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Zinc organic compounds of some oximes coordinated with nickel(II), palladium(II) and copper(II) ions

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Coordinated oximes with nickel(II), palladium(II) and copper(II) ions proved capable of giving substitution reactions with a series of zinc organic compounds. Studies have revealed that, in the cases of dimethylglyoxime and salicylaldoxime, the reaction products result from substitution of the O—H···O hydrogen bridges existing in such compounds by O—Zn—O bridges. All compounds reported in this paper were separated as colored powders and characterized by elemental analyses, IR spectroscopy, X-ray diffraction and magnetic measurements. The new zinc organic compounds form amine adducts. Among the amine adducts, only those with pyridine were isolated and characterized. Copyright © 2001 John Wiley & Sons, Ltd.

KEYWORDS: dimethylglyoxime; salicylaldoxime; diphenylzinc; hydrogen bridges; zinc organic compounds

The reactivity of free and coordinated oximes with bivalent transition metals has been the object of several papers.[1–14] Dimethylglyoxime ($DMGH_2$) and salicyaldoxime ($SALOxH_2$) are two important organic reagents used in analytical chemistry. The importance of the $DMGH_2$ and $SALOxH_2$ compounds goes beyond the field of qualitative and quantitative analytical chemistry, as these compounds are used in different catalytic systems involving polymerization, hydrogenation, oxidation and reduction. The oximes,[9,11,14–22] through a 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 oxime with these metals changes the characteristics of the ligand. Some of characteristic reactions of the functional groups of the ligands are masked or diminished through coordination.[1,5,7–12] The lack of reactivity of the OH groups in the coordinated oximes was assigned to the intramolecular hydrogen bonds,[10,12,14,17,23–27] O—H···O, existing in these compounds.

The reactions of nickel(II), palladium(II) and copper(II) dimethylglyoximates with organometallic compounds[1] have resulted in a new class of compounds corresponding to the formula in Scheme 1.

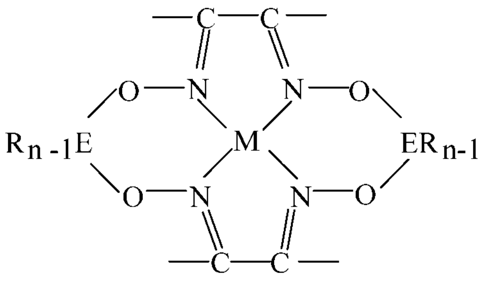
The reaction of zinc organic derivatives with compounds containing active hydrogen atoms[28] has been known for over 100 years. No reports on the chemical interaction between zinc organic derivatives and these compounds of transition metals have so far been found in the literature.

In this paper we report on some compounds resulting from the reaction of $M(II)(DMGH)_2$ and $M(II)(SALOxH)_2$ (M = Ni, Pd, Cu) with $Zn(C_6H_5)_2$ and the characteristic features of the newly synthesized compounds, resulting from IR absorption spectra, X-ray diffraction and from magnetic measurements.

EXPERIMENTAL

Measurements

IR spectra were recorded on a Specord M 90 Carl Zeiss



Scheme 1. E = Zn; *n* = E metal valence; R = C_6H_5; M = Ni, Pd, Cu.

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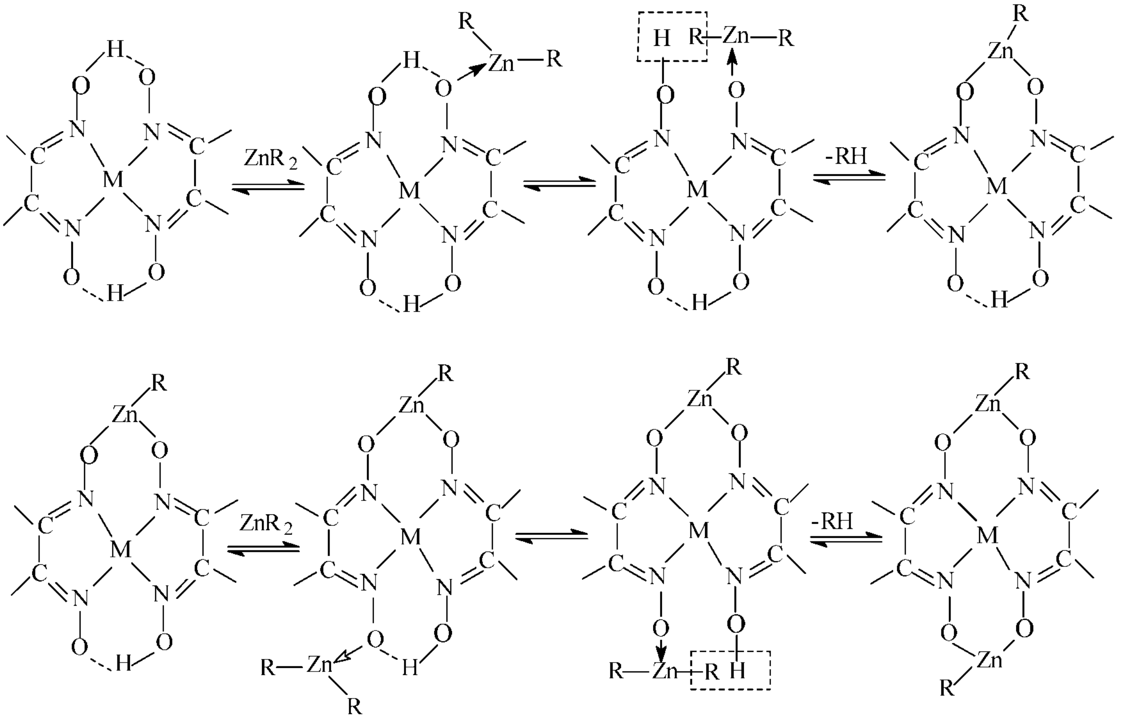

Figure 1. Proposed mechanism for formation of $M(II)(DMG)_2[Zn(C_6H_5)]_2$, where $R = C_6H_5$.

spectrophotometer 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 Kα radiation. Magnetic properties were determined by means of a Gouy balance in a non-homogeneous magnetic field.

Synthesis

All reactions between metaloximates and $Zn(C_6H_5)_2$ and the handling of the new products were carried out in an inert (nitrogen or argon) and dry atmosphere. The solvents used were purified by distillation over metallic sodium.

M(II)(DMGH)$_2$

These compounds were synthesized according to the methods reported in the literature.[4]

M(II)(SALOxH)$_2$

The nickel(II), palladium(II), and copper(II) bis-salicylaldoximates were obtained following the methods given in the

Table 1. The chemical analysis and characteristics of the compounds synthesized

Compound	Color	Analyses (%), calc. (found)				
		C	H	Zn	N	M
$Ni(DMG)_2[Zn(C_6H_5)]_2$	Orange	41.99 (41.60)	3.85 (3.86)	22.88 (22.84)	9.80 (9.40)	10.27 (10.07)
$Pd(DMG)_2[Zn(C_6H_5)]_2$	Yellow	38.76 (38.46)	3.55 (3.84)	21.11 (21.05)	9.04 (8.70)	17.18 (16.90)
$Cu(DMG)_2[Zn(C_6H_5)]_2$	Brown	41.65 (40.90)	3.82 (3.50)	22.69 (22.40)	9.72 (9.50)	11.03 (11.00)
$Ni(DMG)_2[Zn(C_6H_5)]_2 \cdot 2Py$	Orange	49.35 (49.00)	4.38 (4.40)	17.92 (17.50)	11.51 (11.40)	8.05 (7.90)
$Pd(DMG)_2Zn_2(C_6H_5)_2 \cdot 2Py$	Orange	46.32 (46.10)	4.11 (4.20)	16.82 (16.50)	10.80 (10.45)	13.69 (13.50)
$Cu(DMG)_2[Zn(C_6H_5)]_2 \cdot 2Py$	Brown	49.02 (48.90)	4.35 (4.30)	17.80 (17.90)	11.43 (11.30)	8.65 (8.70)
$Ni(II)(SALOx)_2[Zn(C_6H_5)]_2$	Gray violet	50.89 (50.50)	3.26 (3.20)	21.33 (21.19)	4.56 (4.50)	9.62 (9.60)
$Pd(II)(SALOx)_2Zn_2(C_6H_5)_2$	Brown	47.20 (47.00)	3.02 (3.00)	19.66 (19.40)	4.23 (4.10)	16.03 (16.29)
$Cu(II)(SALOx)_2[Zn(C_6H_5)]_2$	Green	50.48 (50.40)	3.23 (3.15)	21.19 (21.33)	4.53 (4.40)	10.35 (10.30)
$Ni(II)(SALOx)_2[Zn(C_6H_5)]_2 \cdot 2Py$	Brown	56.03 (56.00)	3.89 (3.60)	16.99 (16.80)	7.26 (7.10)	7.65 (7.60)
$Pd(II)(SALOx)_2[Zn(C_6H_5)]_2 \cdot 2Py$	Brown	52.75 (52.70)	3.6 (3.60)	15.98 (15.75)	6.83 (6.70)	12.94 (13.00)
$Cu(II)(SALOx)_2[Zn(C_6H_5)]_2 \cdot 2Py$	Green	55.70 (55.60)	3.86 (3.80)	16.88 (16.95)	7.21 (7.10)	8.24 (8.18)

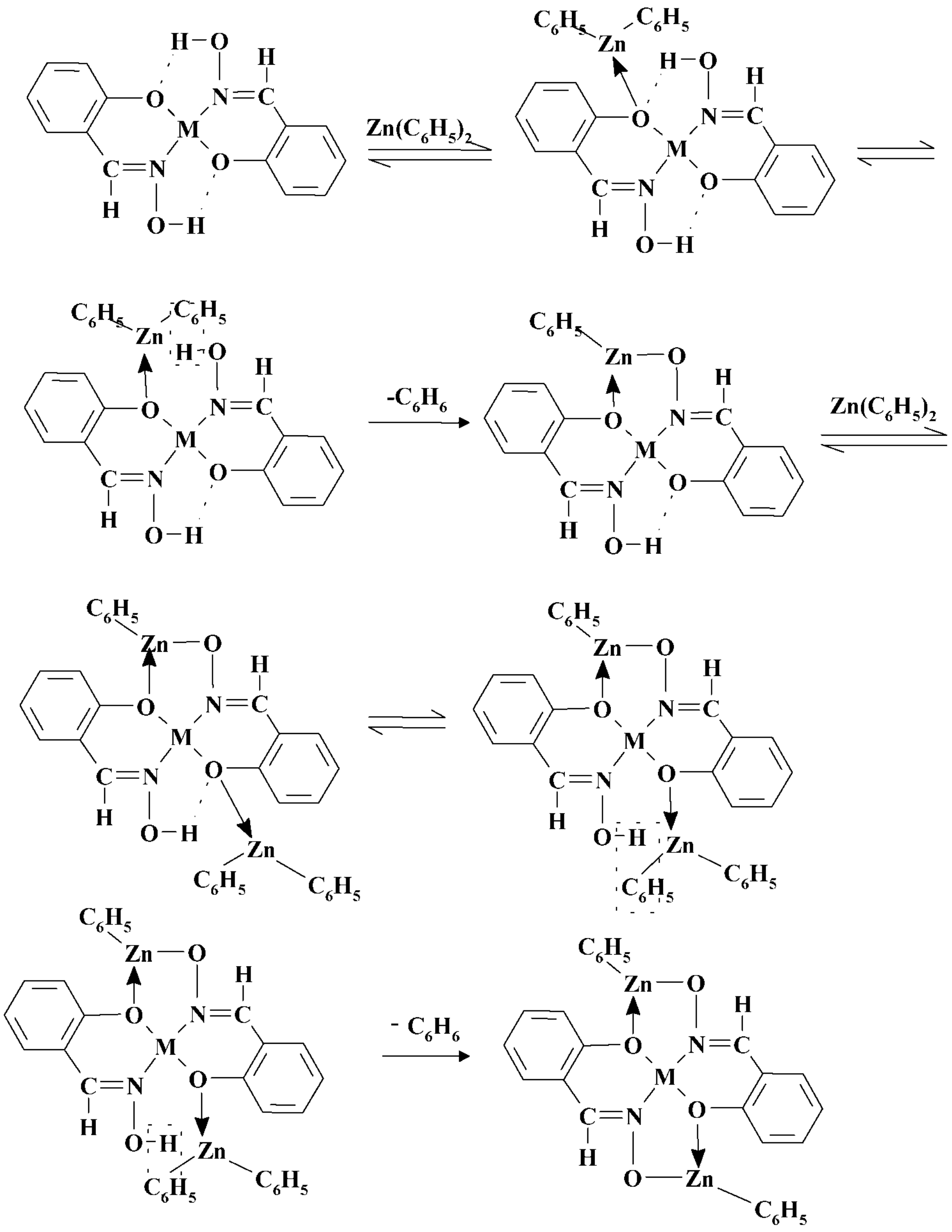

Figure 2. Purposed mechanism for formation of M(II)(SALO$_x$)$_2$[Zn(C$_6$H$_5$)]$_2$.

literature[29,30] and purified by recrystallization from chloroform.

Zn(C$_6$H$_5$)$_2$

This was synthesized according to the Krause and von Grosse[31] method, from diphenylmercury and zinc splinters.

M(II)(DMG)$_2$[Zn(C$_6$H$_5$)]$_2$

To the Zn(C$_6$H$_5$)$_2$ solution in benzene, in a glass apparatus, a suspension of the M(II)(DMGH)$_2$ in benzene was added. The amount of Zn(C$_6$H$_5$)$_2$ taken was somewhat larger than the 1:2 ratio required by the reaction stoichiometry (1:2.5). The reaction was carried out at room temperature, as well as by heating for several hours at solvent reflux temperature. The compounds in the solid state were washed several times with hot benzene to remove any traces of Zn(C$_6$H$_5$)$_2$. The products were dried in vacuum (Table 1).

M(II)(SALOx)$_2$[Zn(C$_6$H$_5$)]$_2$

To the Zn(C$_6$H$_5$)$_2$ solution in benzene a suspension of the metal salicylaldoximate in benzene at 2.5:1 molar ratio was added. A change in color and a slight heating of the reaction vessel took place immediately after mixing the reagents. The mixture was stirred vigorously for a couple of hours at room temperature until complete consumption of the bis-salicylaldoximate had occurred. The solution was concentrated in vacuum. The resulting solid product was separated from the liquid fraction by decanting, washed three or four times with anhydrous ethyl ether and vacuum dried (Table 1).

M(II)(SALOx)$_2$[Zn(C$_6$H$_5$)]$_2$·2Py

Adducts with pyridine of zinc organic derivatives of DMGH$_2$ and SALOxH$_2$ coordinated with nickel(II), palladium(II) and copper(II) ions were obtained by adding pyridine in excess to the solution of M(II)(DMG)$_2$[Zn(C$_6$H$_5$)]$_2$ derivative in benzene {M(II)(DMG)$_2$[Zn(C$_6$H$_5$)]$_2$:amine = 1:8 molar ratio}. The adducts were allowed to deposit and the clear solution was decanted. They were washed several times with ethyl ether and vacuum dried. Although several adducts with amines were studied, only those with pyridine were characterized. The chemical analysis and characteristics of the compounds synthesized are given in Table 1.

RESULTS AND DISCUSSION

The formation of M(II)(DMG)$_2$[Zn(C$_6$H$_5$)]$_2$ and M(II)(SALOx)$_2$[Zn(C$_6$H$_5$)]$_2$ can be summarized by Eqns (1) and (2):

$$\mathrm{M(II)(DMGH)_2 + 2Zn(C_6H_5)_2 \rightarrow}$$

$$\mathrm{M(II)(DMG)_2[Zn(C_6H_5)]_2 + 2C_6H_6} \tag{1}$$

$$\mathrm{M(II)(SALOxH)_2 + 2Zn(C_6H_5)_2 \rightarrow}$$

$$\mathrm{M(II)(SALOx)_2[Zn(C_6H_5)]_2 + 2C_6H_6} \tag{2}$$

For the reaction in Eqn. (1) it seems plausible to suggest a six-stage mechanism comprising four intermediates (see Fig. 1). The first reaction step involves the formation of an unstable adduct between a bisdioximate molecule and a molecule of Zn(C$_6$H$_5$)$_2$ derivative, and thus a coordinate O → Zn bond is formed. As a result of the donor–acceptor bond between zinc and the oxygen of the coordinated oxime, the hydrogen bond is weakened. 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 hydrogen atom, with its higher mobility, would react more quickly and result in the formation of a substituted organozinc derivative and elimination of a hydrocarbon molecule. Similar explanations can be given for the succeeding steps.

The formation mechanism of the M(II)(SALOx)$_2$[Zn(C$_6$H$_5$)]$_2$ is similar to that described for the DMGH$_2$ and the same discussion applies (Fig. 2).

The zinc organic derivatives of the bisoximates with Zn(C$_6$H$_5$) groups are soluble in organic solvents that do not contain chlorine atoms or other functional groups that might react with the compounds. Zinc organic compounds of SALO$_x$H$_2$ and DMGH$_2$ coordinated with nickel(II), palladium(II) and copper(II) ions are readily decomposed by water and alcohols with recovery of the parent chelates.

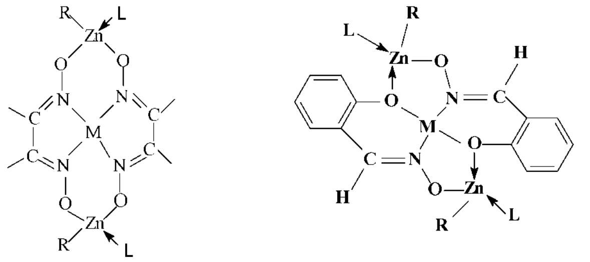

Figure 3. Number of bound amines and bonding manner in the adducts: L = amine; R = C$_6$H$_5$.

The formation of the adducts of M(II)(DMG)$_2$[Zn(C$_6$H$_5$)]$_2$ and M(II)(SALOx)$_2$[Zn(C$_6$H$_5$)]$_2$ with a series of Lewis bases with nitrogen (pyridine, aniline, picoline, lutidine) is weakly exothermal and takes place quite easily, probably owing to the charge in the zinc atom from an unstable three-coordinated state to a stable state in which the zinc atom has the coordination number four. The high chemical stability of the adducts, compared with that of the parent zinc organic derivatives, is probably explained in this manner. The number of bound amine molecules and the bonding manner in the adducts correspond to the formulas given in Fig. 3.

The formation of the adducts produces an intensification in the compound color. The zinc organic derivatives and pyridine-containing adducts shown in Table 1 were isolated as colored powders that were insoluble in liquid hydrocarbons and unstable to water, acids and bases.

The characteristic IR absorptions[15,16,28] of M(II)(DMG)$_2$[Zn(C$_6$H$_5$)]$_2$ are given in Table 2 and compared 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 a variable intensity and position in initial products, is absent in the compounds with zinc. By comparing the IR spectra of these compounds, and the compounds with Zn(C$_6$H$_5$) groups, we notice that the organic groups of the zinc atom do not greatly affect the absorption spectrum of the chelates in the 1650–650 cm^{-1} range. Also, there are no measurable differences

Table 2. IR absorption characteristics (cm^{-1}) of DMGH$_2$ complexes

Compound	(OH)		(C=N)	(NO)	(OH)
Ni(DMGH)$_2$	2350	1780	1560	1235	900
Ni(DMG)$_2$[Zn(C$_6$H$_5$)]$_2$	–	–	1570	1230	–
Pd(DMGH)$_2$	2340	1710	1550	1230	910
Pd(DMG)$_2$[Zn(C$_6$H$_5$)]$_2$	–	–	1660	1235	–
Cu(DMGH)$_2$	2600	1710	1550	1212	860
Cu(DMG)$_2$[Zn(C$_6$H$_5$)]$_2$	–	–	1590	1200	–

Table 3. IR absorption spectra of $M(II)(SALOx)_2[Zn(C_6H_5)]_2$ (cm^{-1})

M = Ni	M = Pd	M = Cu	Assignment
1600	1600	1598	(C=N)
1557	1560	1555	Distortion of (C=N)
1445	1450	1443	Ortho
1340	–	–	
1290	1290	1290	(C–H) in the plane
1200	1200	1200	(N–O)
1125	1130	1123	Vibration due to benzene ring
1020	1020	1018	(C–O)
920	925	920	(N–O)
758	775	760	(CH) out of plane

between the spectra of the compounds with zinc and of their adducts with pyridine in this field.

Absorption bands characteristic of the OH group (Table 3) in $M(II)(SALOxH)_2$ are absent in zinc organic compounds of $SALOxH_2$ coordinated with nickel(II), palladium(II) and copper(II) ions.[32] This absence is the main evidence indicating that the reaction between $M(II)(SALOxH)_2$ and $Zn(C_6H_5)_2$ takes places at the ligand rather than in the main metallic atoms. The positions of absorption maxima of the main ligand (C=O, C=N, NO, ring) are not much changed after substituting hydrogen by the $-ZnC_6H_5$ group.

All the new compounds are diamagnetic, excepting those containing copper. The diamagnetism of the compounds synthesized suggests that the square planar structure and the covalent character of the chelate bonds were not changed by substitution of the hydrogen bridges by $Zn(C_6H_5)$ groups. In the case of the copper derivatives, the paramagnetism is evidence for divalent copper.

Another important result obtained by determining the magnetic properties is the diamagnetism of the adducts with amines, particularly in the case of the nickel derivative. The diamagnetism of the adducts suggests that the ligand is bound to the zinc atom, rather than to the central metallic atom.

The studies carried out here on compounds resulting from the reaction of $M(II)(DMGH)_2$ and $M(II)(SALOxH)_2$ with zinc organic derivatives lead to the following conclusions.

(1) Zinc organic compounds of coordinated oximes result from the substitution of $O-H\cdots O$ hydrogen bonds, existing in chelates, by $O-Zn-O$ zinc bridges.
(2) Substitution of hydrogen bridges in $M(II)(DMGH)_2$ by zinc bridges creates hexa-atomic metallocycles that do not contain carbon atoms.
(3) Substitution of hydrogen bridges in $M(II)(SALOxH)_2$ by zinc bridges creates five-membered metallocycles, $M-O-Zn-O-N$, that do not contain carbon atoms.

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