} \rightarrow Cr^{III} - R_F$$

The likelihood of alternative reactions for the R_F radicals e.g. hydrogen abstraction to form R_FH or coupling to give $R_F–R_F$, is in line with the yields of the organometallics being notably lower than the possible maximum yields of 50% based on chromium(II).

Since the polarity of the C–I bond in R_FI compounds may be considered to be opposite of that in an alkyl halide there remains some ambiguity as to whether the initial attack of chromium(II) is on the α-C or the iodine atom. The evidence of the relative yields of organometallic and iodochromium derivatives appears to support a mechanism requiring an initial halogen attack.

The magnetic moments of several of the complexes at 300 K are given in Table 1, together with their visible absorption bands. The moment of $C_3F_7CrCl_2py_3$ is notably greater than the "spin-only" value for a d^3 ion such as chromium(III) but such high values have been reported for other perfluoroalkylchromium(III) compounds [1,2] as well as some other organometallics [9]. It is, however, unexpected that the pyridine and terpyridyl complexes have rather different room temperature moments since they are considered to have comparable structures (see later discussion) and the electronic fields about the chromium ions might have been expected to be comparable.

The electronic spectra of the complexes (Table 1) show several absorption bands in the region 17000–25000 cm^{-1} of relatively low intensity which are considered due

TABLE 1

ELECTRONIC SPECTRA (cm^{-1}) AND MAGNETIC MOMENTS (BM) (ϵ values given in brackets in units M^{-1} cm^{-1})

Complex	Solvent	Absorption bands			μ_{eff} (300 K)
$C_3F_7CrCl_2py_3$	benzene	17300	21900	24400	3.96
		(64)	(110)	(183)	
$C_3F_7CrCl_2trpy$	acetone	18700	22400	24100	3.83
		(89)	(89)	(146)	
$[C_3F_7CrCl(bpy)_2]PF_6$	THF		22300	23900	3.86
			(135)	(220)	
$C_3F_7CrCl_2bpy$	insol.				3.61
$CrCl_3py_3$ [14]	reflectance	16800	22300		
$CH_3CrCl_2(THF)_3$ [3]	THF	14400		23000	3.96
		(20)		(20)	
	py	16300		25200	

to *d–d* transitions. Since the complexes will all depart considerably from regular octahedral symmetry, it is unlikely that the bands represent the "pure" ${}^4A \rightarrow {}^4T$ transitions expected for d^3 compounds of O_h symmetry. Indeed, the bands may well result from the splitting of one or more of these primary transitions. Alkyldihalochromium derivatives are reported to show only two such bands in tetrahydrofuran solution in the range 14300–23000 cm^{-1} with a shift to higher frequencies in pyridine [3] where no doubt the tris-pyridinate is formed.

The infrared spectra of the complexes all show strong absorptions in the region 1400–1000 cm^{-1} characteristic of C–F stretching frequencies. Five such bands are generally observed for each complex in the regions of 1325, 1220, 1200, 1160 and 1090 cm^{-1}.

None of the perfluoroalkylchromium(III) derivatives react with oxygen in the solid state or in solution in organic solvents. This contrasts with the oxygen sensitivity reported for many other alkyl- and aryl-chromium(III) organometallics [9].

The various compounds are reasonably stable thermally, e.g. $C_3F_7CrCl_2py_3$ does not show decomposition up to 100°C but undergoes breakdown at 115°C while $C_3F_7CrCl_2(phen)_2$ does not decompose below 216°C. The alkylchromium derivatives, $RCrCl_2(THF)_3$ ($R = CH_3$, C_2H_5, C_3H_7) all show decomposition at or close to room temperature [3] with rates increasing with bulk of alkyl groups. However, Nishimura et al. have demonstrated [3] that the attached ligands can greatly modify the thermal stability of such organometallics, $CH_3CrCl_2py_3$ being thermally stable up to 160°C.

There is a notable difference in reaction with water, however, between the perfluoroalkylpyridine derivative and those containing chelating N-heterocyclic ligands. The former complex dissolves readily in water with rapid hydrolysis to very stable perfluoroalkylchromium(III) aquo species. The absorption spectrum of the pink solution (λ_{max} 1.97×10^4, 2.58×10^4 cm^{-1}) is similar to that reported for the brownish-red ion $[CF_3Cr(H_2O)_5]^{2+}$ ion (λ_{max} 2.00×10^4, 2.6×10^4 cm^{-1}) [10]. However, $[CF_3CrF(H_2O)_4]^+$ is also described as "pink" [10] with estimated λ_{max} 1.9×10^4, 2.58×10^4 cm^{-1} and the hydrolysis product of $C_3F_7CrCl_2py_3$ may have contributions from species $[C_3F_7CrX(H_2O)_4]^+$ with X = Cl, I or py. No attempt was made to separate such species. Solid $C_3F_7CrCl_2py_3$ in fact absorbs water from the atmosphere over several months and pyridine is gradually replaced by water molecules.

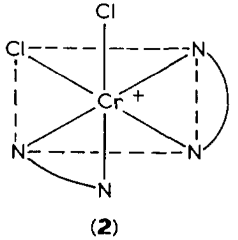
The $C_3F_7Cr^{III}$ compounds containing chelate ligands, bpy, phen and trpy, however, do not react readily with water. The bpy and phen complexes $R_FCrCl_2(chel)_2$ dissolve in water and the complex cations $[R_FCrCl(chel)_2]^+$ can be precipitated by $[PF_6]^-$ anions. The resistance to hydrolysis of other chromium(III) organometallics containing bipyridyl viz. $[R_2Cr(bpy)_2]I$ where R = aryl has been noted previously [11,12,13], whereas other alkyl- and aryl-chromium(III) compounds containing coordinated halide and tetrahydrofuran react very rapidly with water. $C_6H_5CH_2CrCl_2py_3$ has been shown [6] to generate toluene and chromium(III) aquo ions in water via an initial formation of the pentaquo ion $[C_6H_5CH_2Cr(H_2O)_5]^{2+}$.

The lability of the ligands other than C_3F_7 in $C_3F_7CrCl_2py_3$ is shown by their ready replacement with the anions of ligands such as salicylaldehyde or *N,N'*-ethylenebis(salicylaldimine) when the complex reacts with such chelating ligands in the presence of triethylamine forming $C_3F_7Cr(sal)_2py$ and $C_3F_7Cr(salen)py$.

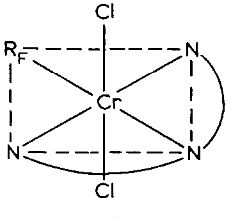
Bipyridyl also can displace ligands directly from $C_3F_7CrCl_2py_3$ to form the monosubstituted $C_3F_7CrCl_2bpy$ rather than the bis compound $C_3F_7CrCl_2(bpy)_2$ isolated from reaction in acetonitrile. The former complex is sparingly soluble and shows a rather low magnetic moment (Table 1) which suggests it may be a chloro-bridged dimer with magnetic interaction between chromium(III) centres leading to a reduced magnetic moment per chromium ion being observed. $CrCl_3bpy$ is considered to be of this type [14].

Structures

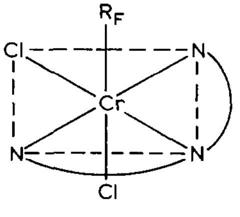
There seems little doubt that the $[C_3F_7CrCl(chel)_2]X$ complexes (chel = bpy, phen; X = Cl, PF_6) contain *cis* type complex cations (**2**) since the interactions between hydrogens *ortho* to the nitrogens on bipyridyl or phenanthroline would prevent two such ligands occupying coplanar *trans* positions with respect to each other. Such arrangements are well authenticated for other organometallic chromium(III) derivatives such as $[(CH_3OC_6H_4)_2 \cdot Cr(bpy)_2]I$ [12] and $[(C_6H_5)_2Cr(bpy)_2]I$ [13]. The structures of $C_3F_7CrCl_2py_3$ and $C_3F_7CrCl_2trpy$ cannot be decided unambiguously in the absence of complete structural analyses but there are a number of indications that both complexes as isolated will have the *mer*-type configuration shown in **1** for a monodentate ligand and for a tridentate ligand in **3** with the R_F group *trans* to a single pyridine or the central ring of trpy.



(**2**)



(**3**)



(**4**)

In the terpyridyl complex, the tridentate ligand, because of its conjugated nature, is constrained to have all three pyridyl components coordinating in the meridional arrangement [15] so that the geometric isomers **3** and **4** are possible. One may distinguish between these two structures on the grounds that the *trans* labilizing influence of the C_3F_7 group should make the Cl^- *trans* to it in structure **4** relatively easily displaced by water whereas in **3** the *trans* influence of the C_3F_7 group on the central pyridyl residue would not be likely to cause dissociation of the entire trichelate group although the Cr–N bond concerned may lengthen. Since $C_3F_7CrCl_2$trpy does not readily react with water structure **3** is favoured. The absorption spectra for $C_3F_7CrCl_2py_3$ and $C_3F_7CrCl_2$trpy are also similar suggesting comparable geometries for both complexes.

Finally, it may be noted that $CrCl_3py_3$ has been shown to have a *mer* arrangement [16] and no other isomeric form has been detected.

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