

Zr (IV) COMPLEXES OF SOME NITROGEN-OXYGEN DONOR LIGANDS (SEMICARBAZONES & SALICYLALDAZINE)

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Abstract

Complexes containing mixed ligands of zirconium (IV) have been synthesized by the reaction of zirconium (IV) nitrate ($Zr(NO_3)_4 \cdot 5H_2O$) with salicylaldazine (SAH_2) and semicarbazone ligands benzaldehyde semicarbazone (BSCH), 4-methoxybenzaldehyde semicarbazone (MBSCH), 2-chlorobenzaldehyde semicarbazone (CISCH) and cinnamaldehyde semicarbazone (CinSCH) forming complexes of the type $[Zr_2(SAH)_2(SCH)_2](NO_3)_8$ and $[Zr_2(SA)_2(SC)_2](NO_3)_2$ in neutral and basic medium respectively. The ligands and their complexes are characterized physico-chemically.

Keywords: ligands, zirconium, semicarbazone, characterization.

Résumé

Des complexes contenant des ligands mixtes de zirconium (IV) ont été synthétisés par la réaction du nitrate du zirconium (IV) ($Zr(NO_3)_4 \cdot 5H_2O$) sur le salicylaldazine (SAH_2) et les ligands semicarbazone benzaldehyde semicarbazone (BSCH), le semicarbazone 4-méthoxybenzaldehyde (MBSCH), le semicarbazone 2-chlorobenzaldehyde (CISCH) et le semicarbazone de cinnamaldehyde (CinSH) formant des complexes du type $[Zr_2(SAH)_2(SH)_2](NO_3)_8$ et $[Zr_2(SA)_2(SC)_2](NO_3)_2$ dans des milieux neutre et basique respectivement. Les ligands et leurs complexes sont caractérisés physico-chimiquement.

Mots clés: ligands, zirconium, semicarbazone, caractérisation.

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ملخص

تم دراسة تكوين معقدات الزركونيوم (IV) مع مزيج من ليكاندات السيميكاربازون (التي تشمل بنز الديهايد السيميكاربازون أو 4 - ميثوكسي بنز الديهايد سيميكاربازون أو 2 - كلوروبنز الديهايد سيميكاربازون أو سينمالديهايد سيميكاربازون) مع الساليسادازين، واقترح الصيغ التالية $[Zr_2(SAH)_2(SCH)_2](NO_3)_8$ و $[Zr_2(SA)_2(SC)_2](NO_3)_2$ للمعقدات الناتجة في كل من المحيط المتعادل والقاعدي على التوالي، وشخصت المعقدات الناتجة باستخدام الأشعة تحت الحمراء وفوق البنفسجية وطيف الرنين النووي المغناطيسي والتحليل الدقيق للعناصر وقياس التوصيلية الكهربائية. **الكلمات المفتاحية:** ليكاندات، زركونيوم، السيميكاربازون، تحليل.

The azines are ligands which coordinate in different manners [1,2]. Number of metal-azine complexes have been studied [3,5].

Semicarbazones are ligands bonding through the nitrogen and oxygen atoms to the central metal ion forming an important class of biologically active ligands and provide models for metal-ligand bonding sites in several enzymes [6]. Semicarbazone complexes of some transition elements have been reported [7,9].

There has been a considerable interest, recently, in the study of mixed ligands complexes of transition and non transition metals [10, 13] due to their important role in biological processes [14].

In view of this, and since mixed ligands complexes with zirconium (IV) ion have not yet been reported, it is a matter of interest to determine the extent to which the biological properties of these ligands would be affected by incorporating the Zr (IV) ion. This information can be gained by biological examination of the various complexes derived from the azine and semicarbazones which would be synthesized.

In the present work, new zirconium (IV) complexes with mixed ligands (salicylaldazine and semicarbazones) have been synthesized and characterized by elemental analysis, molar conductance values, infrared, ultraviolet and nuclear magnetic resonance spectral data. The structures of the ligands are shown in Figure 1.

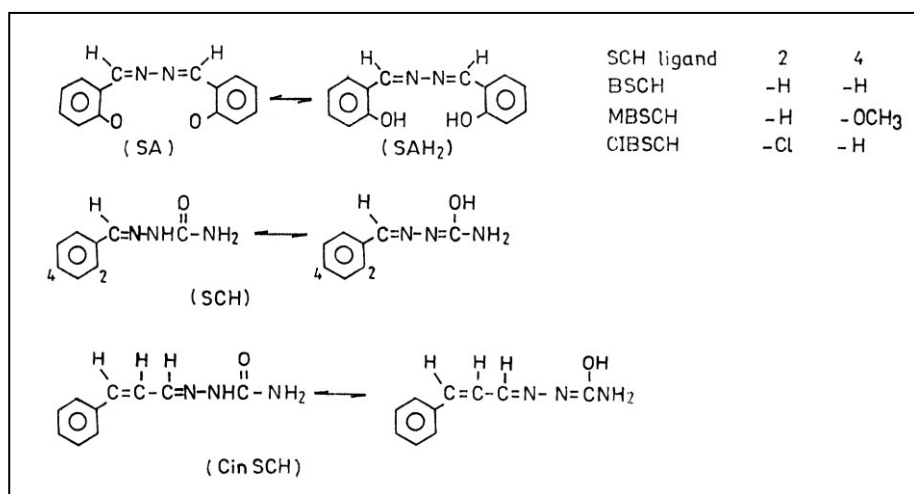


Figure 1: Model structures of the ligands.

EXPERIMENTS

A- Chemicals

The following chemicals are used as supplied: hydrazine sulfate, semicarbazide hydrochloride, ethanol, diethyl ether, ammonium hydroxide (BDH) and dimethylformamide, $Zr(NO_3)_4 \cdot 5H_2O$ (Fluka). Whereas, the chemicals benzaldehyde, cinnamaldehyde, 4-methoxybenzaldehyde (Fluka) and 2-chlorobenzaldehyde (BDH) were used after purification by distillation.

B- Preparation of the ligands

Salicylaldazine have been prepared according to the standard method [15]. A mixture of 2.4g powdered hydrazine sulfate, 18 ml water and 2.4 ml concentrated ammonium hydroxide has been stirred. 52.94g salicylaldehyde was added with continuous stirring over a period of 30-60 minutes. The mixture has been stirred for a further hour. The solid product was separated by filtration, washed with water, recrystallized from 8 ml rectified spirit. Yellow crystals were obtained (m.p.220-222°C).

Semicarbazone ligands have been prepared according to the standard method [9]: 10g of semicarbazide hydrochloride and 15 g sodium acetate dissolved in 100 ml water were mixed with 10 g of the aldehyde. The mixtures were shaken and heated on a water bath for few minutes. On cooling, the solid products were separated, filtered off, washed with water, recrystallized from ethanol and dried. White crystals were obtained (m.p. of BSCH = 200°C, MBSCH= 212°d, CIBSCH= 224°d and CinSCH = 230°C).

C- Preparation of the complexes

1- Neutral medium

Complexes of the types $[Zr_2(SAH)_2(SCH)_2](NO_3)_8$ have been prepared by the reaction of aqueous solution of $Zr(NO_3)_4 \cdot 5H_2O$ with ethanolic solution of salicylaldazine and semicarbazone ligands in 2: 2: 2 molar ratio. The mixtures have been refluxed for 3 hrs, evaporated to about half their volumes and cooled. The resulting products were filtered off, washed with diethyl ether and dried.

2- Basic medium

Complexes of the type $[Zr_2(SA)_2(SC)_2](NO_3)_2$ have been prepared by the reaction of aqueous solution of $Zr(NO_3)_4 \cdot 5H_2O$ with ethanolic solution of salicylaldazine and semicarbazone ligands in 2: 2: 2 molar ratio. NaOH solution was added until the pH of the solutions was 8-8.5. The mixtures were heated for a few minutes then cooled in ice bath. The solid products were filtered off, washed with diethyl ether and dried.

D- Analytical and physical measurements

Elemental analyses for some complexes have been carried out on a CHN analyser, type 1106 (Carlo-Erba) at the Department of Chemistry, College of Science, University of Mosul, Mosul-Iraq. The metal contents have been determined by a standard precipitation method [16].

Molar conductivities of the complexes have been measured in an electrolytic conductivity measuring set LF-42 using $10^{-3}M$ dimethyl formamide (DMF) at room temperature.

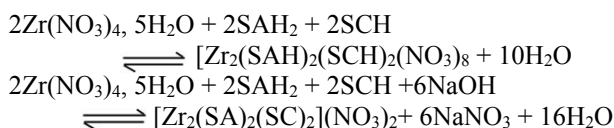
IR spectra of the ligands and their complexes have been recorded on a Pye-Unicam 1100 spectrophotometer in the 400-4000 cm^{-1} rang using KBr pellets.

UV spectra have been recorded on a Pye-Unicam 8000 spectrophotometer for $10^{-5}M$ solution of the ligands and their complexes in dimethylformamide at 25°C, using a 1cm cell.

1H NMR spectra of the ligands and some of their complexes have been recorded on Hitachi Perkin Elmer NMR spectrometer (60 MHz).

RESULTS AND DISCUSSION

The reaction of $Zr(NO_3)_4 \cdot 5H_2O$ with salicylaldazine and the semicarbazone ligands in 2: 2: 2 molar ratio in both neutral and basic medium may be represented by the following reactions:



The resulted complexes are colored, solid, moderately soluble in ethanol, soluble in DMF and soluble in DMSO. The elemental analyses reveal that the complexes have the compositions $[Zr_2(SAH)_2(SCH)_2](NO_3)_8$ and $[Zr_2(SA)_2(SC)_2](NO_3)_2$ in neutral and basic medium, respectively (Table 1). The molar conductivities of the complexes in $10^{-3}M$ DMF are determined, the values shown in Table 1 approach those expected for 1: 8 and 1: 2 electrolytes [17] for complexes of type I and II, respectively.

According to the analytical and physical data of the metal complexes, the central metal atoms are probably hexacoordinated leading to binuclear complexes.

N°	Compound	Color	M.P. °C or d*	Λ_M $\Omega^{-1}\text{cm}^2 \text{mol}^{-1}$ DMF	% Analysis (Cal./Obs.)			Zr
					C	H	N	
1	$[\text{Zr}_2(\text{BSCH})_2(\text{SAH}_2)_2](\text{NO}_3)_8$	Yellow	246d	720	35.57 (35.0)	2.83 (2.81)	9.43 (9.0)	12.29 (12.50)
2	$[\text{Zr}_2(\text{MBSC})_2(\text{SAH}_2)_2](\text{NO}_3)_8$	Yellow	235d	700				
3	$[\text{Zr}_2(\text{CIBSCH})_2(\text{SAH}_2)_2](\text{NO}_3)_8$	Yellow	62	730	33.99 (33.7)	2.57 (2.77)	9.01 (9.87)	11.74 (11.55)
4	$[\text{Zr}_2(\text{CinSCH})_2(\text{SAH}_2)_2](\text{NO}_3)_8$	Yellow	220d	700				
5	$[\text{Zr}_2(\text{BSC})_2(\text{SA}_2)](\text{NO}_3)_2$	Yellow	222	170				
6	$[\text{Zr}_2(\text{MBSC})_2(\text{SA}_2)_2](\text{NO}_3)_2$	Yellow	214	170	47.32 (47.7)	3.43 (3.02)	12.00 (12.08)	15.64 (15.50)
7	$[\text{Zr}_2(\text{CIBSC})_2(\text{SA}_2)_2](\text{NO}_3)_2$	Yellow	236d	150				
8	$[\text{Zr}_2(\text{CinSC})_2(\text{SA}_2)_2](\text{NO}_3)_2$	Yellow	240d	160	48.74 (48.7)	2.36 (3.03)	12.36 (12.08)	16.11 (16.50)

Table 1: Analytical data and physical properties. M.P. = Melting point. d* = decomposed. Λ_M = Molar conductivity.

Compounds*	$\nu_{\text{C=N}}$ azine	$\nu_{\text{N=N}}$ azine	$\nu_{\text{C-O}}$ azine	ν_{OH} azine	$\nu_{\text{C=N}}$	ν_{NH}	$\nu_{\text{C=O}}$	ν_{NH_2}	ν_{NO_3}	$\nu_{\text{Zr=O}}$	$\nu_{\text{Zr=N}}$	Other bands
BSC & SA	1635	950	1290	3130-3180	1580	3500	1675	1450	-----	-----	-----	-----
1	1570	990	1340	3350-3450	1545	3500	1630	1450	1380	450,500	580	-----
5	1580	990	1320	-----	1550	3500	-----	1450	1380	500	560	-----
MBSC & SA	1635	950	1290	3130-3180	1580	3600	1690	1490	-----	-----	-----	C-O-C 1190
2	1575	990	1320	3200-3400	1530	3600	1625	1490	1375	450-505	600	C-O-O 1190
6	1590	990	1350	-----	1520	3600	-----	1490	1375	520	570	C-O-O 1190
CIBSC & SA	1635	950	1290	3130-3180	1590	3510	1690	1480	-----	-----	-----	C-Cl 700
3	1580	980	1325	3200-3400	1560	3510	1640	1480	1380	450,500	590	C-Cl 700
7	1570	990	1355	-----	1550	3510	-----	1480	1380	500	570	C-Cl 700
CinSC & SA	1635	950	1290	3130-3180	1590	3500	1680	1460	-----	-----	-----	-----
4	1575	990	1320	3300-3450	1560	3500	1640	1460	1385	450,490	560	-----
8	1590	990	1330	-----	1550	3500	-----	1460	1385	500	560	-----

Table 2: IR spectra of the ligands and their complexes (frequencies expressed in cm^{-1}).

* Compound 1-8 corresponds to complexes in table 1.

IR spectra

The infra red spectra of semicarbazone ligands show a strong band at $1675\text{-}1690 \text{ cm}^{-1}$ which is attributed to the C=O group [7]. This value shifts towards a lower frequency on coordination, in neutral medium, indicating the formation of a chelation between the oxygen of the carbonyl oxygen and the metal ion [7]. Meanwhile, in basic medium this band disappears in the complexes and a new band is observed at $1340\text{-}1360 \text{ cm}^{-1}$ due to C-O group, thereby establishing coordination of the ligand through enolic oxygen atom [9]. The next strong band at $1580\text{-}1590 \text{ cm}^{-1}$ which is attributed to C=N group [7] shifts towards lower frequency on coordination [7] which is due to the decrease of the bond order as a result of metal nitrogens bond formation [7]. The position of the ligands in the range $3500\text{-}3600 \text{ cm}^{-1}$ remain unaltered in the complexes indicating that there is no coordination through the NH group [9]. The spectra of salicyldazine show a strong band in the region 1635 cm^{-1} as due to the C=N stretching vibration [1]. This band shifts towards a lower frequency (Table 2); this demonstrate that the two azine nitrogens are coordinated to the metal ion. Moreover, the positive shift in N-N vibration on complexation can be added as a further support to the coordination of the azine nitrogen to the metal ion [1]. The next broad band in the region $3130\text{-}3180 \text{ cm}^{-1}$ which is attributed to the stretching vibration of OH

group shifts from the normal position as due to the hydrogen bonding [18]. The broadening of this band is also a consequence of the hydrogen bonding phenomenon. This band, however, is shifted to higher values in the complexes prepared in neutral medium, indicating the breaking down of the hydrogen bonding and formation of the chelate ring between the phenolic oxygen and azine nitrogen to the metal atom. In basic medium, there is no new band in this region, an indication that the OH group of the azine ligand undergoes deprotonation. Furthermore, an important band in the azine ligand is found at 1290 cm^{-1} attributed to the phenolic C-O stretching vibration [8]. This band shifts to a higher frequency on complexation, as a result of bonding of phenolic oxygen to the metal atom [19]. The infra red spectra of the complexes show a strong band at $1375\text{-}1385 \text{ cm}^{-1}$ due to the ionic NO_3^- group [20]. On the other hand, the spectra of all complexes show new bands around $420\text{-}440 \text{ cm}^{-1}$ and $400\text{-}410 \text{ cm}^{-1}$ due to the $\nu_{\text{Zr-O}}$ and $\nu_{\text{Zr-N}}$ respectively [21].

UV spectra

The electronic spectra of the ligands and their complexes in DMF solution have been recorded. The maximum at about $240\text{-}255 \text{ nm}$ in case of the ligands are due to $\pi\text{-}\pi^*$ (benzenoid) electronic transition [7]. This band is almost unchanged in the complexes. Moreover, the

spectra of the ligands show a broad band at about 325-330 nm which is due to the $n-\pi^*$ transition within the $C=N$ chromophore. On complexation, a blue shift (305-515 nm) is observed due to the polarization in the $C=N$ bond caused by the metal-ligand electron interaction during the chelation [5,7]. This shift is due to the donation of nitrogen lone pair of the azomethine group to the zirconium atom [22]. However, in the visible region, at about 405-420 nm, a band is observed which can be related to the charge transfer from ligand to metal orbitals. This ligand metal charge transfer absorption band is possibly responsible for the colors of these complexes [5, 13].

^1H NMR spectra

The coordination of the ligands have been further substantiated by ^1H NMR spectra of the ligands and some of their complexes in deuterated DMSO with internal reference.

In the spectra of the ligands, the protons observed at (δ 8.0-8.1 ppm) shift downfield in the spectra of the complex (δ 8.5-8.7 ppm). This deshielding is possibly due to the donation of the lone pair of electrons by the azomethine nitrogen to the metal atom resulting in the formation of a coordination bond [7]. The other protons of NH and NH_2 remain unaltered in the complexes and confirm the bonding through the $C=O$ and $C-O$ groups in neutral and basic medium, respectively. The proton of OH, observed at δ 5.5 ppm in free SAH_2 ligand, shifts downfield for the complexes in neutral medium. This downfield shift (\sim 3.5 ppm) indicate that the OH group is deshielded, possibly due to the donation of the lone pair of electrons by the oxygen to the metal atom, whereas, for the prepared complexes in basic medium, the OH proton has disappeared, due to the deprotonation that takes place and to the coordination between oxygen and the metal atom.

From the present study, we can conclude that the complexes having the formula $[\text{Zr}_2(\text{SAH})_2(\text{SCH})_2](\text{NO}_3)_8$ and $[\text{Zr}_2(\text{SA})_2(\text{SC})_2](\text{NO}_3)_2$ in neutral and basic medium, have the following proposed geometry (Fig. 2).

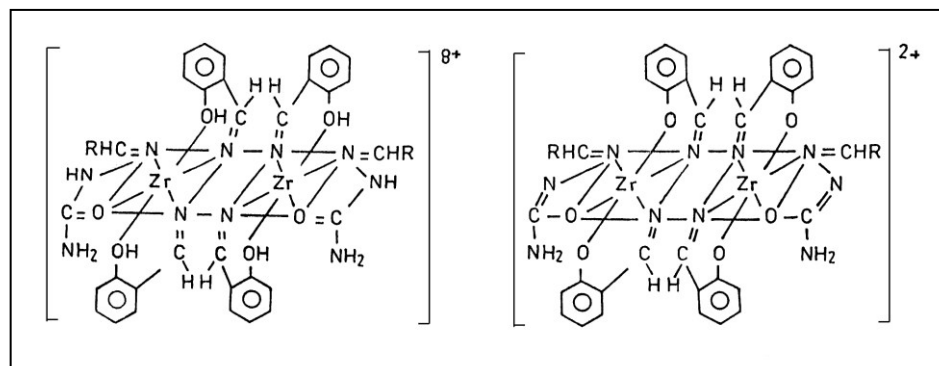


Figure 2 : Model structures of the complexes.

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