

Bimetallic μ -Oxoalkoxides. X. A New Class of Polynuclear Complexes

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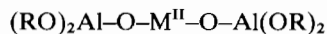
Cryoscopic data, as well as electronic, NMR and mass spectra are presented for a variety of bimetallic μ -oxoalkoxides: they indicate that, like simple metal alkoxides, these compounds are associated in organic solution. The importance of these intermolecular associations is related to the nature of the metals, but also to the structure of the alkoxy groups.

Introduction

Mixed metal oxides, specially those of transition metals, are well known for their interesting properties which have led to key applications in such fields as solid state physics and heterogeneous catalysis. In this frame, it was obviously tempting to undertake the tentative synthesis of molecules including $-M_1-O-M_2-$ units, soluble in organic media, but which would still mimic at least some of the important properties of the usual inorganic mixed oxides. These substances, enjoying combined properties due to the presence of different metals, could be of great interest in modelling the synergistic effects existing between oxo-bridged metals: such interactions usually result in extremely interesting electronic delocalizations and magnetic exchanges¹.

On the other hand, they could also represent good models of biologically important molecules, *i.e.* polynuclear complexes involving $M-O$ bonds in molecular oxygen binding and activation.

In these prospects, we have accordingly prepared a series of compounds corresponding to the general formula



where M is Cr^{II} , Mn^{II} , Fe^{II} , Co^{II} , Zn^{II} , Mo^{II} and R an alkyl group (most often propyl or butyl).

These compounds, called μ -oxoalkoxides, were synthesized by two different methods. The first one involves a thermal condensation reaction between aluminum trialkoxide and a metal(II) acetate^{2a}, while the

second one is based on a carefully controlled hydrolysis of Meerwein's 2:1 double alkoxide complexes^{2b}.

It has already been shown that some of these μ -oxoalkoxides are excellent catalysts for the ring-opening polymerization of heterocyclic compounds such as oxiranes, thiiranes and lactones³. Moreover, the Fe(II) and Mo(II) derivatives are found to bind very rapidly molecular oxygen⁴.

The kinetics of these processes depend very strongly on the nature of the metals and of the alkoxy groups.

It is the purpose of this paper to study the physical properties of the μ -oxoalkoxide complexes in organic solution.

Results

The μ -oxoalkoxides display an amazingly high solubility in most organic solvents and particularly in hydrocarbons (see Experimental). This property can be explained by an intermolecular association giving an aggregate in which a core of μ -oxo bridged metals is surrounded by a lipophylic layer of alkoxy groups. This association obviously results from the tendency of these metals to fulfill their coordination number by forming intra- and intermolecular metal-oxygen bonds, a phenomenon which is already well known for simple metal alkoxides⁵.

The mean degrees of association (\bar{n}) of the μ -oxoalkoxides are measured by cryoscopy in benzene and cyclohexane with a good accuracy and reproducibility. The results are shown in Table I. As expected, it is observed that \bar{n} strongly depends on the nature of the metals, the alkoxy groups and the solvent. Moreover, the μ -oxoalkoxides are systematically less associated in benzene, a behaviour which is probably due to the coordination power of this solvent.

In addition, within the concentration range studied, \bar{n} remains independent of the concentration (within limits of experimental errors). Nevertheless, such a behaviour is not observed for the $ZnO_2Al_2(On-C_4H_9)_4$ and $FeO_2Al_2(On-C_4H_9)_4$ compounds for which \bar{n} clearly depends on the concentration of the solution and also on the method of preparation.

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TABLE I. Molecular Association of Bimetallic μ -Oxoalkoxides, $(RO)_2Al-O-M^{II}-O-Al(OR)_2$.

M^{II}	R	Solvent	\bar{n}	Concentration Range Examined <i>M</i>	Colour
Fe ^{II}	iso-C ₃ H ₇	Benzene	1	(0.09–0.2)	Dark Green
		Cyclohexane	2.1	(0.06–0.12)	Dark Green
	n-C ₄ H ₉	Benzene	1–3	} variable with concentration	Dark Green
		Cyclohexane	2–8		Dark Green
	sec-C ₄ H ₉	Benzene	1.1	(0.06–0.10)	Dark Green
		Cyclohexane	2.0	(0.08–0.14)	Dark Green
ter-C ₄ H ₉	Benzene	1.1	(0.04–0.08)	Dark Green	
	Cyclohexane	4.1	(0.04–0.06)	Dark Green	
Co ^{II}	iso-C ₃ H ₇	Benzene	2.0	(0.3–0.6)	Violet–Red
		Cyclohexane	3.0	(0.02–0.1)	Violet–Red
	n-C ₄ H ₉	Benzene	4.1	(0.2–0.8)	Blue
		Cyclohexane	6.2	(0.02–0.12)	Blue
Mo ^{II}	iso-C ₃ H ₇	Benzene	1.1	(0.08–0.8)	Deep Red
		Cyclohexane	2.1	(0.09–0.18)	Deep Red
	n-C ₄ H ₉	Benzene	3.0	(0.18–0.35)	Deep Green
Cr ^{II}	iso-C ₃ H ₇	Benzene	1.1	(0.05–0.12)	Blue
		Cyclohexane	2.0	(0.05–0.08)	Blue
Zn ^{II}	n-C ₄ H ₉	Benzene	4–8	} variable with concentration	Pale Yellow
	sec-C ₄ H ₉	Benzene	4–8		Pale Yellow

On the other hand, we have also studied other structural properties of these compounds in solution and in vapour phase.

Colour and Visible Absorption Spectra

The electronic absorption spectra of these compounds also strongly depend on the molecular association. The visible spectra exhibit two bands at 375 and 490 nm for the $MoO_2Al_2(Oiso-C_3H_7)_4$ compound and only one distinct absorption band at 750 nm for the $MoO_2Al_2(Osec-C_4H_9)_4$ compound (Fig. 1). Moreover, these absorption bands are not dependent on the nature of the solvent and can thus be attributed to electronic transitions between molecular orbitals which have predominantly metal *d* orbital character.

An additional interesting feature is the striking difference in extinction coefficients between these two different compounds (Fig. 1) (see below).

These results indicate the great influence of the nature of the alkoxy groups on the *d*-metal orbitals splitting and consequently on the electronic visible transitions which affect the colour of the complexes (Table I).

NMR Spectra

Figure 2 shows the proton-decoupled ¹³C NMR spectrum of the $MoO_2Al_2(Oiso-C_3H_7)_4$ compound

which is non-associated ($\bar{n} \approx 1$) in benzene (table I). Two peaks are observed at 26.0 and 28.4 ppm (from TMS) which can be attributed to two different CH₃ groups, as well as two other peaks at 63.6 and 69.2 ppm attributed to CH groups.

This spectrum clearly indicates the presence of two different isopropoxy groups in this compound: two peaks (28.4 and 69.2 ppm) correspond to the carbon atoms of the bridging isopropoxy groups (weak field values), and the others to the carbon atoms of the non-bridging groups (high field values).

The NMR spectrum of this mononuclear species is very simple, and this method is thus very convenient for the study of the intramolecular coordination of the alkoxy groups. On the opposite, the proton-decoupled ¹³C NMR spectra of the polynuclear species are more complex. In the case of $ZnO_2Al_2(Osec-C_4H_9)_4$ for which \bar{n} is greater than one (Table I), we can also observe the peaks expected for the different carbon atoms of the molecule (Fig. 3). Nevertheless, they are not simple and, for the CH peak, we observe again two distinguishable *sec*-butoxy groups in the molecule, although the phenomenon is less marked for the other resonance peaks. This result indicates also the presence of bridging and non-bridging isobutoxy groups.

However, from these sole observations, it is unfortunately not possible to distinguish the inter- and the intramolecular bridging groups.

Mass Spectrometry

The molecular association of the μ -oxoalkoxides, in the vapour phase, has also been explored by mass spectrometry. Molecular ion peaks have been observed at $m/e = 292, 336, 351, 395$ and 454 , with important relative intensities, for the $\text{FeO}_2\text{Al}_2(\text{Oiso-C}_3\text{H}_7)_4$ compound. These peaks correspond to aggregate fragments which have lost a propene molecule from one of the isopropoxy groups. Such fragmentation schemes have also been observed for $\text{Al}(\text{Oiso-C}_3\text{H}_7)_3$.⁶ The results, quoted in Table II, confirm the intermolecular coordinations between oxygen and metal atoms in the vapour

TABLE II. Molecular Ion Peaks of the $\text{FeO}_2\text{Al}_2(\text{Oiso-C}_3\text{H}_7)_4$ Complex.

Observed m/e Values	Aggregate Fragment	Relative Abundance ^a
292	$\text{Fe}(\text{Oiso-C}_3\text{H}_7)_4$	30
336	$\text{FeO}_2\text{Al}_2(\text{OH})(\text{Oiso-C}_3\text{H}_7)_4$	45
351	$\text{Fe}(\text{Oiso-C}_3\text{H}_7)_5$	59
395	$\text{FeO}_2\text{Al}_2(\text{OH})(\text{Oiso-C}_3\text{H}_7)_4$	28
454	$\text{FeO}_2\text{Al}_2(\text{OH})(\text{Oiso-C}_3\text{H}_7)_5$	10

^a Estimated with respect to the C_3H_7^+ peak, taken equal to 100.

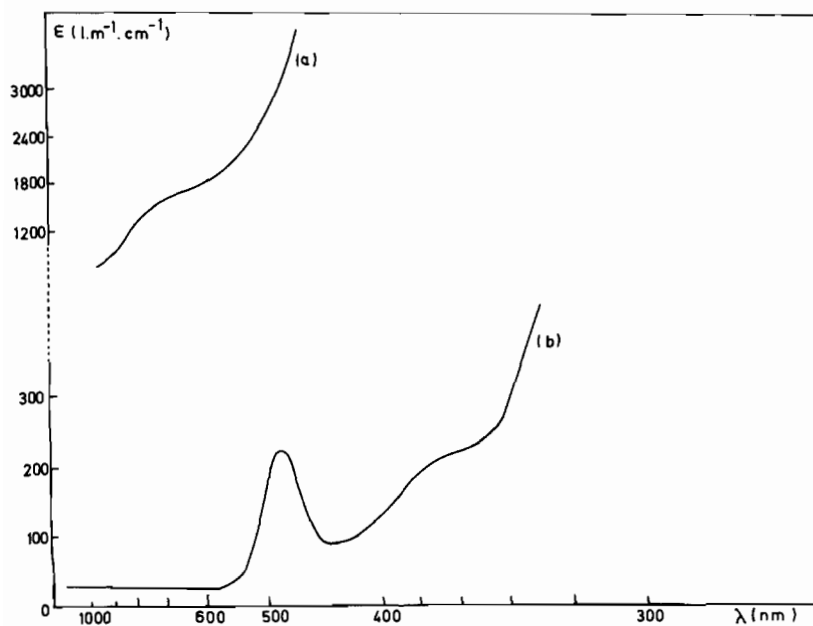


Figure 1. Electronic spectra of $\text{MoOAl}_2(\text{OR})_4$ in cyclohexane. a) $\text{R} = \text{n-butyl } 1.25 \times 10^{-3} \text{ M}$; b) $\text{R} = \text{isopropyl } 10^{-2} \text{ M}$.

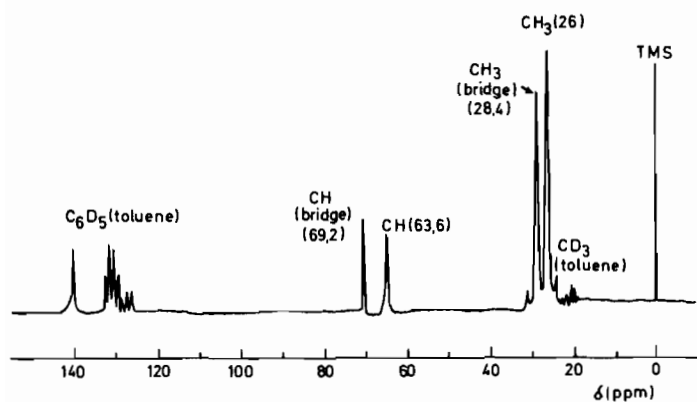


Figure 2. ^{13}C NMR spectrum of $\text{MoO}_2\text{Al}_2(\text{Oiso-C}_3\text{H}_7)_4$.

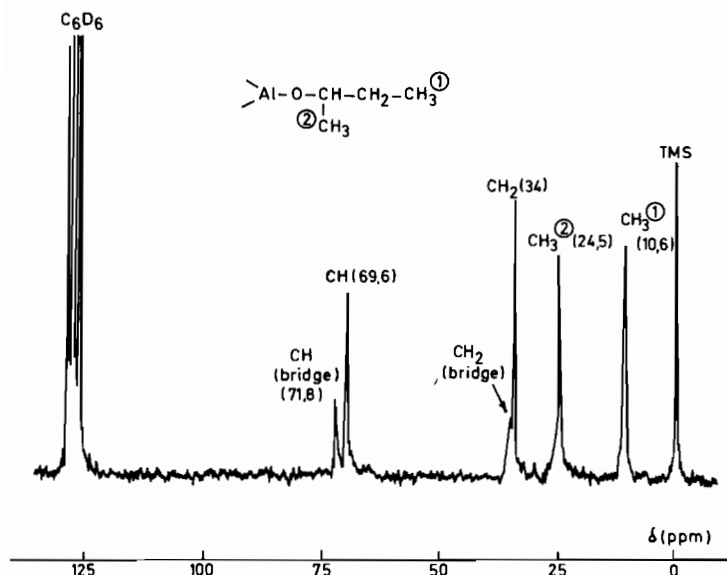


Figure 3. ^{13}C NMR spectrum of $\text{ZnO}_2\text{Al}_2(\text{Osec-C}_4\text{H}_9)_4$.

phase, and can be correlated with the previous observations made on solutions.

Discussion

From the results gathered in Table I, the most interesting conclusion is that the mean degree of association (\bar{n}) depends on the nature of the alkoxy groups: of course, the strength of the metal–oxygen bonds increases with the basicity of the alkoxy groups; but on the other hand, this tendency is opposed by steric factors, which increase as the size of the alkoxy groups increases. The value of \bar{n} depends accordingly on the relative importance between basicity and steric effects, as it has already been observed for simple metal alkoxides⁵.

As might be expected, the degree of molecular association is also directly dependent on the nature and the coordination number of the central metal atom M^{II} . However, this latter parameter is controlled by the nature of the alkoxy groups: their effect on the geometry and the molecular energy levels of the complex is strongly marked, for example by the different colours and electronic absorption spectra of both $\text{MoO}_2\text{Al}_2(\text{Oiso-C}_3\text{H}_7)_4$ and $\text{MoO}_2\text{Al}_2(\text{On-C}_4\text{H}_9)_4$ compounds. Moreover, the high intensity of the $\text{MoO}_2\text{Al}_2(\text{On-C}_4\text{H}_9)_4$ compound can be related to an electronic delocalization in this molecular aggregate. Such ascertaining has been made by different authors which have studied the electronic spectra of strongly delocalized polynuclear compounds⁷.

Finally, the nature of the solvent has also a great importance: the lower values of \bar{n} observed in benzenic solution are probably due to the coordination power of this solvent.

The NMR spectra of polynuclear aggregates are very complex, since the peaks corresponding to bridged and non-bridged alkoxy groups are due to the presence of both inter- and intramolecular interactions: it is not possible at present to estimate the relative importance of both interactions and further studies are necessary to propose detailed molecular models for these aggregates.

Within the temperature and the concentration ranges quoted in Table I, we observe that the mean degree of association of these compounds remains generally independent of the concentration. Moreover, these values are generally close to integers and this is probably due to the predominance of one well-defined and thermodynamically favoured species in solution. These effects are consistent with those reported by Mazzei⁸ for poly(*N*-alkyliminoalanes) and Owens⁹ for organo-aluminum compounds.

Nevertheless, in some cases, the values of \bar{n} are not close to integers and are dependent on the concentration of the solution and of the method of synthesis (Table I). This result implies probably the existence of different species which are in equilibrium and confirms the great complexity of the overall structure of these μ -oxoalkoxides.

In conclusion, it appears that this new family of coordination compounds, mostly present as molecular aggregates in organic solution, can be compared to small fragments of mixed oxides (formally similar to

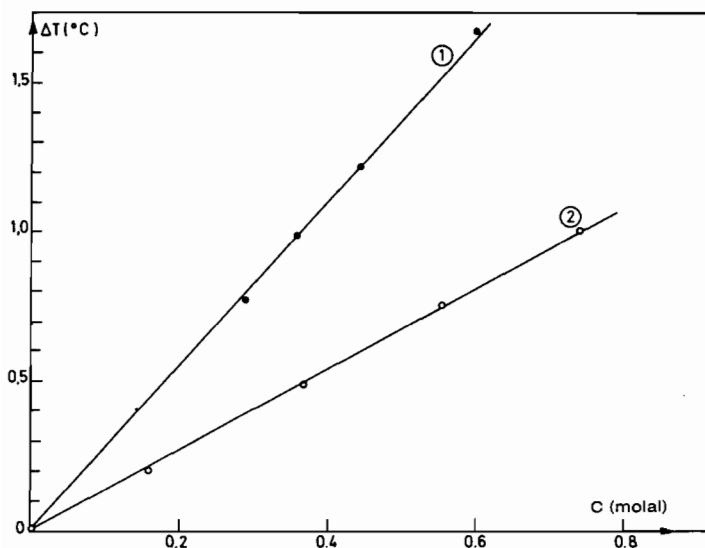


Figure 4. Degree of association of $\text{CoO}_2\text{Al}_2(\text{OR})_4$ in benzene. 1) R = isopropyl; 2) R = n-butyl.

spinels when $\bar{n} = 4$), solubilized by a lipophilic layer of alkoxy groups. As such, they enjoy interesting physical properties characteristic of oxides with electronic delocalization, but they also represent an attractive frontier model between homogeneous and heterogeneous catalysis: this latter aspect will be developed in future publications.

Experimental

All solvents were dried over LiAlH_4 or CaH_2 before distillation, and the experiments were performed under inert atmosphere (argon).

The preparation of the μ -oxoalkoxide compounds was described in details elsewhere².

These complexes are very soluble in most organic solvents. In fact, several of them (for which the alkyl group contains four or more carbon atoms) are practically miscible to alkanes or benzene in every proportion. For instance, a perfectly clear solution is obtained from 10 gr of $\text{ZnO}_2\text{Al}_2(\text{O}n\text{-C}_4\text{H}_9)_4$ and 8 ml of n-heptane. Moreover, the solubility decreases for smaller alkoxy groups; for instance, the isopropoxy compounds are less soluble than the butoxy ones.

The mean degrees of association (\bar{n}) were determined in a cryometer conceived to operate under an argon atmosphere, and the solutions were injected in the apparatus with hypodermic syringes through a septum. \bar{n} was obtained from the slope of the graph ΔT versus molal concentration C ($\Delta T = K C/\bar{n}$ where the cryoscopic constant of the solvent, $K = 5.1$ and 20.5 for benzene and cyclohexane, respectively) (Fig. 4).

The ^1H and ^{13}C NMR spectra were recorded on Varian (T 60) and Brücker (HFX 90) spectrometers with TMS as internal reference, using 0.3 M solutions in perdeuteriated benzene or toluene.

Visible absorption spectra of the compounds in benzene, toluene and cyclohexane solutions were recorded on a Zeiss apparatus (the concentrations of the solutions are quoted in Figure 1), and the mass spectra on an Itachi-Perkin Elmer RMU-6 D spectrometer.

Acknowledgments

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