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Aluminiumorganic compounds of coordinated salicylaldoxime and their adducts with nitrogen Lewis bases

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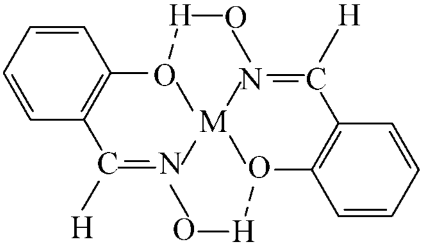
Aluminiumorganic compounds of a coordinated salicylaldoxime resulted from reaction of $M(II)(SALOxH)_2$ (where M(II) = Ni(II), Pd(II) and Cu(II); SALOx represents the divalent radical of the salicylaldoxime) with AlR_3(R = CH_3,C_2H_5,i-C_4H_9,C_6H_5 and Cl). Copper(II) bis-salicylaldoximate reacting with Al(i-C_4H_9)$_3$ does not form a compound similar to those obtained with nickel and palladium. Aluminiumorganic compounds of the coordinated salicylaldoxime result from the substitution of O—H···O hydrogen bonds, existing in chelates, 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. The new aluminiumorganic compounds form adducts with amine. Among the amine adducts, only the adducts with pyridine were isolated to confirm their formula and the mode of binding. Copyright © 2001 John Wiley & Sons, Ltd.

KEYWORDS: salicylaldoxime; chelate; triisobutylaluminium; triphenylaluminium; hydrogen bridges

The theoretical and practical aspects of the use of salicylaldoxime ($SALOxH_2$) in chemical analysis have been discussed in several papers.[1–8] Those papers also dealt with the structure and changes taking place on chelation by different metallic ions. The oximes,[9–19] through a rigorous control of precipitation pH, form selectively, extremely stable coloured chelate compounds with nickel(II), palladium(II) and copper(II) ions. The bis-salicylaldoximates studied by us correspond to the formula:



where M = Ni(II), Pd(II), Cu(II).

Some of the characteristic reactions of the functional groups of the free ligands are masked or diminished through coordination, which may also be supposed to occur in the case of the salicylaldoxime. We have synthesized a series of i-butyl- and phenyl-aluminiumorganic derivatives of the nickel(II), palladium(II) and copper(II) bis-salicylaldoximates, as well as their adducts with amines.

EXPERIMENTAL

Measurements

IR spectra were recorded on a Specord M 90 Carl Zeiss spectrophotometer by the KBr pellet technique. X-ray diffraction images of the compounds were obtained by the Debye Scherer method with URK-5 and TUR M-60 apparatus by using Cu Kα radiation and a nickel filter. 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. Magnetic properties were determined by means of a Gouy balance in a non-homogeneous magnetic field. The presence of C_4H_9 radicals only in the soluble compounds synthesized was revealed using a Jeol 60 MHz NMR spectrometer, with tetramethylsilane as the internal reference, at room tempera-

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ture. The results of the NMR study of these compounds will be publish in a future paper. They can be summarized as follows: The $M(II)(SALOx)_2Al_2(i\text{-}C_4H_9)_4$ (M(II) = Ni, Pd) derivatives exhibit a 1:2 ratio between the protons of $M(II)(SALOxH)_2$ and the methyl protons of the isobutyl radical, according to the proposed structure. The proton signals from $M(II)(SALOxH)_2$ shift downfield in the new compounds due to the formation of Al—O bonds. Also, the formation of Al—O bonds determines the downfield shift of the isobutyl proton signals in these compounds. The nature of the central metal does not affect the isobutyl proton signals.

Synthesis

M(II)(SALOxH)₂

The nickel(II), palladium(II), and copper(II) bis-salicylaldoximates were obtained by methods given elsewhere.[1] $Al(C_6H_5)_3$ was obtained starting from $Hg(C_6H_5)_2$ and aluminium powder, by heating to 130–140 °C, and was purified by recrystallization from benzene and *n*-hexane. $Al(i\text{-}C_4H_9)_3$ was purchased from Merck. All reactions and the handling of the new compounds were carried out in an inert and moisture-free atmosphere.

M(II)(SALOx)₂Al₂(C₆H₅)₄

The syntheses of the aluminiumorganic derivatives of the nickel(II), palladium(II) and copper(II) bis-salicylaldoximates were carried out in Schlenk vessels by adding a benzene solution of $Al(C_6H_5)_3$ to the finely ground and dried chelate powders. The amount of $Al(C_6H_5)_3$ taken was somewhat larger than the 1:2 ratio (1.5:2) required by the reaction stoichiometry. The reactions were carried out at room temperature, as well as by heating for several hours, at the solvent reflux temperature. In both cases, coloured powders, insoluble in benzene, were obtained. These were washed several times with hot benzene to remove any traces of $Al(C_6H_5)_3$. The products were dried in vacuum. Independently of processing temperature, the resulting compounds have the same chemical characteristics and structure.

M(II)(SALOx)₂Al₂(i-C₄H₉)₄

These compounds were obtained by adding triisobutylaluminium solution in *n*-heptane to a dried and crushed powder of $M(II)(SALOxH)_2$. The amount of chelate taken was somewhat larger than the 1:2 ratio (1.5:2) required by the reaction stoichiometry. During the reaction the flask was thoroughly cooled with ice. After the reaction was finished the reaction vessel was kept at low temperature for 20 min. The resulting compounds are soluble in *n*-heptane. The solvent was removed by evaporation in vacuum to obtain coloured powders of the new compounds.

The reaction between $Cu(II)(SALOxH)_2$ and $Al(i\text{-}C_4H_9)_3$ took place under the same conditions as for the nickel (II) and palladium(II) derivatives. After the reaction was finished the reaction vessel was kept in ice for a few hours, a solid fraction during which time (insoluble in *n*-heptane) and a liquid orange-coloured fraction separated. The liquid phase was concentrated in vacuum until complete removal of the solvent. The solid compound thus obtained does not contain copper. It has a chemical composition similar to that obtained by direct reaction between $SALOxH_2$ and $Al(i\text{-}C_4H_9)_3$. The solid fraction was washed several times with *n*-heptane and dried under vacuum. The product obtained is black in colour and does not contain $Al(i\text{-}C_4H_9)_2$ groups.

M(II)(SALOx)₂Al₂R₄·2L

The adducts with amine were obtained by two methods. In the first method the previously dried amine (dried on KOH and freshly distilled) was added to the new compounds in powder form. The powders are solvated by the amines and changed their colour. The reaction was accompanied by a slight release of heat and did not require cooling of the reaction vessel. The separation of the adducts was carried out by removing the amine by evaporation in vacuum.

In the second method, the reaction took place directly between AlR_3 and $M(II)(SALOxH)_2$ in the amine solution. In this case, the reaction vessel was cooled with ice. The excess amine was removed by evaporating at low pressure. Whichever method was used the resulting compounds have the same qualities and chemical structure. Though adducts are humidity resistant, the reactions were carried out in an inert and moisture-free atmosphere.

The chemical analysis and characteristics of the compounds synthesized are given in Table 1, but only the adducts with pyridine are listed.

RESULTS AND DISCUSSION

Determinations of the structure have pointed out that in bis-salicylaldoximates the hydrogen bonds are very short and probably asymmetrical. This asymmetry may be explained through the interpolation of the hydrogen between the oxygen atom of the oximic group and the oxygen atom of the phenolic group.

Some of the characteristic reactions of the functional groups of the free ligands are masked or diminished through coordination. The lack of reactivity of the OH groups in the coordinated oximes was caused by the O—H···O intramolecular hydrogen bonds existing in these compounds.[11,14,20–26] These changes were not much studied. We have synthesized a series of phenylaluminiumorganic derivatives of the nickel(II), palladium(II), and copper(II) bis-salicylaldoximates. The formation may be described by Eqn. (1):

$$M(II)(SALOxH)_2 + 2AlR_3 \longrightarrow M(II)(SALOx)_2Al_2R_4 + 2RH \quad (1)$$

where M = Ni, Pd and Cu; R = C_6H_5 and $i\text{-}C_4H_9$. A six-stage mechanism, comprising four intermediates, is suggested (see Fig. 1).

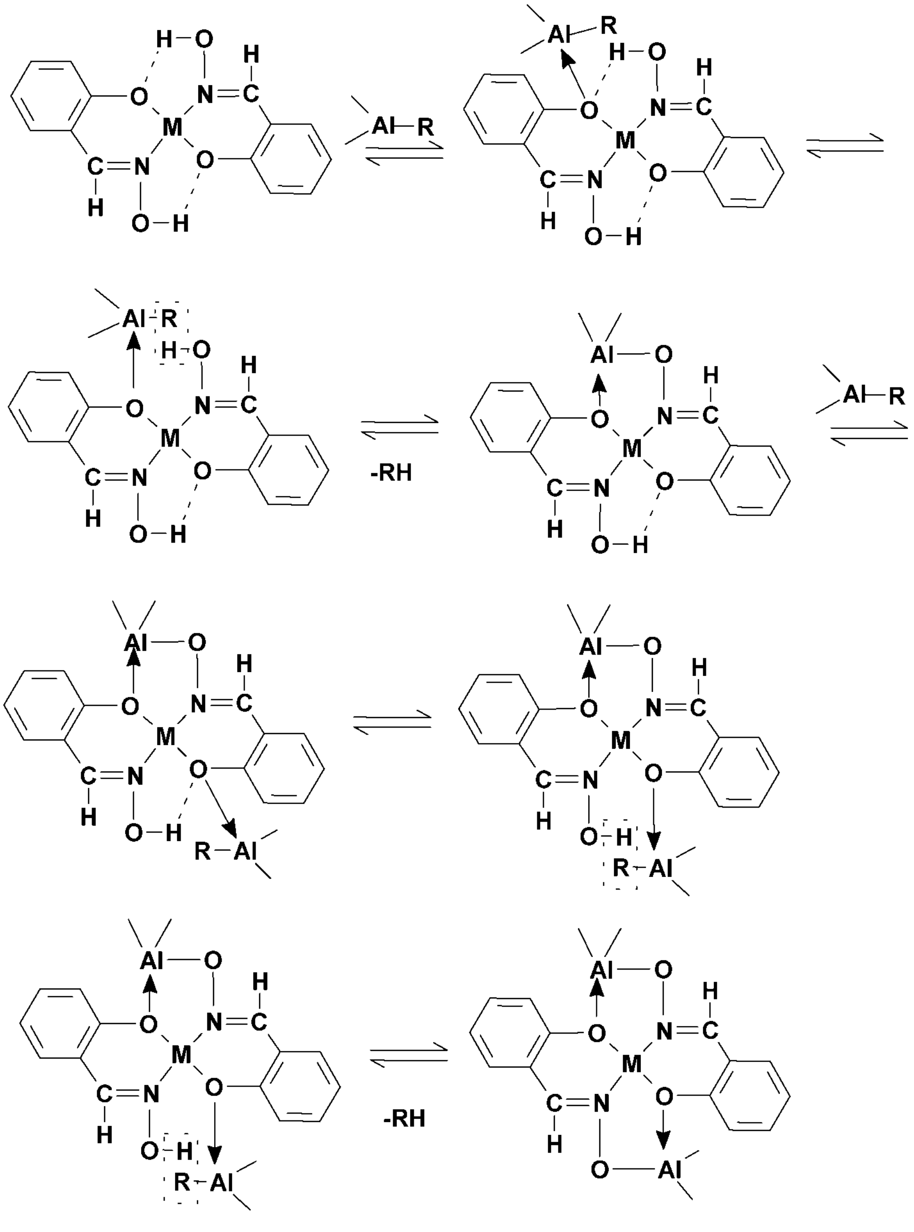


Figure 1. Mechanism for formation of M(II)(SALOx)$_2$Al$_2$R$_4$.

The first reaction step involves the formation of an unstable adduct between a bis-salycyldioximate molecule and a molecule of AlR$_3$, and thus a coordinate O $\rightarrow$ Al bond is formed. 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. This highly mobile hydrogen atom reacts quickly, resulting in the formation of a substituted organoaluminium derivative and elimination of a hydrocarbon molecule. Similar explanations can be given for the succeeding steps.

The final formula is corroborated by chemical analyses (Table 1) and the magnetic characteristics, as well by the IR spectra of the compounds (Table 2).

Cu(II)(SALOxH)$_2$ reacting with Al(i-C$_4$H$_9$)$_3$ has a different behaviour than that of similar nickel(II) and palladium(II) derivatives. Under the working conditions mentioned, we have obtained the aluminiumorganic derivative of the uncoordinated salicylaldoxime. The result of the reaction is as expected, if we take into account the reduction character of the aluminiumorganic derivative and the ease with which bivalent copper passes to a lower valence.[27]

Table 2 gives the approximate values of the characteristic absorption maxima in the 1650–650 cm^{-1} range assigned to the corresponding vibrations. The high frequencies found

Table 1. Analyses and characteristics of the products synthesized

Compound	Colour	Analysis, calc. (found) (%)				
		C	H	Al	N	M
$Ni(C_7H_5O_2N)_2Al_2(C_6H_5)_4$	Yellowish-brown	66.02 (66.04)	4.34 (4.32)	7.81 (7.84)	4.05 (4.05)	8.50 (8.51)
$Pd(C_7H_5O_2N)_2Al_2(C_6H_5)_4$	Grey	61.75 (61.80)	4.06 (4.08)	7.31 (7.31)	3.78 (3.75)	14.40 (14.43)
$Cu(C_7H_5O_2N)_2Al_2(C_6H_5)_4$	Green	65.56 (65.60)	4.31 (4.32)	7.76 (7.75)	4.02 (4.04)	9.13 (9.13)
$Ni(C_7H_5O_2N)_2Al_2(C_6H_5)_4 \cdot 2Py$	Yellow	67.88 (67.85)	4.71 (4.73)	6.36 (6.36)	6.59 (6.60)	6.92 (6.96)
$Pd(C_7H_5O_2N)_2Al_2(C_6H_5)_4 \cdot 2Py$	Grey	64.25 (64.30)	4.46 (4.45)	6.02 (6.00)	6.24 (6.25)	11.87 (11.90)
$Cu(C_7H_5O_2N)_2Al_2(C_6H_5)_4 \cdot 2Py$	Yellow–green	67.48 (67.50)	4.68 (4.65)	6.32 (6.35)	6.56 (6.58)	7.44 (7.44)
$Ni(II)(C_7H_5O_2N)_2Al_2(i\text{-}C_4H_9)_4$	Brown	58.91 (58.80)	7.52 (7.48)	8.83 (8.85)	4.58 (4.55)	9.65 (9.63)
$Pd(II)(C_7H_5O_2N)_2Al_2(i\text{-}C_4H_9)_4$	Grey–black	54.62 (54.53)	6.97 (6.97)	8.19 (8.23)	4.42 (4.24)	16.23 (16.18)
$Ni(II)(C_7H_5O_2N)_2Al_2(i\text{-}C_4H_9)_4 \cdot 2Py$	Greenish brown	62.41 (62.10)	7.28 (7.28)	7.02 (7.13)	7.28 (7.28)	7.67 (7.65)
$Pd(II)(C_7H_5O_2N)_2Al_2(i\text{-}C_4H_9)_4 \cdot 2Py$	Grey–brown	58.75 (58.44)	6.85 (6.85)	6.60 (6.68)	6.85 (6.85)	13.09 (13.05)

The reaction between $Cu(II)(SALOxH)_2$ and $Al(i\text{-}C_4H_9)_3$ took place under the same conditions as for the nickel (II) and palladium(II) derivatives. In these conditions was obtained a solid compound that does not contain copper. It has a chemical composition similar to that obtained by direct reaction between $SALOxH_2$ and $Al(i\text{-}C_4H_9)_3$. The $Cu(C_7H_5O_2N)_2Al_2(C_6H_5)_4$ and $Cu(C_7H_5O_2N)_2Al_2(C_6H_5)_4 \cdot 2Py$ compounds are paramagnetic.

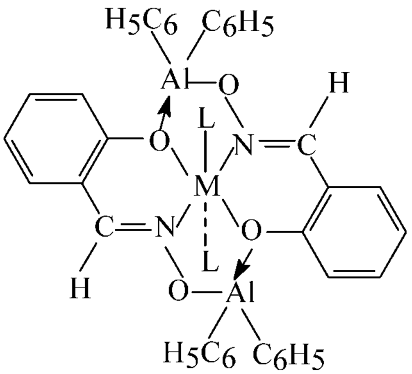
between 1650 and 1640 cm^{-1} in the salicylaldoximates (due to the OH groups) are not found in the aluminiumorganic compounds of the chelates, thus confirming the substitution of the hydrogen by $A1R_2$ groups. The fact that the characteristic absorptions[28] of the C=N groups are only very slightly affected by substitution of the hydrogen suggests that this group does not change its reactivity. However, substitution of the hydrogen by the $A1R_2$ group changes the position of the N−O absorption maximum, displacing it towards higher frequencies. This displacement towards higher frequencies is probably due to a polar structure.

By comparing the IR spectra of the $Pd(II)(C_7H_5O_2N)_2Al_2(i\text{-}C_4H_9)_4$ and the compounds with $Al(C_6H_5)_2$ groups, we notice that the organic groups of the aluminium atom do not greatly affect the absorption spectra of the chelates in the 1650–650 cm^{-1} range. Also, there are no measurable differences between the spectra of the compounds with aluminium and their adducts with pyridine in this range.

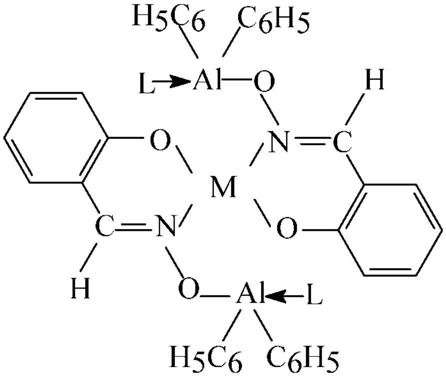
The X-ray diffraction images of the new compounds are characteristic of amorphous substances. Hydrolysis restores the crystalline structure, owing to a reconfiguration of the chelates. The diamagnetism of the new compounds (not those of copper) suggests conservation of the square-planar structure of the chelates, even after creation of the chelate–A1R bond. The aluminiumorganic salicylaldoximate compounds synthesized react with amines to form stable compounds in the solid state. Our attempts to obtain compounds corresponding to the formula a Scheme 1, through the reaction of the organoaluminium derivatives of the nickel(II), palladium(II), and copper(II) salicylaldoximates with amines (pyridine, aniline, picoline, lutidine), did not produce paramagnetic compounds corresponding to the

Table 2. IR absorption spectra (cm^{-1}) of $M(C_7H_5O_2N)_2Al_2R_4$

Nickel		Palladium		Copper	Assignment
$(i\text{-}C_4H_9)$	(C_6H_5)	$(i\text{-}C_4H_9)$	(C_6H_5)	(C_6H_5)	
1635	1610	1620	1600	1618	(C=N)
1553	1558	1558	1555	1560	Distorsion of (C=N)
1490, 1460	1496	1495, 1458	1492	1500	Ortho
1363, 1327	1460		1480	1464	
1293	1322	1338, 1302	1300	1303	(C−H) in the plane
1230, 1205	1280	1215	1200	1215	(N−O)
1152, 1124	1158	1157, 1120	1150	1160	Vibration due to the benzene
1068	1125	1060	1122	1135	Ring
1025	1040	1040	1035	1045	(C−O)
920	924	924	922	938	(N−O)
850, 752	760	820, 750	760	775	Stretching (CH)



Scheme 1.



Scheme 2.

octahedral configuration. Similar explanations can be given for the formation of $Ni(II)(C_7H_5O_2N)_2Al_2(i\text{-}C_4H_9)_4 \cdot 2Py$ and $Pd(II)(C_7H_5O_2N)_2Al_2(i\text{-}C_4H_9)_4 \cdot 2Py$.

The diamagnetism of these compounds (not copper) forces us to suppose that the corresponding adducts are obtained through an acid–base Lewis reaction[29] in which the acid part is played by the aluminium atom of the aluminiumorganic salicylaldoximate derivatives (Scheme 2).

The square-planar structure is thus not changed, and consequently neither is the diamagnetism. The ease with which the adducts with amines are obtained is a confirmation of the fact that the aluminium atom is not strongly bound to the phenolic oxygen atom. The number of amine molecules bound to the solid compound is confirmed by chemical analysis (Table 1).

Studies carried out until now[30] on compounds resulting from the reaction of dioximates of some transition metals with aluminiumorganic derivatives lead to the conclusion that the aluminiumorganic compounds of coordinated oximes result from the substitution of O—H…O hydrogen bonds, existing in chelates, by O—Al—O aluminium bridges.

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