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Alumino-organic derivatives of some dioximes

Nicolae Voiculescu*

"P. Poni" Institute of Macromolecular Chemistry, Iasi, Aleea Gr. Ghica Voda 41 A, Iasi 6600, Romania

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The alumino-organic combinations of the dioximes ($DOxH_2$) examined in this paper result from the substitution of the hydrogen bonds of oximes by alumino-organic groups. Relative to the same alumino-organic derivatives, diphenylglyoxime ($DPGH_2$) behaves similarly to dimethylglyoxime ($DMGH_2$). The chemical reactivity of $DPGH_2$ towards these alumino-organic compounds is, however, less than in the case of $DMGH_2$. An exception is the monomer state of $(DPG)[Al(i\text{-}C_4H_9)_2]_2$ in benzene solution. The behavior relative to amines of alkyl derivatives is similar to that found in coordinated oximes. In contrast, phenylaluminum derivatives of $DMGH_2$ and $DPGH_2$ are not soluble in amines. All compounds reported in this paper were separated from the reaction mixture as colored powders and were characterized by chemical analyses, IR spectroscopy, X-ray diffraction spectra and ^1H NMR. Finally, a comparison between the reactivity of free and coordinated dioximes is briefly considered. It is hoped that such comparisons will throw light on the problems associated with the reactivity of free and coordinated oxides versus alumino-organic compounds. Copyright © 2002 John Wiley & Sons, Ltd.

KEYWORDS: dimethylglyoxime; diphenylglyoxime; alumino-organic compounds; hydrogen bridges

INTRODUCTION

Dimethylglyoxime ($DMGH_2$) is an important organic reagent used in analytical chemistry. The importance of $DMGH_2$ compounds has succeeded beyond the field of qualitative and quantitative analytical chemistry, and these compounds are used in such diverse catalytic systems as polymerization, hydrogenation, and oxidation or reduction.

Some oximes,[1–9] through rigorous control of the pH on precipitation, have the capacity to form selective and extremely stable colored chelate compounds with nickel(II), palladium(II) and copper(II) ions. The coordination of the oximes with these metals changes the characteristics of the ligand. The lack of the reactivity of the OH groups in the coordinated oximes was ascribed[10–18] to the intramolecular hydrogen bonds $O{-}H\cdots O$, existing in these compounds. The hydrogen bonds existing in the free oximes differ from those in the chelates in the way they are achieved and by their strength. In $DMGH_2$,[19] the hydrogen bonds are intermolecular and are established between the oximic oxygen and the nitrogen atom of the next molecule. The hydrogen bonds tie the molecules together to form infinite chains. The atoms in the $O{-}H\cdots N$ bond are not set in a straight line, but in the shape of a 140° angle.[20] It is interesting to note that the hydrogen-bonding network itself is approximately planar (see Fig. 1). The hydrogen bond system in diphenylglyoxime ($DPGH_2$) is almost identical to that in $DMGH_2$.

No reports on the chemical interaction between alumino-organic derivatives and the oximes examined in this paper have so far been found in the literature.

The present experimental results will be discussed, along with the previous ones, and the discussion will take account of IR absorption spectra, X-ray diffraction, and ^1H NMR.

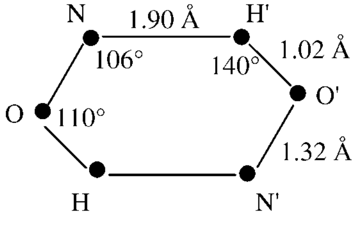

Figure 1. Hydrogen bonding network in $DMGH_2$.

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*Correspondence to: N. Voiculescu, "P. Poni" Institute of Macromolecular Chemistry, Iasi, Aleea Gr. Ghica Voda 41 A, Iasi 6600, Romania.
E-mail: nicvoic@icmpp.tuiasi.ro

EXPERIMENTAL

Measurements

The IR spectra were recorded on a Specord M 90 Carl Zeiss spectrophotometer using the KBr pellet technique. The X-ray diffraction patterns of compounds were obtained by the powder method on a TUR M-60 apparatus, using Cu Kα radiation. To avoid any trace of humidity, the test samples were inserted into sealed glass tubes. Working with the URK-5, the exposures were carried out in a vacuum chamber at 40 kV and 25 mA, for 2 h.

The molecular masses of the alkyl derivatives of the oximes were determined cryoscopically in benzene. The presence of C_4H_9 and C_2H_5 radicals only in the soluble synthesized compounds was revealed on a Jeol 60 MHz NMR spectrometer, using tetramethylsilane as the internal reference, at room temperature. The ^1H NMR spectra of oximes were measured in ≤ 5 mol% solution in deuterated dimethylsulfoxide.

Synthesis

$Al(C_6H_5)_3$ was obtained[21] starting from $Hg(C_6H_5)_2$ and aluminum powder, by heating to 130–140 °C, and was purified by recrystallization from benzene and *n*-hexane. $Al(i\text{-}C_4H_9)_3$, $Al(C_2H_5)_3$, $Al(C_2H_5)_2Cl$, $DMGH_2$, and $DPGH_2$ were purchased from Merck.

All alumino-organic compounds were handled either under an atmosphere of dry nitrogen or in a glass vacuum line of conventional design. Oxygen and moisture were rigorously excluded from all reactions.

The method of obtaining $(DMG)_2[Al(i\text{-}C_4H_9)_2]_4$ is published elsewhere.[10]

$(DMG)_2[Al(C_2H_5)_2]_4$ was obtained by adding $Al(C_2H_5)_3$ dissolved in *n*-heptane over a suspension of dried $DMGH_2$ in *n*-heptane ($DMGH_2$:$Al(C_2H_5)_3$ = 1:4 molar ratio). It was heated at the reflux temperature of the solvent, until the whole quantity of $DMGH_2$ processed was transformed into a red syrup, which deposited at the bottom of the flask. The syrupy residue was washed several times with *n*-heptane to remove any traces of $Al(C_2H_5)_3$ and was dried in vacuum.

$(DMG)_2[Al(C_6H_5)_2]_4$ was obtained by adding $Al(C_6H_5)_3$ dissolved in benzene on $DMGH_2$ powder ($DMGH_2$: $Al(C_6H_5)_3$ = 1:6 molar ratio). It was heated to the reflux temperature of the solvent, until the whole quantity of $DMGH_2$ processed had been transformed into a brown powder. The total heating time was 40 h. The resulting product was decanted and washed several times with benzene to remove the $Al(C_6H_5)_3$ added in excess, and was dried in vacuum.

$(DMG)_2[Al(C_2H_5)Cl]_4$ was obtained by adding $Al(C_2H_5)_2Cl$ dissolved in *n*-heptane over a suspension of dried $DMGH_2$ in *n*-heptane ($DMGH_2$:$Al(C_2H_5)_2Cl$ = 1:4 molar ratio). It was heated at the reflux temperature of the solvent, until the whole quantity of $DMGH_2$ processed was transformed into a red syrup, which deposited at the bottom of the flask. The syrupy residue was separated from the liquid fraction by decanting and was dried in vacuum.

$(DPG)[Al(i\text{-}C_4H_9)_2]_2$ was obtained by mixing a triisobutilaluminum benzene solution with a suspension of $DPGH_2$ in benzene at a 3:1 molar ratio. The reaction mixture was stirred vigorously for several hours at room temperature. The excess unreacted $DPGH_2$ was separated from the liquid fraction by decanting. It was repeatedly washed with benzene and dried in vacuum.

The chemical analysis, molecular weight, and characteristics of the compounds synthesized are given in Table 1.

$(DPG)[Al(C_2H_5)_2]_2$ was obtained in a similar manner to the preparation of $(DPG)[Al(i\text{-}C_4H_9)_2]_2$.

$(DPG)[Al(C_6H_5)_2]_2$ was obtained by mixing $Al(C_6H_5)_3$ with $DPGH_2$, similar to the preparation of $(DPG)Al_2(i\text{-}C_4H_9)_4$. The mixture was heated with stirring for several days until a homogeneous brown, solid compound was obtained. The solid product was separated from the liquid

Table 1. Analysis, molecular, weight and characteristics of the products synthesized

Compound	Molecular weight, Calc. (found)	Color	Analyses, [calc.], Found (%) C	H	Al	N
$(DMG)_2[Al(i\text{-}C_4H_9)_2]_4$	792, (760)	Orange	[60.60] 59.63	[10.60] 10.60	[13.63] 13.80	[7.07] 7.16
$(DMG)_2[Al(C_2H_5)_2]_4$	568, (560)	Orange	[50.70] 50.41	[9.15] 9.10	[19.01] 19.15	[9.85] 9.80
$(DMG)_2[Al(C_6H_5)_2]_4$	952, (–)	Brown	[70.58] 69.87	[5.46] 5.46	[11.34] 11.40	[5.88] 5.80
$(DPG)[Al(i\text{-}C_4H_9)_2]_2$	520, (538)	Orange	[69.23] 68.95	[8.84] 8.63	[10.38] 10.43	[5.38] 5.23
$(DPG)[Al(C_2H_5)_2]_2$	408, (–)	Orange	[64.70] 64.55	[7.35] 7.35	[13.23] 13.35	[6.86] 6.85
$(DPG)[Al(C_6H_5)_2]_2$	600, (–)	Brown	[76.00] 75.74	[5.00] 4.87	[9.00] 9.24	[4.66] 4.62
$(DMG)_2[Al(C_2H_5)Cl]_4$[a]	852, (861)	Orange–red	[31.78] 31.10	[5.29] 5.25	[17.88] 18.05	[9.27] 9.27
$(DPG)[Al(C_2H_5)Cl]_2$[b]	421, (–)	Orange–red	[51.30] 50.61	[4.75] 4.75	[12.82] 12.90	[6.65] 6.55

[a] Cl%: calc., 25.16; found, 25.08.

[b] Cl%: calc., 16.86; found, 16.80.

fraction by decanting. It was repeatedly washed with warm benzene and dried in vacuum.

(DPG)[Al(C_2H_5)Cl]$_2$ was obtained in a similar manner to the preparation of (DMG)$_2$[Al(C_2H_5)Cl]$_4$.

RESULTS AND DISCUSSION

The experimental data obtained in this investigation establish that the reactions of alumino-organic derivatives with free dioximes can be described by the following equation:

$$\mathrm{DOxH_2 + 2AlR_3 \rightarrow (DOx)[AlR_2]_2 + 2RH} \qquad (1)$$

where R = i-C_4H_9, C_2H_5, C_6H_5, Cl; DOx = DMG, DPG.

The reaction of Al$(C_2H_5)_2$Cl with free oximes may occur in two ways. In the first, the Al—Cl bond would break with the release of hydrochloric acid; in the second, the Al—C bond would break with the release of ethane. The reaction products found confirm the latter is the case.

The stoichiometric data on the reactions and analysis of the amorphous products is consistent with Eqn. (1). For these reactions, it seems plausible to suggest a six-stage mechanism comprising four intermediates in the case of DPGH$_2$, as shown in the case of coordinated oximes,[22] and a ten-stage mechanism comprising five intermediates in the case of DMGH$_2$.

In both cases, the first reaction step probably involves the formation of an unstable adduct between the alumino-organic derivative and the oxime, as shown in Fig. 2. The adduct formation takes place through the binding of the aluminum atoms to the oxime nitrogen and thus a coordinate N → Al bond is formed. As a result of the donor–acceptor bond between aluminum and the nitrogen of the oxime, the hydrogen bond is weakened. The formation of the adduct causes the appearance of a free hydroxyl group, which has a more mobile hydrogen atom than those of the oximes, where they are engaged in O—H···N bonds. Therefore, it would be expected that reaction at the hydrogen atom with a higher mobility would react more react quickly, resulting in the formation of a covalent alumino-organic derivative and elimination of a hydrocarbon molecule. Similar explanations can be given for the succeeding steps.

(DMG)$_2$[Al(i-C_4H_9)$_2$]$_4$, (DMG)$_2$[Al(C_2H_5)Cl]$_4$ and (DMG)$_2$[Al$(C_2H_5)_2$]$_4$ are dimers in the solid phase. The dimerization is represented by the last two steps, nine and ten, in which the closure by the hexa-atomic heterocycles, Al—O—N—Al—O—N, without carbon atoms produces a very interesting macrocycle. The dimerization results from binding of the aluminum atom to the nitrogen atom of the next molecule, as shown in Fig. 2.

The DMGH$_2$ molecule must first rotate 180° about the central carbon–carbon bond. This rotation occurs when DMGH$_2$ is dissolved in a solvent. The 'anti' form that appears through a revolution of the DMGH$_2$ molecule around the central C—C bond is necessary for the formation of the dimer. The molecular weight measurements (Table 1) correspond to the dimer state. The formation of the dimer may be explained either by binding of the aluminum atoms by the hydrocarbon radicals, or by binding of the aluminum atoms only to the oxygen atoms. Dimerization by the hydrocarbon radicals would lead to hybrid bonds of the aluminum atoms between sp^3 and sp^2, which are less stable than the sp^3 bonds formed by nitrogen binding. Formation through O—Al—O bonds is also unlikely, because the aluminum atoms are interposed between the atoms participating in the hydrogen bond, atoms which, in the case of the DMGH$_2$, are nitrogen and oxygen atoms, O—H···N.

The monomer state of (DPG)[Al(i-C_4H_9)$_2$]$_2$ is probably due to the influence of phenyl groups in DPGH$_2$: some steric hindrances probably to allow DPGH$_2$ to participate in the reaction only in 'anti' form. However, it is possible that this monomer state may exist only in benzene solution, with the solid-state compounds being polymerized, through Al—N bonds between the adjacent molecules. This supposition is supported by X-ray diffraction spectra of compounds, indicating an amorphous state, specific to polymer compounds.[20,22]

The alumino-organic derivatives of oximes described in this paper are colored solid substances, unstable towards water, alcohols, acids and bases. Hydrolysis rebuilds the oximes and their properties to form colored complexes with nickel(II), palladium(II), and copper(II) ions.

The behavior relative to amines is similar to that found in alumino-organic compounds of DMGH$_2$ and DPGH$_2$ coordinated with nickel(II), palladium(II), and copper(II) ions.[22] Alkyl derivatives are soluble in tertiary amines, with color intensification. Nevertheless, no attempts have been made to isolate adducts with amines. In contrast to the alkylalumino-organic derivatives, all phenylalumino-organic derivatives of oximes are insoluble in amines.

The replacement of oximic hydrogen atoms by AlR$_2$ groups also brings about changes in the IR absorption spectrum (Table 2). In the 3600–650 cm^{-1} range, the absorption spectrum of alumino-organic combinations of DMGH$_2$ and DPGH$_2$ is characterized by the absence of the absorption maxima characteristic of the OH group and by the position change of the absorption maxima of the CN and NO groups. The two absorption maxima of the CN and NO groups of (DOx)[AlR$_2$]$_2$ appear at much higher frequencies than for DOxH$_2$, or even for chelates.[22] The character of the radicals left at the aluminum atom determines the magnitude of the displacement and decreases in the following order:

$$\mathrm{Al(C_2H_5)Cl > Al(i\text{-}C_4H_9)_2,\ Al(C_2H_5)_2 > Al(C_6H_5)_2}$$

X-ray diffraction images of all new compounds show their amorphous state. In the case of alkylaluminum, compounds of oximes, informative results for the soluble synthesized compounds could be obtained by NMR spectrometry. It has been found that α-dioximes generally exhibit an OH proton signal[23] in the range 11 to 11.9 ppm. This signal is quite broad and exhibits considerable concentration dependence. These phenomena are caused by self-association through hydrogen bonding.

The ^1H NMR data (Table 3) are in good agreement with the IR spectra and are in favor of the substitution of hydrogen bonds with alumino-organic bridges. Thus, the NMR spectra of the aluminio-organic derivatives of oximes did not shown hydroxyl absorption. Also, the ratios between the signals of DMG methyl protons, and the methyl protons of the alkyl radical in $(DMG)_2[Al(i\text{-}C_4H_9)_2]_4$, $(DMG)_2[Al(C_2H_5)_2]_4$, and $(DMG)_2[Al(C_2H_5)Cl]_4$ are 1:4, 1:2 and 1:1, according to the proposed structure (Fig. 2).

We found that the signals of the protons in oxime AlR_2 groups appear at a lower field than in AlR_3 at room

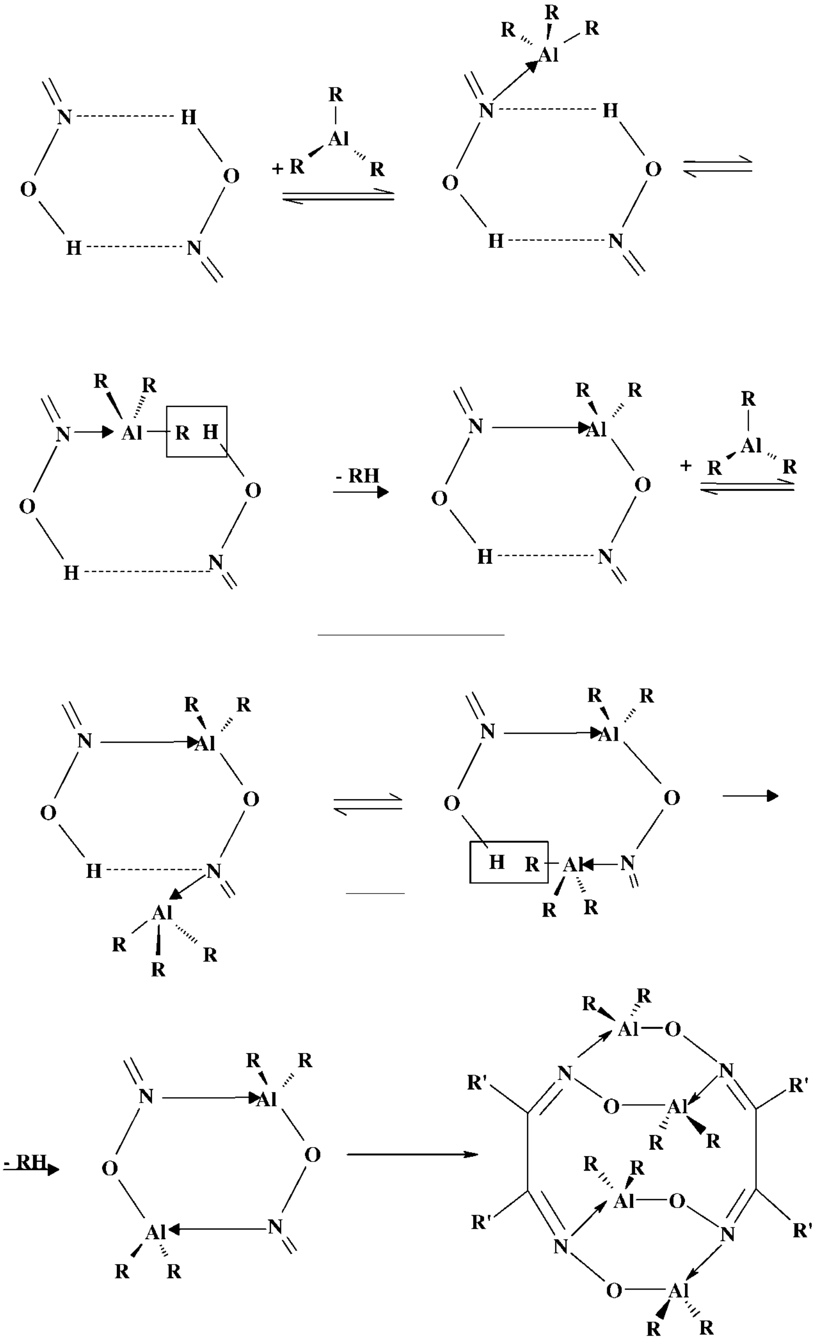

Figure 2. Mechanism for formation of $(DOx)[AlR_2]_2$; R = $i\text{-}C_4H_9$, C_2H_5, C_6H_5, Cl, R′ = CH_3 and C_6H_5.

Table 2. IR absorption spectra of the alumino-organic derivatives of dioximes (cm^{-1})

Compound	(C=N)	(NO)
$(DMG)_2[Al(C_2H_5)_2]_4$	1625	1250
$(DMG)_2[Al(i\text{-}C_4H_9)_2]_4$	1630	1250
$(DMG)_2[Al(C_2H_5)Cl]_4$	1640	1095
$(DMG)[Al(C_6H_5)_2]_2$	1595	1080
$(DPG)[Al\ (C_2H_5)_2]_2$	1585	1150, 1090
$(DPG)[Al(i\text{-}C_4H_9)_2]_2$	1590	1150, 1090
$(DPG)[Al\ (C_6H_5)_2]_2$	1585	1140, 1090
$(DPG)[Al\ (C_2H_5)Cl]_2$	1650	1160, 1095

temperature. On the other hand, the methyl signals in the DMG show a shift to a higher field from the position in DMGH$_2$. This seems to be due to the saturation of the C=N bonds in the alumino-alkyl derivatives of oximes.

Our results tend to be in agreement with the literature data.[23–26]

Studies carried out on the compounds resulting from the reaction of alumino-organic derivatives with free dioximes lead to the following conclusions:

- alumino-organic compounds of free dioximes result from the substitution of O—H···N hydrogen bonds, existing in dioximes, by O—Al—N aluminum bridges,
- alkylalumino-organic derivatives of dioximes are dimer substances and dimerization creates hexa-atomic metallocycles, Al—O—N—Al—O—N, without carbon atoms.
- Studies carried out on compounds resulting from the reaction of alumino-organic derivatives with free and coordinated dioximes[22] lead to the following findings, grouped into similiarities and differences. The similiarities observed consist of:
- The alumino-organic combinations of the free and coordinated dioximes appear through the substitution of hydrogen bonds by alumino-organic groups; the aluminum atom is interposed between the atoms participating in the hydrogen bond and forms an sp^3 bond.
- The resulting compounds are colored solid substances unstable towards water, alcohol, acids, and bases. Alcoholysis and hydrolysis bring the ligand back to its state before the reaction.

Table 3. ^{1}H NMR chemical shifts (ppm) for the soluble products

	δ (CH$_3$)		δ	δ (CH)		δ
Product	Oxime	Alkyl	(CH$_2$)	Oxime	Alkyl	(OH)
DMGH$_2$	1.94	–	–	–	–	11.37
DPGH$_2$	–	–	–	7.40	–	11.54
$(DMG)_2[Al(i\text{-}C_4H_9)_2]_4$	1.60	1.25	0.16	–	1.29	–
$(DMG)_2[Al(C_2H_5)_2]_4$	1.60	1.24	0.33	–	–	–
$(DPG)[Al(i\text{-}C_4H_9)_2]_2$	1.60	1.25	0.16	7.40	1.29	–
$(DMG)_2[Al(C_2H_5)Cl]_4$	1.60	1.25	0.31	–	–	–

- The chemical reactivity is determined by the character of the radicals of the aluminum atom and decreases in the following order:

$$Al(C_2H_5)_2Cl > Al(i\text{-}C_4H_9)_3,\ Al(C_2H_5)_3 > Al(C_6H_5)_3$$

- The compounds resulting in both cases form adducts with amines through the aluminum atoms.

The differences consist of:

- The chemical reactivity of free dioximes *versus* alumino-organic derivatives is smaller than in the coordinate state.
- The alumino-organic derivatives of the free dioximes result through the replacement of the intermolecular hydrogen bonds.
- The aluminum atoms bind differently, forming an O—Al—N bond in dioxime compounds, and an O—Al—O bond in the others.
- These differences are the result of the influence exercised by the central metallic atoms on the progress of the reaction, the binding, and the behavior of the derivatives obtained.

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