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(FLUOROALKYL)COBALT(III) SCHIFF-BASE COMPLEXES

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SUMMARY

The (fluoroalkyl)cobalt(III) Schiff-base complexes $R_fCoChelL$ ($R_f = CF_3$, C_2F_5, C_3F_7; Chel = Salen, Acacen, Tfacacen, Bzacacen*; L = —, H_2O, pyridine) have been synthesised by oxidative addition of R_fI to tetrahydrofuran solutions of sodium reduced cobalt Schiff-base chelates. The ^1H NMR spectra of the complexes show that less electron density is transmitted via the cobalt atom to the planar chelate groups from the R_f group than from the analogous R group. ^{19}F NMR spectra show that the α-CF_2 resonances do not undergo the pronounced low-field shifts experienced by low-valent metal fluoroalkyl compounds.

INTRODUCTION

Considerable interest has been shown recently in the simple chemical models of Vitamin B_{12} of the type RCoChelL where R = alkyl, aryl, cyano, etc.; Chel = Salen[1-3], Acacen[4,5], Dmg_2[6] ("cobaloxime"); L = H_2O, pyridine, Ph_3P, etc. We report the synthesis and NMR spectral properties of the analogous fluoroalkyl Schiff-base compounds $R_fCoChel$ where $R_f = CF_3$, C_2F_5, C_3F_7. Despite the numerous reports[7] of low-valent cobalt carbonyl fluoroalkyl compounds, there is little previous data on higher-valent cobalt fluorocarbon compounds. A brief mention was made of CF_3CoDmg_2[8] and a bridged fluoroalkyl derivative[9] $\{[(CN)_5CoCF_2]_2\}^{6-}$ has been reported.

RESULTS AND DISCUSSION

Synthesis and properties

(Fluoroalkyl)cobalt(III) derivatives have been prepared in good yields by the addition of perfluoroalkyl iodides to tetrahydrofuran solutions or suspensions of sodium salts of cobalt(I)–Schiff-base ligands.

The reaction occurs rapidly at −78° and the red-brown complexes can be precipitated by addition of the reaction mixture to water. It has been observed that [CoChel]I is also formed in the reaction in amounts which vary depending on the ligand being used from a negligible amount in the CoAcacen reaction to about 25% of the total Co for CoSalen.

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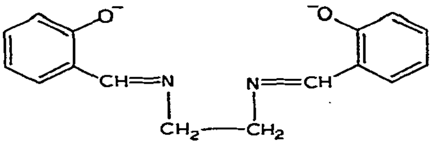
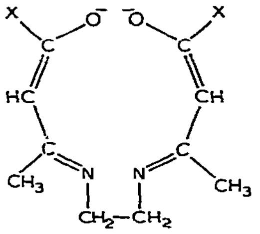
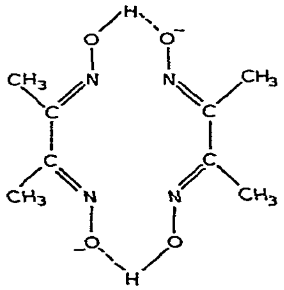
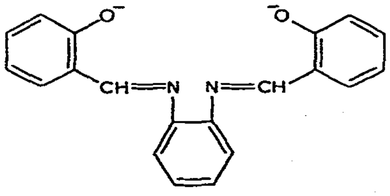
* See Table 1 for abbreviations of ligands.

C_3F_7CoSalen has also been prepared by the reaction of CH_3CoSalen with C_3F_7I in ethylene glycol dimethyl ether at reflux temperature. The less soluble C_3F_7CoSalen precipitates and is obtained in almost quantitative yield. The exchange occurs slowly at room temperature and can be followed by measuring the ^{19}F resonance of the complex as it forms.

The use of Schrauzer's method[10] (BH_4^- in alkaline solution) as an alternative route to CoSalen fluoroalkyl derivatives also gave low yields of the required compounds.

TABLE 1

ABBREVIATIONS USED FOR LIGANDS

Salen	
Acacen, $X=CH_3$ Tfacacen, $X=CF_3$ Bzacacen, $X=C_6H_5$	
Dmg_2	
Salphen	

The fluoroalkyl derivatives in general were isolated as hexacoordinate aquo derivatives but several pentacoordinate complexes were also obtained directly from aqueous systems. This variation in ease of binding water has been observed for alkyl derivatives of CoSalen and CoAcacen[1,4] and may be attributed to the pronounced donor effect of the alkyl groups[11] attached to cobalt on which is superimposed a subtle interplay of effects due to specific organo groups and ligands. All the aquated compounds can be dehydrated readily by heating at 80° under vacuum. The sixth coordination position can be readily filled by pyridine and other nitrogenous bases by recrystallizing either anhydrous or aquo derivatives from the pure ligand.

As is often found for other organometallic fluorocarbon derivatives[7] the cobalt fluoroalkyl compounds are more "stable" than their alkyl counterparts. Thus the complexes are stable towards ultaviolet radiation in solution over periods of at least seven days and sulphur dioxide will not react with the cobalt–carbon bond in contrast to the insertion obtained for Co–alkyl derivatives[12].

NMR spectra

The ^1H NMR spectra of the R_fCoChelL compounds are given in Table 2 together with those of the corresponding RCoChelL for comparison. The solvent $(CD_3)_2SO$ was used, where possible, to overcome solubility problems and to avoid solvent shifts. In the β-ketoimine complexes, for a particular R_f group, variation of the side-chain substituent X causes a downfield shift of all planar ligand proton resonances in the order $C_6H_5 > CF_3 > CH_3$. A similar sequence has been observed[13] in

TABLE 2

^1H NMR SPECTRA OF (FLUOROALKYL)- AND ALKYLCOBALT(III) SCHIFF-BASE CHELATES
In $(CD_3)_2SO$ relative to TMS (δ 0 ppm).

Compound	Planar ligand			
	=CH	CH=N	C_2H_4	CH_3
$CF_3CoAcacen \cdot H_2O$	5.17		3.67	2.22 2.32
$CH_3CoAcacen^a$	5.12		3.40	2.03 2.09
$CF_3CoSalen \cdot H_2O$		8.42	4.09	
$CH_3CoSalen \cdot H_2O$		8.02	3.57	
$C_2F_5CoAcacen$	5.19		3.75	2.20 2.31
$C_2H_5CoAcacen^a$	5.08		3.40	2.01 2.07
$C_2F_5CoTfacacen \cdot H_2O$	5.82		3.91	2.56
$C_2H_5CoTfacacen \cdot H_2O$	5.69		$\sim$3.6	2.39
$C_2F_5CoBzacacen \cdot H_2O$	6.09		3.96	2.58
$C_2F_5CoSalen$		8.45	4.20	
$C_2H_5CoSalen$		8.0	3.55	
$C_3F_7CoAcacen \cdot H_2O$	5.32		3.91	2.33 2.45
$C_3F_7CoSalen$		8.45	4.24	

[a] In $CDCl_3$.

the planar divalent metal complexes and has been attributed to resonance effects in the chelate rings. Replacement of the R group by the related fluoroalkyl group R_f likewise causes a downfield shift in the ligand proton positions. This is in accord with a ground state *cis* effect[14] whereby the cobalt atom transmits less electron density from the more electronegative R_f group with a concomitant decrease in shielding. Within the R_fCoSalen and R_fCoAcacen series there is a less well defined trend of the shifts to low field in order $C_3F_7 > C_2F_5 > CF_3$.

The ^{19}F NMR spectra are given in Table 3. The fluorine resonances on the carbon atoms bonded directly to cobalt are broadened to the extent of ca. 10 Hz when $R_f = C_2F_5$ and ca. 30–50 Hz when $R_f = C_3F_7$. Wilkinson and Mays[9] observed a similar broadening of 60 Hz in the compounds $\{[(CN)_5CoCF_2]_2\}^{6-}$ and $[(CN)_5CoC_2F_4H]^{3-}$ and attributed it to incomplete averaging of spin coupling with the ^{59}Co nucleus ($I = \frac{7}{2}$). The shifts of the α-CF_2 resonances are of particular interest. The δ values are ca. 90–95 ppm compared with 80–85 ppm in the pentacyano compounds. These values are intermediate between those observed in non-transition-metal compounds of the types R_fSnR_3 and $(R_f)_2PCl$ ($\delta \sim 120$ ppm) and transition-metal derivatives with π-type ligands of the types $R_fMn(CO)_5$, $(R_f)_2Fe(CO)_4$, $R_fCoC_5H_5(CO)I$ ($\delta = 55$–75 ppm). This large shift to low-field in the latter type of transition-metal compound is also observed in the fluoroalkyl halides and is thought[15] to be due to increased paramagnetic shielding arising from the presence of low lying excited states in the M–C_α or halogen–C_α bonds. Assuming this interpretation to be correct we can therefore see that the intermediate shifts in the present chelates and the pentacyano derivatives arise from electronic effects of these ligand groupings being transmitted via the cobalt atom

In the trifluoromethyl compounds the CF_3 resonance does experience a large shift to low field, $\delta \sim 25$ ppm, but again this is less than in $CF_3Mn(CO)_5$, $CF_3Co(CO)_4$ or $CF_3Fe(CO)_4I$ where $\delta = -9$ to $+14.7$ ppm.

A possible reaction mechanism

The successful reaction of perfluoroalkyl iodides with d^8 Co^I complexes to

TABLE 3

^{19}F NMR SPECTRA OF (FLUOROALKYL)COBALT(III) SCHIFF-BASE CHELATES

In $(CD_3)_2SO$ relative to $CFCl_3$ (δ 0 ppm); δ values upfield from $CFCl_3$; br=broad, t=triplet.

Compound	Fluoroalkyl group			
	α-CF_3	α-CF_2	β-CF_2	γ-CF_3
$CF_3CoAcacen \cdot H_2O$	25.7			
$CF_3CoSalen \cdot H_2O$	25.3 br			
$C_2F_5CoAcacen$		96.7 br		79.7
$C_2F_5CoSalen$		94.1 br		78.8
$C_2F_5CoTfacacen$		95.3 br		80.0[a]
$C_2F_5CoBzacacen \cdot H_2O$		96.5 br		79.7
$C_3F_7CoAcacen \cdot H_2O$		93.5 br	121.8	78.0 t[b]
$C_3F_7CoSalen$		91.0 br	121.0	78.4 t[b]
C_3F_7I		68.4	119.1	79.4

[a] Ligand CF_3 712 ppm. [b] $J_{\alpha\gamma}$ 12 Hz.

TABLE 4

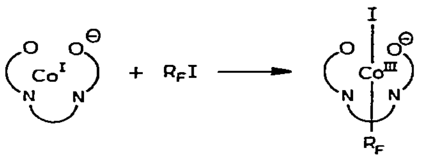
ANALYSES

Py = pyridine; Pic = picoline.

Compound	Formula	Found (calcd.) (%)			
		C	H	N	F
$CF_3CoAcacen \cdot H_2O$	$C_{13}H_{20}CoF_3N_2O_3$	42.0 (42.4)	5.5 (5.5)	7.1 (7.6)	15.1 (15.5)
$CF_3CoSalen \cdot H_2O$	$C_{17}H_{16}CoF_3N_2O_3$	49.3 (49.5)	4.0 (3.9)	6.7 (6.8)	12.7 (13.8)
$CF_3CoSalen \cdot Py$	$C_{22}H_{19}CoF_3N_3O_2$	56.6 (54.7)	6.4 (6.1)	8.7 (8.7)	10.4 (11.7)
$C_2F_5CoAcacen$	$C_{14}H_{18}CoF_5N_2O_2$	42.4 (42.0)	4.5 (4.5)	6.9 (7.0)	23.3 (23.7)
$C_2F_5CoSalen$	$C_{18}H_{14}CoF_5N_2O_2$	49.9 (48.7)	4.3 (3.2)	6.9 (6.3)	21.4 (21.4)
$C_2F_5CoSalen \cdot Py$	$C_{23}H_{19}CoF_5N_3O_2$	53.8 (53.5)	3.7 (3.7)	8.3 (8.1)	18.0 (18.4)
$C_2F_5CoTfacacen \cdot H_2O$	$C_{14}H_{14}CoF_{11}N_2O_3$	32.0 (31.9)	2.7 (2.7)	5.3 (5.3)	39.6 (39.7)
$C_2F_5CoBzacacen \cdot H_2O$	$C_{24}H_{24}CoF_5N_2O_3$	53.6 (53.1)	4.6 (4.5)	5.0 (5.1)	16.9 (17.5)
$C_3F_7CoAcacen \cdot H_2O$	$C_{15}H_{20}CoF_7N_2O_3$	39.7 (38.5)	4.3 (4.3)	6.8 (6.0)	27.7 (28.4)
$C_3F_7CoSalen$	$C_{19}H_{14}CoF_7N_2O_2$	45.9 (46.1)	2.8 (2.8)	5.6 (5.7)	28.4 (26.9)
$C_3F_7CoSalen \cdot 1\frac{1}{2} Py$	$C_{21.5}H_{16.5}CoF_7N_{2.5}O_2$	51.1 (51.9)	3.6 (3.5)	8.3 (8.0)	23.6 (21.7)
$C_3F_7CoSalen \cdot \alpha\text{-}Pic$	$C_{25}H_{21}CoF_7N_3O_2$	50.9 (51.7)	3.6 (3.6)	7.5 (7.2)	23.4 (22.9)
$C_3F_7CoSalen \cdot \gamma\text{-}Pic$	$C_{25}H_{21}CoF_7N_3O_2$	53.6 (51.7)	4.1 (3.7)	8.6 (7.2)	20.5 (22.9)

give (perfluoroalkyl)cobalt derivatives is in contrast to the reaction observed with the d^8 system, $[Mn(CO)_5]^-$, where $IMn(CO)_5$ and fluorocarbons are formed[16,17]. Alkyl halides however react to give $RMn(CO)_5$[18].

The polarity of the C–I bond is believed to control the mode of reaction with $[Mn(CO)_5]^-$, it being $C^{\delta-}$–$I^{\delta+}$ in R_f–I and $C^{\delta+}$–$I^{\delta-}$ for alkyl iodides. Schrauzer[19] has presented evidence that Co^I compound react with alkyl halides by an S_N2 reaction and therefore perfluoroalkyl iodides would be expected to follow a polarity-controlled reaction path and give predominantly iodo derivatives in reactions with Co^I complexes. Although small yields of [CoChel]I have been observed in a few reactions in the present work the major yield is of R_f–Co^{III}Chel. This suggests that the transition state may initially form by nucleophilic attack of a Co^I complex on the $I^{\delta+}$ of R_f–I followed by either release of R_f^- and formation of [CoChel]I, NaF and fluorocarbons or addition of R_f to the Co thus completing an oxidative addition reaction[20,21]. These types of reactions involving RX or R_f–I are already well known for other square planar d^8 systems of Co^I [22], Ir^I [23] and Rh^I [22]. The hexacoordinate intermediate could then lose I^- preferentially because of the pronounced labilizing effect on the 6th coordination position[11] due to the organic group in the 5th position.



This latter aspect of the hypothesis assumes that *trans* addition would be most likely to aid removal of I^- and therefore the mechanism might be expected to depend on the ease with which the ligands already attached to Co could distort in order to accommodate such an addition. The yield of [CoChel]I may thus be greater as the second step of the proposed mechanism becomes more difficult. In this regard an examination of models suggests that the increasing degree of "inflexibility" to bonding or twisting for three ligands examined is Acacen < Salen < Salphen, and the amount of [CoChel]I recovered does increase from CoAcacen to CoSalphen. In fact, in the latter case only [CoSalphen]I was detected, no R_fCoSalphen being isolated. It could be argued similarly that when complete oxidative addition is blocked as in the reaction of R_fI with the pentacoordinate $[Mn(CO)_5]^-$ then R_f^- elimination would be the favoured reaction and an iodo derivative would be the sole product.

The concept of a free-radical-controlled mechanism as supported by the work of Halpern[24] on Co^{II} compounds reacting with alkyl halides cannot be precluded for the perfluoroalkyl halide reactions but it seems less applicable to Co^I systems than the oxidative addition concept.

EXPERIMENTAL

NMR spectra

These were recorded on a Varian 56.4/60 A spectrometer, with $(D_3C)_2SO$ as solvent. ^1H shifts were downfield relative to TMS and ^{19}F upfield relative to $CFCl_3$.

Air sensitivity

All the cobalt(II) complexes and the Na-reduced species are air sensitive and all work was carried out under nitrogen.

Cobalt(II) Schiff-base complexes

CoSalen[25] and CoAcacen[26] were prepared by literature methods. CoBzacacen[27] was prepared by a modification of earlier methods. An ethanol solution of the ligand (1 mole) was added to $CoCl_2 \cdot 6\,H_2O$ (1 mole) in water. Additional ethylenediamine (2 moles) was added and the resulting orange solution refluxed. Orange needles separated on cooling and were recrystallized from benzene/petroleum ether. (Found: C, 65.1; H, 5.42; N, 6.83. $C_{22}H_{22}CoN_2O_2$ calcd.: C, 65.2; H, 5.47; N, 6.91%.)

CoTfacacen. This complex has not been previously reported and proved difficult to prepare in high yields. Two methods were devised:

1. Trifluoroacetylacetone (0.02 mole, 3.1 g) was cooled to 0° and ethylenediamine (0.01 mole, 0.6 g) added slowly with stirring. When reaction had ceased the solid product was melted and kept at its melting point (157°) until all water was evaporated. The ligand was heated to reflux in benzene with anhydrous $CoAcac_2$ (0.01 *M*, 2.6 g) for 30 min. The mixture was then evaporated to dryness under vacuum,

redissolved in benzene and the process repeated. After a third treatment the residue was recrystallized from benzene giving the complex (50% yield). (Found: C, 37.1; H, 2.9; F, 28.9; N, 7.2. $C_{12}H_{12}CoF_6N_2O_2$ calcd.: C, 37.0; H, 3.1; F, 29.3; N, 7.2%.)

2. Cobalt acetate tetrahydrate was digested with ethanol until the initial red solution had deposited a pale pink amorphous powder. This solid was filtered, washed with ethanol and resuspended in ethanol with the ligand. The mixture was heated until the solid had dissolved, evaporated to half volume and de-aerated water added. The precipitate was filtered and recrystallized from benzene (yield <20%).

(Fluoroalkyl)cobalt(III) compounds

(*a*). A mixture of a cobalt(II) complex and excess sodium sand or sodium amalgam was stirred in tetrahydrofuran until reduction was complete. The reduced solutions were deep green in colour except for that derived from CoBzacacen which was an intense red.

The solutions were freed from excess reductant by either filtration or decantation, cooled to −78° and excess fluoroalkyl iodide added. A colour change to brown-green occurred. Water was added to the solution and the mixture concentrated to yield crystals of the (fluoroalkyl)cobalt complex. The products were recrystallized from benzene/petroleum ether or methanol/water. Further purification by chromatography on neutral alumina columns was required in some cases.

In a number of cases the filtrate was coloured red-orange and further evaporation yielded samples of [CoChel]I together with NaI. When CoSalophen was reduced with Na/Hg the deep green reduced product reacted with C_3F_7I or C_2F_5I to give solely [CoSalphen]I and fluorocarbons. No (fluoroalkyl)cobalt complexes could be isolated.

(*b*). CH_3CoSalen (5 mmoles) dissolved in ethylene glycol dimethylether (10 ml) was refluxed with C_3F_7I (25 mmoles) for 2 h. On cooling C_3F_7CoSalen crystallized (yield >95%).

(*c*). Salen (0.01 mole, 2.68 g) and $CoCl_2 \cdot 6\,H_2O$ (0.01 mole, 2.4 g) were dissolved in methanol (50 ml) and sodium hydroxide (0.02 mole, 0.8 g) dissolved in the minimum amount of water was added. A brown precipitate formed and further sodium hydroxide (1.3 g) was added followed by sodium borohydride (0.1 g) in methanol. Several drops of a solution of $PdCl_2$ in dilute HCl were added and reduction to a deep green solution occurred. Excess heptafluoropropyl iodide was added and an immediate colour change to orange occurred. Water was added to precipitate the (perfluoroalkyl)cobalt complex which was subsequently recrystallized from methanol/water (yield 10%).

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