

FLUORO- AND CHLOROALKOXIDES OF SOME TRANSITION METALS

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A series of fluoro- and chloroalkoxy derivatives, $M(OR)_3$, $MCl(OR)_2$, $MCl_2(OR)$, $M^1(OR)_3$ and $M^1Cl(OR)$ where M = Vanadium(III), Chromium(III), Iron(III); M^1 = Cobalt(II), Copper(II) and R = $-OCH_2CH_2Cl$, $-CH_2CCl_3$ and $-CH_2CF_3$ have been synthesised. In addition, $Ni(OCH_3)-(CH_2CCl_3)_2$, $CrO_2(OR)_2$ and $CrO_2Cl(OR)$ have also been prepared. Their stereochemistry has been adduced from their IR spectra, magnetic susceptibility, electronic spectra and NMR data. The observed cryoscopic and conductance data for some of them agree with the contention that they are dimers/polymers in solid state but split into ion-pairs in polar solvents.

The effect of electron-withdrawing substituent in the alkoxy group on the acceptor properties of these derivatives, when compared with normal alkoxides, is observed. Unlike the latter, the halo-alkoxides form stable adducts with oxygen and nitrogen donor ligands (L) and the possible geometry for these adducts have also been suggested. The Mössbauer spectra for the adducts of iron(III) derivatives are consistent with $L_4Fe(\mu-OR)_2Fe(OR)_4$ structure. Tetrahedral cobalt(II) alkoxides and their adducts with ligands have been stabilised with simple 2,2,2-trifluoroethoxy and 2,2,2-trichloroethoxy ligands.

Key Words: 2-Chloroethoxy-, 2,2,2-Trichloroethoxy- and 2,2,2-Trifluoroethoxy Derivatives of 3d-Metals; Ligand Adducts of Metal Alkoxides

INTRODUCTION

METAL alkoxides have long been known¹ but the corresponding fluoro- and chloro-alkoxides have been relatively unknown and of these the 2-chloroethoxy, 2,2,2-trichloroethoxy and 2,2,2-trifluoroethoxy derivatives of 3d-metals have not been reported except for some reports on titanium(IV).²⁻⁶ Further, metal alkoxides do not normally react with ligands to yield adducts since they prefer to an alkoxy-bridged⁷ autocomplexation.⁸ However, substitution of electron-withdrawing atom/atoms in the alkyl group of $-OR$ moiety is known to reduce the extent and strength⁹ of such auto-complexation and this may lead to the ligand coordination.

Our earlier work on the syntheses and characterization of these new derivatives and their adducts is briefly presented alongwith the new data with an aim to throw light on the nature of these compounds.

FLUORO- AND CHLOROALKOXIDES OF VANADIUM(III), CHROMIUM(III) AND IRON(III)

Reaction of anhydrous MCl_3 ($M = V(III)$, $Cr(II)$ and $Fe(III)$) with $LiOR$ ($R = -CH_2CH_2Cl$, $-CH_2CCl_3$ and $-CH_2CF_3$) in 1:3, 1:2 and 1:1 molar proportions yield the corresponding alkoxides $M(OR)_3$, $-MCl(OR)_2$ and $MCl_2(OR)$.¹⁰⁻²¹ The solubility of these derivatives in EtO_2 enables their separation from $LiCl$.

Magnetic moments of these derivatives were found to be depressed when compared with those of the high spin ions in octahedral sites and this observation is indicative of antiferromagnetism involving alkoxy-bridging. Infrared spectra support this since $M(OR)_3$ and $MCl(OR)_2$ derivatives show both terminal and bridging $C-O-M$ frequencies. The reflectance spectra are characteristic of an octahedral geometry for them. The mass spectral data¹⁴ for some of them show m/e peaks at positions higher than those required for monomers which confirm the above findings.

Solutions in $PhNO_2/CH_3CN$

Conductance and UV-visible spectral data of haloalkoxides of vanadium(III)¹³ are characteristic of tetrahedral geometry and it is obvious that the octahedral geometry in solid state undergoes a complete reorganisation. The conductance and cryoscopic studies¹⁷ on the corresponding iron(III) derivatives is more interesting and reveal that these compounds are dimers in solid state but dissociate into ion-pairs in solution.

¹H NMR spectra of some of these derivatives^{13-16,21} as their pyridine solutions show slightly broad singlets arising from the $-CH_2$ protons and this may account for the possibility of monomeric adducts $M(NOR_N)(C_5H_5N)_{6-N}$ in pyridine solution.

FLUORO- AND CHLORO-ALKOXIDES OF DIOXOCHROMIUM(VI)

Reaction of CrO_2Cl_2 with $LiOR$ in 1:2 and 1:1 molar ratio in Et_2O yields dark brown solid compounds formulated as $CrO_2(OR)_2$ and $CrO_2Cl(OR)$, respectively ($R = -CH_2CH_2Cl$, $-CH_2CCl_3$, $-CH_2CF_3$).²² These compounds are predominantly covalent as shown by their conductance data and the cryoscopic studies of their solutions in nitrobenzene at varied concentration show the increase in molecular weight with increased concentration. At low concentration, these data reveal that they are monomeric but at higher concentration, the molecular weight value approaches that required for the dimers. Apparently, they are present as dimers in the solid state. The infrared spectra of $CrO_2(OR)_2$ show two bands in the $C-O$ region at 1060-90 and 1000-1050 cm^{-1} characteristic of the terminal and bridging $C-O$ vibrations, respectively while the compounds formulated as $CrO_2Cl(OR)$ show only one band at the position where the $C-O$ bridging absorbs. In addition, the $O=Cr=O$ asymmetric and symmetric stretching frequencies appear at 930-960 and 910-940 cm^{-1} respectively. These findings are in accord with an alkoxy-bridged dimeric structure for these compounds.

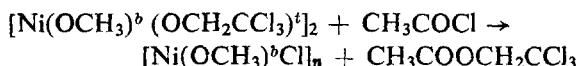
Their ¹H NMR spectra show distinct sharp resonances assigned to the terminal and bridging $-OCH_2$ groups²² in the compounds $CrO_2(OR)$ whereas

$\text{CrO}_2\text{Cl}(\text{OR})$ type of compounds show only one sharp singlet assigned to the bridging $-\text{OCH}_2$ group. The ^{19}F NMR spectra for the compounds $\text{CrO}_2(\text{OCH}_2\text{CF}_3)_2$ and $\text{CrO}_2\text{Cl}(\text{OCH}_2\text{CF}_3)_2$ appear at 78.6 and 80ppm, respectively.

The mass spectrum of $\text{CrO}_2\text{Cl}(\text{OCH}_2\text{CF}_3)$ shows evidence of its being dimeric in nature and the species originating from a dimer split to give m/e peak at the position of a monomer.

CHLORO AND FLUORO-ALKOXIDES OF NICKEL(II), COBALT(II) AND COPPER(II)

Nickel(II) methoxide does not undergo alcoholysis reaction with other alcohols even under forcing conditions.²³ Such an alcoholysis reaction has been characterized as a first example²⁴ in the reaction of nickel(II) methoxide with 2,2,2-trichloroethanol yielding the mixed alkoxy-compound formulated as $\text{Ni}(\text{OCH}_3)(\text{OCH}_2\text{CCl}_3)$. Its magnetic moment and reflectance spectral data²³ are characteristic of a tetrahedral structure for this compound. Such a structure may be visualised in terms of a dimeric framework through $-\text{OCH}_3$ bridges since such bridging may be preferred over to $-\text{OCH}_2\text{CCl}_3$ bridging on simple steric consideration. Infrared spectrum supports this as it shows two bands at 1070 and 1020 cm^{-1} assigned to the terminal and bridging C-O stretching frequency. Further, a support to the preferential $-\text{OCH}_3$ -bridged structure is adduced from the following reaction :-



The mass spectrum confirms the dimeric structure of this compound.

Copper(II) yields a variety of fluoro- and chloro-alkoxides viz. $\text{Cu}(\text{OCH}_2\text{CF}_3)_2$, $\text{CuCl}(\text{OCH}_2\text{CF}_3)$,²⁵ $\text{CuCl}(\text{OCH}_2\text{CCl}_3)$ and $\text{Cu}(\text{OCH}_3)(\text{OCH}_2\text{CCl}_3)$.²⁶ These halo-alkoxides have tetragonally distorted octahedral geometry as evidenced by their reflectance spectral data.

The interest in the syntheses of cobalt(II) fluoro- and chloroalkoxides has been two-fold. Firstly, such derivatives have not been reported and secondly, the known derivatives $\text{Cu}(\text{OR})_2$ ($R=\text{CH}_3$, C_2H_5 etc.) have the octahedral geometry¹ and no cobalt(II) alkoxide with a tetrahedral geometry has been reported, despite the fact that there is expected to be very small stability difference between the octahedral and tetrahedral cobalt(II) complexes with the same ligand.

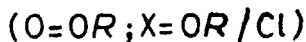
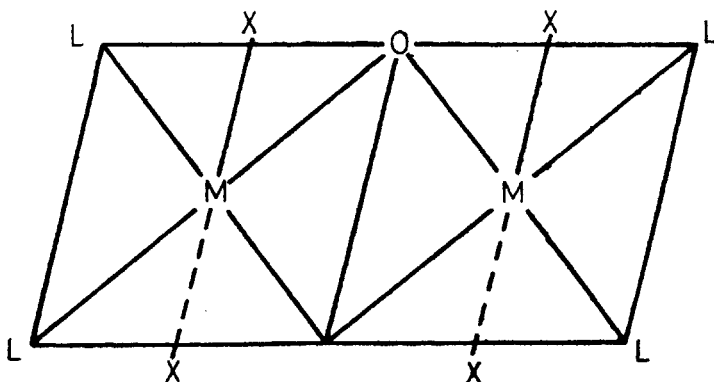
Reaction of anhydrous cobalt(II) chloride with $\text{LiOCH}_2\text{CCl}_3$ in 1 : 2 and 1 : 1 molar proportions gives intense blue compounds formulated as $\text{Co}(\text{OCH}_2\text{CCl}_3)_2.L$ and $\text{CoCl}(\text{OCH}_2\text{CCl}_3).L$ respectively ($L = \text{tetrahydrofuran}$ or dioxan).²⁷ The stereochemistry of cobalt(II) in these derivatives has been identified with definiteness from their electronic spectra, which are clearly characteristic of tetrahedral geometry. The position of the bands are almost same in the reflectance and solution spectra which confirms the retention of tetrahedral geometry even in solution. The IR spectra show the trichloroethoxy bridged structure and the position of Co-Cl stretching frequency in $\text{CoCl}(\text{OCH}_2\text{CCl}_3).L$

was found to be 300cm^{-1} and the position of this band is characteristic of tetrahedral geometry since $(\text{CoCl}_4)^{2-}$ ion is known to give $\nu(\text{Co-Cl})$ at 294 cm^{-1} .

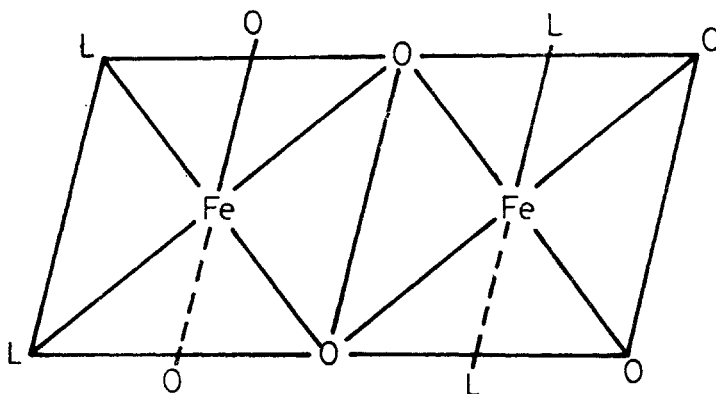
Interestingly, these paramagnetic compounds show relatively sharp single ^1H NMR resonances in HCONH_2 solutions. The signals appear at $\delta = 4.15\text{ppm}$ for CH_2 or $-\text{OCH}_2\text{CCl}_3$ in $\text{Co}(\text{OCH}_2\text{CCl}_3)_2 \cdot \text{C}_4\text{H}_8\text{O}_2$ and at $\delta = 4.3\text{ppm}$ for $-\text{CH}_2$ of $-\text{OCH}_2\text{CCl}_3$ in $\text{CoCl}(\text{OCH}_2\text{CCl}_3) \cdot \text{C}_4\text{H}_8\text{O}$. These observations very likely convey the possibility of the presence of monomeric species such as $\text{Co}(\text{OCH}_2\text{CCl}_3)_2(\text{HCONH}_2)_{N-2}$ in solution ($N=6$ or 4).

REACTION OF FLUORO- AND CHLORO-ALKOXIDES WITH LIGANDS

The fluoro- and chloro-alkoxides react exothermally with oxygen and nitrogen donor ligands to yield stable adducts having 1:1 or 1:2 stoichiometries.^{10-22,25-28,29} The magnetic moment, reflectance and IR spectral data suggest an octahedral geometry with bridging halo-alkoxy group for these adducts. The adducts of the type $M(\text{OR})_{3-n}\text{Cl}_n \cdot 2L$ ($n = 0, 1, 2$, and L is monodentate ligand) have the following structure where the ligand are possibly *cis*- to each other as revealed by their IR data, showing split bands for coordinated ligands.



The structure of the adducts of iron(III) halo-alkoxides has been further probed from their Mössbauer data^{18,20} which are indicative of two quadrupole split doublets and the presence of two kinds of iron. The Mössbauer parameters are consistent with iron(III) high spin complexes in octahedral symmetry. Furthermore, the independence of quadrupole splitting of temperature confirm the high spin state for both the sites in agreement with the μ_{eff} data. The possibility of having two sites with difference in the ligand arrangements such as represented by the figure below could not fit into the Mössbauer results with the corresponding adducts with bipyridyl. The Mössbauer parameters for the latter were nearly similar to the *bis*-adducts with the monodentate ligands



(L = Monodentate ligand ; O = OCH₂ CCl₃)

and bipyridyl would be constrained to *trans*-chelation. The only alternative structure,³⁰ which may satisfy the data for the adducts with monodentate and bidentate ligands, is $L_4Fe-(\mu-OR)_2Fe(OR)_4$ and structure such as this would be consistent with a two-site arrangement and would also provide an obvious mode of cleavage in polar solvents to give the postulated ions as evidenced by molar conductance.¹⁷

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