

Bis(2,2,2-trifluoroethoxy)copper(II) & (Chloro)(2,2,2-trifluoroethoxy)copper(II): Synthesis & Coordination Chemistry

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Bis(2,2,2-trifluoroethoxy)copper(II) and (chloro)(2,2,2-trifluoroethoxy)copper(II) have been synthesized. They form adducts of the types $\text{Cu}(\text{OCH}_2\text{CF}_3)_2 \cdot \text{L}$ and $\text{CuCl}(\text{OCH}_2\text{CF}_3) \cdot \text{L}$ with various O- and N-donors. The parent complexes as well as the adducts have been characterized on the basis of various physico-chemical studies. The magnetic moment values of the complexes indicate the presence of antiferromagnetic interaction. The electronic spectra of these complexes are in favour of a distorted octahedral geometry. Infrared spectra are consistent with an alkoxy-bridged polymeric structure.

Metal alkoxides have been widely synthesized and studied^{1,2}; the corresponding fluoroalkoxides are, however, relatively unknown, and of these the fluoroalkoxides of copper(II) have not been reported so far. An important difference between the alkoxides and halo-alkoxides is that the former usually do not further react with ligands^{1,3} but the latter may do so as found in the cases of tris(2,2,2-trichloroethoxy)iron(III)⁴, tris(2,2,2-trifluoroethoxy)vanadium(III) and (chloro)bis(2,2,2-trichloroethoxy)vanadium(III)^{5,6}. We report here the preparation, characterization and reactivity with lewis bases of two fluoroalkoxides, i.e., $\text{Cu}(\text{OCH}_2\text{CF}_3)_2$ and $\text{CuCl}(\text{OCH}_2\text{CF}_3)$.

The complexes were prepared and handled using a vacuum line set up having an arrangement for occasional flushing with dry oxygen-free nitrogen.

Preparation of bis(2,2,2-trifluoroethoxy)copper(II)

To a known amount of $\text{Cu}(\text{OCH}_3)_2$ (ref. 2) in benzene was added 2,2,2-trifluoroethanol slightly in excess that that calculated for 1:2 molar ratio and the contents were stirred for ~4 hr. The reaction mixture was refluxed azeotropically using a Dean and Stark apparatus for 30 days till methanol ceased to come out. Excess of 2,2,2-trifluoroethanol and benzene were pumped off and the compound was dried *in vacuo* to get a blue solid.

Preparation of (chloro)(2,2,2-trifluoroethoxy)copper(II)

To the chilled bis (2,2,2-trifluoroethoxy)-

copper(II) in dry benzene was added freshly distilled acetyl chloride in 1:1 molar ratio and the contents were stirred for ~6 hr. The reaction mixture was refluxed for ~8 hr when a green product separated; it was washed repeatedly with CCl_4 and dried under high vacuum to obtain a bluish green solid.

Preparation of the adducts

The adducts were prepared by dissolving the fluoroalkoxides in respective ligands and inducing precipitation of the products by the addition of dry ether. The solid adducts were filtered washed with CCl_4 and dried *in vacuo*.

The adducts with solid ligands (Py-O, α -pic-O and α, α' -bipyridyl) were prepared by using their solutions in chloroform.

Copper and chlorine were estimated gravimetrically⁷ and carbon and hydrogen were estimated by microanalysis. Infrared spectra were recorded in nujol and hexachlorobutadine mulls on a Perkin Elmer 621 spectrophotometer. The diffuse reflectance spectra were recorded on Unicam Sp-700 and Hitachi model-330 spectrophotometers. Magnetic susceptibilities were determined by the Gouy method.

Bis(2,2,2-trifluoroethoxy)copper(II), $\text{Cu}(\text{OCH}_2\text{CF}_3)_2$, and (chloro)(2,2,2-trifluoroethoxy)copper(II), $\text{CuCl}(\text{OCH}_2\text{CF}_3)$, are hygroscopic solids which do not melt but decompose on heating and are insoluble in common organic solvents. Magnetic moment at room temperature of $\text{Cu}(\text{OCH}_2\text{CF}_3)_2$ is 1.1 B.M. which is considerably below the value for one unpaired electron. This may be due to the antiferromagnetic coupling⁸ with neighbouring copper atoms through the bridging $-\text{OCH}_2\text{CF}_3$ groups in a polymeric structure. The magnetic moment of $\text{CuCl}(\text{OCH}_2\text{CF}_3)$ (2.08 B.M.) is comparable with that reported² for $\text{Cu}(\text{OCH}_3)_2$ (2.30 B.M.) and this may be explained on the basis of spin-orbital interaction⁹.

Infrared spectra of these compounds show the characteristic C—O stretching frequency¹⁰ as a broad band at 1090 and 1070 cm^{-1} respectively. The bands which appear at 540-550 and 430-440 cm^{-1} respectively may be assigned to the asymmetric and symmetric Cu—O vibrations¹¹. $\text{CuCl}(\text{OCH}_2\text{CF}_3)$ shows a band at 350 cm^{-1} which may be assigned to $\nu(\text{Cu-Cl})$ ¹².

The reflectance spectra of these compounds show broad bands at 14300 and 13250 cm^{-1} respectively arising from $2E_g \rightarrow {}^2T_{2g}$ transition which is characteristic of tetragonally distorted¹³ octahedral copper(II)

Table 1 — Characterisation Data of $\text{Cu}(\text{OCH}_2\text{CF}_3)_2$, $\text{CuCl}(\text{OCH}_2\text{CF}_3)$ and Their Adducts

Complex	Colour	Found (Calc.), %				μ_{eff} (B.M.)	λ_{max} (cm^{-1})
		Cu	Cl	C	H		
$\text{Cu}(\text{OR})_2$	Blue	25.02 (24.29)	—	18.05 (18.35)	1.35 (1.52)	1.10	14300
$\text{CuCl}(\text{OR})$	Bluish green	31.67 (32.19)	18.11 (17.89)	11.96 (12.11)	1.13 (1.00)	2.08	13250
$\text{Cu}(\text{OR})_2\text{DMF}$	Dark green	18.13 (18.99)	—	24.97 (25.11)	3.15 (3.28)	—	13250
$\text{CuCl}(\text{OR})\text{DMF}$	-do-	23.81 (23.44)	12.93 (13.09)	21.76 (22.13)	3.15 (3.32)	—	13100
$\text{CuCl}(\text{OR})\text{NMA}$	-do-	23.59 (23.44)	13.40 (13.09)	21.65 (22.13)	3.18 (3.32)	—	13100
$\text{Cu}(\text{OR})_2\text{TMU}$	-do-	15.75 (16.83)	—	27.95 (28.60)	4.15 (4.23)	1.31	13920
$\text{CuCl}(\text{OR})\text{TMU}$	Green	20.15 (20.23)	10.63 (11.30)	26.31 (26.75)	2.10 (2.32)	—	13750
$\text{CuCl}(\text{OR})\text{HMPA}$	Dark green	16.65 (16.85)	9.88 (9.41)	25.13 (25.46)	5.11 (5.30)	—	13670
$\text{Cu}(\text{OR})_2\alpha\text{-pic-O}$	-do-	16.54 (17.14)	—	—	—	1.707	13250
$\text{CuCl}(\text{OR})\text{Py-O}$	-do-	21.23 (21.64)	11.85 (12.11)	—	—	1.223	—
$\text{CuCl}(\text{OR})\text{Py}$	Dark green	22.31 (22.93)	12.95 (12.80)	34.97 (35.36)	2.56 (2.94)	1.65	13850
$\text{Cu}(\text{OR})_2\alpha\text{-pic}$	-do-	17.46 (17.91)	—	32.65 (33.84)	3.09 (3.10)	1.403	13650
$\text{Cu}(\text{OR})_2\beta\text{-pic}$	-do-	17.14 (17.91)	—	32.15 (33.84)	3.01 (3.10)	1.44	13300
$\text{CuCl}(\text{OR})\text{DMSO}$	-do-	22.10 (22.64)	12.25 (12.89)	—	—	—	13870
$\text{Cu}(\text{OR})_2\text{Bipy}$	Green	14.65 (15.21)	—	39.78 (40.21)	4.13 (4.78)	1.49	13800

$\text{R} = \text{CH}_2\text{-CF}_3$

complexes. This rules out square-planar or tetrahedral geometry for these complexes because the former shows absorption above 15000 cm^{-1} ($15000\text{--}20000\text{ cm}^{-1}$) whereas the latter does not have absorptions in the visible region¹⁴.

$\text{Cu}(\text{OCH}_2\text{CF}_3)_2$ and $\text{CuCl}(\text{OCH}_2\text{CF}_3)$ react with dimethylformamide (DMF), N-methylacetamide (NMA), tetramethylurea (TMU), hexamethylphosphoramide (HMPA), α -picoline-N-oxide (α -pic-N-O), pyridine-N-oxide (Py-N-O), pyridine (Py), α - and β -picolines (α,β -pic), dimethyl sulphoxide (DMSO) and α,α' -bipyridyl (Bipy) to form adducts having 1:1 stoichiometry (Table 1). An alteration in the molar ratio of the reactants and an increase in the contact time had no effect on the nature of products. $\text{Cu}(\text{OMe})_2$ and $\text{Cu}(\text{OEt})_2$ do not form adducts with the present ligands and it is evident that the incorporation of electron withdrawing atom/atoms in $-\text{R}$ group or in place of $-\text{OR}$ of $\text{Cu}(\text{OR})_2$ has induced the metal to act as a better acceptor. These adducts do not melt but decompose on heating and

are insoluble in common organic solvents. These facts suggest that the adducts are also polymeric, probably through the formation of $-\text{OCH}_2\text{CF}_3$ bridges. Their low values of magnetic moments also show antiferromagnetic exchange interactions⁸ between neighbouring metals.

The IR spectra of the adducts show a single broad band in the region $1045\text{--}1060\text{ cm}^{-1}$ which may be assigned to $\nu\text{C}-\text{O}$ ¹⁰ and two bands at ~ 550 and $\sim 440\text{ cm}^{-1}$ which may be assigned to the symmetric and asymmetric Cu-O stretching vibrations; the latter band may be attributed to $\nu(\text{Cu}-\text{O} \rightarrow \text{Cu})$ ¹¹ also. These data clearly favour a structure with $-\text{OCH}_2\text{CF}_3$ bridging groups and this gets support from the fact that intermolecular alkoxy bridging is also enthalpically favoured². The spectra of the complexes $\text{CuCl}(\text{OCH}_2\text{CF}_3)_2\text{L}$ show additional bands at $360\text{--}330\text{ cm}^{-1}$ which may be assigned to the Cu-Cl stretching vibrations^{3,10,15}; this assignment rules out the Cl-bridged structure for them since $\nu(\text{Cu}-\text{Cl} \rightarrow \text{Cu})$ absorbs at $\sim 260\text{--}280\text{ cm}^{-1}$ (refs 3, 15).

The coordination of ligands in the present complexes is evident from the changes^{16,17} in their characteristic frequencies on complexation. The reflectance spectra of the adducts show a single, somewhat broad band at $13000\text{--}14000\text{ cm}^{-1}$ which is characteristic of the tetragonally distorted octahedral geometry¹³ of the complexes.

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