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Aluminiumorganic compounds of some metaldioximates

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Coordinated dioximes with nickel(II), palladium(II) and copper(II) ions proved capable of giving substitution reactions with a series of aluminiumorganic compounds. Studies made on the reaction products have revealed that in the case of both dimethylglyoxime and diphenylglyoxime. The reaction products result from substitution of the O—H···O hydrogen bridges existing in such compounds by O—Al—O bridges. All compounds reported in this paper were separated from the reaction mixture as coloured powders and were characterized by chemical analyses, IR spectroscopy, X-ray diffraction spectra, proton NMR spectra and magnetic properties. Copyright © 2001 John Wiley & Sons, Ltd.

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1. INTRODUCTION

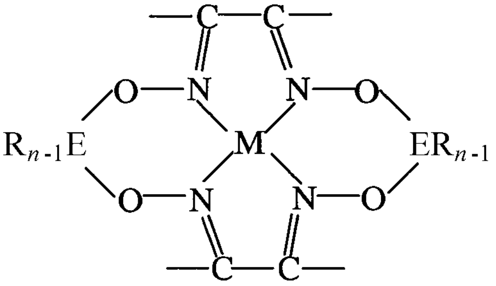
Reactions of coordinated compounds can be classified in four categories,[1] namely:

- substitution of a ligand by another;
- intramolecular isomerization;
- reaction of the central metallic atom;
- reactions of the coordinated ligands.

Special interest is shown in the literature only to the first three types of reaction. Only a few papers have dealt with the reaction of coordinated ligands. The reactivity of free and coordinated oximes with bivalent transitional metals was the object of several papers.[2–14] Dimethylglyoxime ($DMGH_2$) and diphenylglyoxime ($DPGH_2$) are two important organic reagent used in analytical chemistry. The oximes,[9,11,14–22] through a rigorous control of precipitation pH, have the ability to form selectively, very stable coloured chelate compounds with nickel(II), palladium(II) and copper(II) ions. The coordination of the dioxime with these metals determines the screening of the ligand characteristic properties. The lack of reactivity of the OH groups in the coordinated oximes was caused by the intramolecular hydrogen bonds,[10,12,14,17,23–27] O—H···O, existing in these compounds.

Experiments on the reactivity of nickel(II), palladium(II) and copper(II) dimethylglyoximates with boron, aluminium and zinc compounds have resulted in a new class of compounds corresponding to the formula given in Fig. 1.

In this paper we give preparation methods and some physico-chemical characteristics of the compounds resulting from the reactions of $Al(C_6H_5)_3$ and $Al(i\text{-}C_4H_9)_3$ with $M(II)(DO_XH)_2$ [M(II) being nickel(II), palladium(II) and copper(II); DO_xH is the coordinated dimethylglyoxime and diphenylglyoxime species].



E = Al, B, Zn; *n* is the E metal valence

R = CH_3, C_2H_5, C_6H_5, $i\text{-}C_4H_9$, Cl

Figure 1 Formula for new class of compounds.

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Table 1 Analysis, molecular weight and characteristics of products synthesized

Compound	Molecular weight (calc./found)	Colour	Analysis (%)									
			C		H		Al		N		M	
			calc.	found	calc.	found	calc.	found	calc.	found	calc.	found
$Ni(DMG)_2Al_2(i\text{-}C_4H_9)_4$	569/587	orange	50.61	50.30	8.43	8.58	9.49	9.45	9.84	9.62	10.31	10.31
$Pd(DMG)_2Al_2(i\text{-}C_4H_9)_4$	792/940	green yellowish	46.70	46.63	7.78	7.63	8.75	8.70	9.07	9.30	17.25	17.29
$Ni(DMG)_2Al_2\ (C_6H_5)_4$	649/–	brown	59.16	58.80	4.93	5.11	8.32	8.32	8.62	8.61	9.09	9.10
$Pd(DMG)_2Al_2\ (C_6H_5)_4$	696/–	greenish grey	55.09	55.05	4.59	4.58	7.74	7.70	8.03	8.02	15.35	16.11
$Ni(DPG)_2Al_2(i\text{-}C_4H_9)_4$	817/805	dark red	64.62	64.23	6.83	6.85	6.61	6.66	6.85	6.81	7.22	7.17
$Pd(DPG)_2Al_2(i\text{-}C_4H_9)_4$	865/856	green yellowish	61.04	60.84	6.47	6.45	6.24	6.26	6.47	6.43	12.02	12.13
$Ni(DPG)_2Al_2\ (C_6H_5)_4$	897/–	brown	69.56	69.31	4.45	4.42	6.02	6.15	6.24	6.21	6.57	6.34
$Pd(DPG)_2Al_2\ (C_6H_5)_4$	945/–	grey	66.03	65.94	4.23	4.21	5.71	5.82	5.92	5.88	11.32	11.18

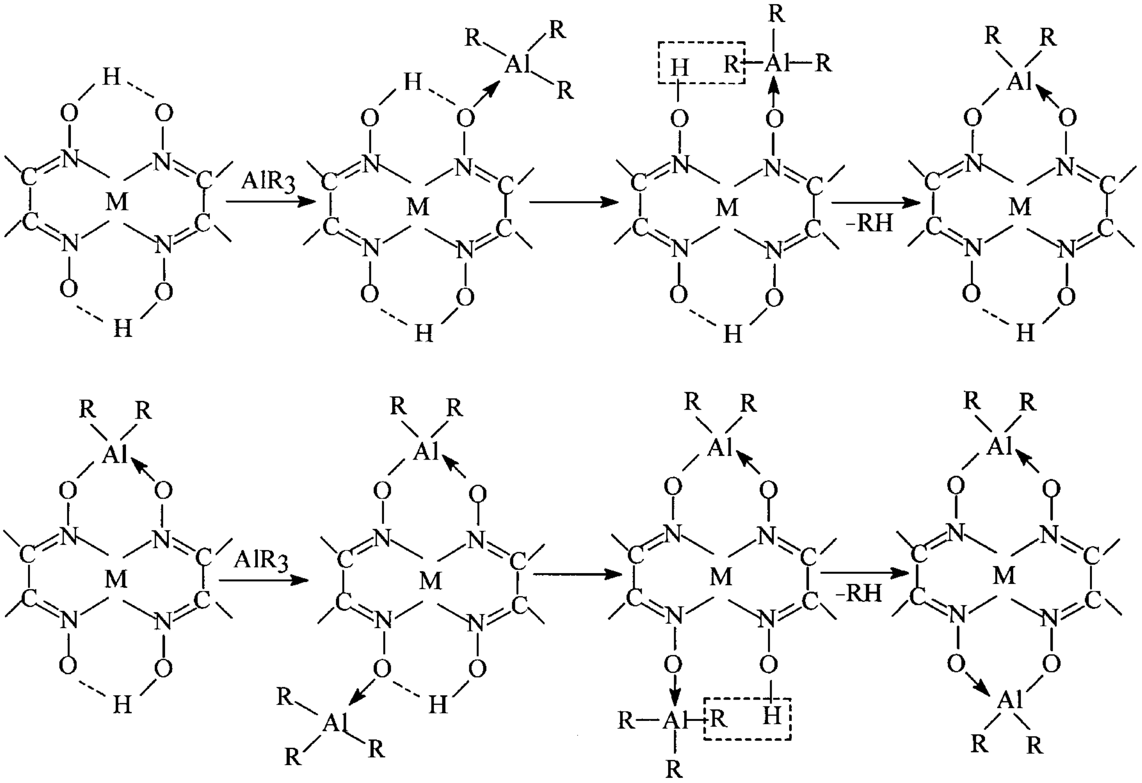

Figure 2 Mechanism for formation of $M(II)(DO_x)_2Al_2R_4$.

2. EXPERIMENTAL

2.1 Measurements

IR spectra were recorded on a Specord M90 Carl Zeiss spectrophotometer by using the KBr pellet technique. X-ray diffraction patterns of compounds were obtained by the powder method on a TUR M-60 apparatus, using Cu K_α radiation. Magnetic properties were determined by means of a Gouy balance in a non-homogeneous magnetic field. Molecular masses of compounds with isobutyl groups were determined by cryoscopic measurements in benzene and are presented in Table 1. The molecular masses of derivatives with phenyl groups could not be determined, since these compounds are not totally soluble in benzene. The presence of butyl radicals in the soluble compounds synthesized was revealed using a Jeol 60 MHz NMR spectrometer, with TMS as the internal reference, at room temperature. The results of the NMR study of these compounds will be published in a forthcoming paper.

2.2 Synthesis

2.2.1 $M(II)(DO_xH)_2$

These were synthesized according to methods reported in the literature.[4] The working procedure for obtaining triphenylaluminium was described in a previous paper.[5] The solvents used were purified by distillation on metallic sodium. All reactions between $M(II)(DO_xH)_2$ and AlR_3 and the handling of the new products were carried out in an inert (nitrogen or argon) and dry atmosphere.

2.2.2 $M(II)(DO_x)_2Al_2(C_6H_5)_4$

To a $Al(C_6H_5)_3$ solution in benzene, in a glass apparatus, a suspension of the $M(II)(DO_xH)_2$ in benzene was added. The amount of triphenylaluminium taken was somewhat larger than the 1:2 ratio (1.5:2) required by the reaction stoichiometry. The reaction was carried out at room temperature, as well as by heating for several hours at solvent reflux temperature. The powder resulting from the reaction is insoluble in benzene and was separated by decanting. The compounds in the solid state

Table 2 IR absorption characteristics (values in cm^{-1})

Compound	(OH)	(C=N)	(NO)	(OH)
$Ni(DMGH)_2$	2350;1780	1560	1235	900
$Pd(DMGH)_2$	2340;1710	1550	1250	910
$Ni(DMG)_2Al_2(i\text{-}C_4H_9)_4$	–	1600	1230	–
$Pd(DMG)_2Al_2(i\text{-}C_4H_9)_4$	–	1630	1250	–
$Ni(DMG)_2Al_2(C_6H_5)_4$	–	1590	1240	–
$Pd(DMG)_2Al_2(C_6H_5)_4$	–	1590	1230	–
$Ni(DPG)_2Al_2(i\text{-}C_4H_9)_4$	–	1580	1295	915
$Pd(DPG)_2Al_2(i\text{-}C_4H_9)_4$	–	1575	1240	990
$Ni(DPG)_2Al_2(C_6H_5)_4$	–	1590	1290	998
$Pd(DPG)_2Al_2(C_6H_5)_4$	–	1580	1290	1070

were washed several times with hot benzene to remove any traces of $Al(C_6H_5)_3$. The products were dried in vacuum.

2.2.3 $M(II)(DO_x)_2Al_2(i\text{-}C_4H_9)_4$

These were obtained by adding triisobutylaluminium solution in toluene to the dried and crushed powder of the $M(II)(DO_xH)_2$. The amount of chelate taken was somewhat larger than the 1:2 ratio (1.5:2) required by the reaction stoichiometry. The reaction mixture was heated and stirred for several days at room temperature. The excess unreacted dioximate was separated from the liquid fraction by decanting. The solid compounds was separated from the liquid fraction by removing the solvent under vacuum.

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

3. RESULTS AND DISCUSSION

The formation of $M(II)(DO_x)_2Al_2R_4$ can be rationalized by an insertion of AlR_2 into $M(II)(DO_xH)_2$. The formation of $M(II)(DO_x)_2Al_2R_4$ can be summarized by Eqn [1]:

$$\begin{aligned} &M(II)(DO_xH)_2 + 2M(II)(DO_x)_2Al_2R_4 \\ &\quad \rightarrow M(II)(DO_x)_2Al_2R_4 + 2RH \end{aligned} \qquad [1]$$

where $R = i\text{-}C_4H_9$ and C_6H_5. A six-stage mechanism, comprising four intermediates, is suggested (see Fig. 2).

The first reaction step involves the formation of an unstable adduct between a bisdioximate molecule and a molecule of the AlR_3 derivative, thereby forming a coordinate O → Al bond. As a result of the donor–acceptor bond between aluminium and the oxygen of the coordinated oxime, the hydrogen bond is weakened. The adduct formation causes the appearance of a free hydroxyl group, which has a more mobile hydrogen atom than in the starting chelate. Therefore, it would be expected that this more mobile hydrogen atom would react quickly, resulting in the formation of a substituted organoaluminium derivative and the elimination of a hydrocarbon molecule. Similar explanations can be given for the subsequent steps.

Though, to date, we have no firm proof, we believe that the aluminium atom holds a nearly symmetrical position between the two oxygen atoms, owing to an intramolecular rearrangement. Chemical analyses of the powders (Table 1) show that the Al/M(II) ratio is two for all products, this value showing the maximum number of AlR_3 molecules entering into reaction with each molecule of bisdioximate under the above reaction conditions. The aluminiumorganic derivatives of the bisdioximates with $Al(i\text{-}C_4H_9)_2$ groups are soluble in organic solvents that do not contain chlorine atoms or other functional groups that might react with the compounds. Compounds with $Al(C_6H_5)_2$ groups are slightly soluble in the same solvents. They are decomposed by water, acids and bases.

The characteristic IR absorptions[15,16,28] of this series are given in Table 2, together with those of the original chelates. The 3500–650 cm^{-1} spectral range is characterized by the disappearance of the absorption maximum of the OH groups of the bioximates. Similarly, the band appearing as a shoulder in the 1600–1800 cm^{-1} range, with variable intensity and position in the initial materials, is absent in the compounds with aluminium.

The interpretation and the assignment of absorption bands in the 700–300 cm^{-1} range is difficult, due to lack of premiers spectral studies in this area. IR absorptions in this range of aluminiumorganic derivatives of coordinated $DMGH_2$ and $DPGH_2$ exhibit bands at about 490, 520 and 680 cm^{-1}. These absorption bands[9,10,28] can be attributed to the Al—O, M—N and M—C bonds.

The derivatives with $Al(i\text{-}C_4H_9)_2$ groups have a crystalline ordered structure. X-ray diffraction spectra of compounds with phenyl groups show that they are typically amorphous, differing fundamentally from the starting compounds. All new compounds are diamagnetic. The diamagnetism of the compounds synthesized suggests that the planar structure of the chelates is not changed by substitution of the hydrogen bridges by the AIR_2 groups.

$Ni(II)(DMGH)_2$ and $Pd(II)(DMGH)_2$ are very stable combinations, compared with Cu(II) $(DMGH)_2$, and this difference probably determines their different behaviour from that of the aluminium organic derivatives. This different behaviour of $Cu(II)(DMGH)_2$, (it is reduced to Cu(0)) compared with that of the AIR_3 derivatives, is not observed at the ligand site, but at the central metallic ion, which, in reaction with AIR_3, leaves the coordination sphere as a pure metal (Cu(0)) or is reduced to a valence of one. The reaction by which the reduction of the copper takes place implies a role for water molecules. The existence of water in the system is not excluded, as even $Cu(II)(DMGH)_2$ binds a water molecule, removable with difficulty.

Studies carried out to date on compounds resulting from the reaction of bisdimethylglyoximates and bisdiphenylglyoximates of some transition metals with aluminiumorganic derivatives lead to the following conclusions:

- aluminiumorganic compounds of coordinated oximes result from the substitution of O—H···O hydrogen bonds, existing in chelates, by O—Al—O aluminium bridges;
- the substitution of hydrogen bridges by aluminium bridges determines the ring closure of hexa-atomic metallocycles without carbon atoms, leading to the formation of macrocyclic compounds.

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