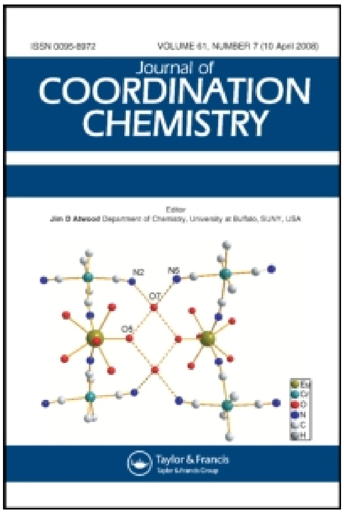

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SYNTHESIS AND CHARACTERIZATION OF SCHIFF BASE COMPLEXES WITH ZINC HALIDES

F. A. Bottino[a]; P. Finocchiaro[a]; E. Libertini[a]
[a] Faculty of Engineering, Institute of Chemistry, Catania, Italy

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SYNTHESIS AND CHARACTERIZATION OF SCHIFF BASE COMPLEXES WITH ZINC HALIDES

F.A. BOTTINO, P. FINOCCHIARO† and E. LIBERTINI

Institute of Chemistry, Faculty of Engineering, Viale A. Doria 6, 95125 Catania, Italy

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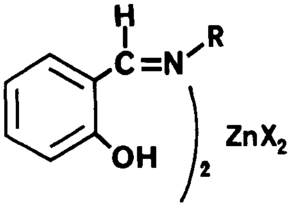
New complexes with Schiff bases and $ZnX_2(X=Cl \cdot I)$ have been synthesized. Infrared, CIMS (NH_3) and ^{13}C-NMR studies have been used in order to elucidate their structures.

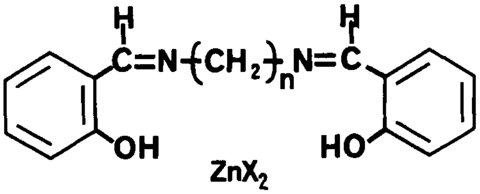
Keywords: Zinc, schiff base, complex, synthesis, salen

INTRODUCTION

In previous work[1–4] we have studied the stereochemistry of *bis*-chelate complexes with group II metals; addition compounds with bifunctional tetradentate Schiff base ligands have been reported with emphasis on tin derivatives.[5–7] In order to examine the behaviour of Schiff bases towards $ZnCl_2$ and ZnI_2, and to evaluate the influence



I



II

① R= $CH(CH_3)_2$, X=Cl
② R= $CH(CH_3)_2$, X=I
③ n=2 X=Cl
④ n=2 X=I
⑤ n=4 X=Cl
⑥ n=4 X=I
⑦ n=6 X=Cl
⑧ n=6 X=I

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†Author for correspondence.

of the length of the methylenic chain of the base on their conformation and starting with ZnX_2 in methanol solution, we have obtained 1:1 Zn(II) addition compounds with ligands II (**3**–**6**). Unfortunately they are almost completely dissociated in polar solvents and insoluble in other common organic solvents. Therefore we have attempted to throw some light on their structures by spectrometric analyses in the solid state.

EXPERIMENTAL

Instrumentation

Proton and carbon nmr spectra were recorded on a Bruker WP-80FT spectrometer, at 25°C in nearly saturated DMSO solutions, with TMS as internal standard.

Mass spectra were obtained using an LKB 9000 mass spectrometer together with a Kratos MS 50S double focusing mass spectrometer equipped with an Eclipse 120 data system from Data General employing DS 55 Kratos software. Chemical Ionization (CI) was performed using ammonia (99.998%) as the reagent gas (Matheson Gas Products).

The Schiff bases were obtained by direct reaction between salicylaldehyde and the appropriate diamine. The adducts were synthesised by adding a methanolic solution of the anhydrous ZnX_2 salt to an equimolar solution of the Schiff base in the same solvent. The mixture was stirred and the yellow coloured adducts precipitated almost quantitatively. The product was filtered off, washed with the same solvent and dried *in vacuo*. Only the compounds **1** and **2** exhibit macroscopic crystallinity; they are stable in air, but almost completely dissociate in polar solvents.

Infrared spectra of the adducts were recorded on a Perkin-Elmer 684 spectrometer in KBr and CsI pellets. The main frequencies, together with melting points and the elemental analyses, are summarized in Table I.

The elemental analyses are in accordance with compounds of stoichiometry $ZnX_2 \cdot L_2$ for **1** and **2** and $ZnX_2 \cdot L$ for **3**–**8**. No adducts with a metal: ligand ratio other 1:1 could be obtained in the presence of an excess of the ligand.

TABLE I
Characteristic data for the adducts

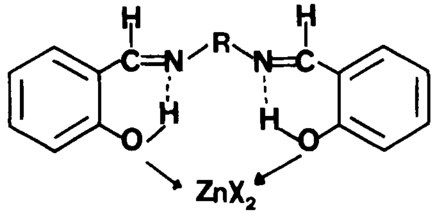
Compound	m.p.(°C)	Analyses found (calc.) (%) C	H	N	$\nu(C=N)/cm^{-1}$	$\nu(C-O)/cm^{-1}$	$\nu(O-H)/cm^{-1}$	$\nu(Zn-Cl)/cm^{-1}$
1	167	51.16 (51.92)	5.79 (5.66)	6.41 (6.05)	1650	1545	1290	310
2	242	37.91 (37.21)	3.91 (4.02)	4.38 (4.33)	1650	1547	1285	
3	274(d)	47.98 (47.51)	3.62 (3.95)	7.26 (6.92)	1640	1550	1285	355
4	300(d)	33.02 (32.71)	2.54 (2.72)	4.91 (4.76)	1645	1540	1285	
5	267	49.81 (49.99)	4.68 (4.62)	6.50 (6.47)	1640	1530	1280	315
6	280(d)	35.41 (35.13)	3.23 (3.25)	4.73 (4.55)	1652	1548	1280	
7	263	52.98 (52.16)	5.31 (5.21)	6.41 (6.08)	1655	1545	1290	310
8	261	37.52 (37.33)	3.81 (3.72)	4.71 (4.28)	1655	1545	1285	

RESULTS AND DISCUSSION

The IR spectra show no band in the region 3700–3500 cm^{-1} attributable to the stretching vibration of the free phenolic hydroxyl group and in the adducts an intramolecular hydrogen bond is present as is evident from the broad bands in the region 3100–2800 cm^{-1} which overlap with the ν(C–H) vibrations.[8] In all spectra C=N stretching vibration at ~1635 cm^{-1} is present; this band is shifted by about 5–10 cm^{-1} towards higher frequencies in the adducts, contrary to other chelate complexes, where the absorption shifts to lower frequencies, indicating less double-bond character in the C=N bond.[9] The spectra show absorptions at ~1580 cm^{-1} in the ligands which shift to ~1540 cm^{-1} in the adducts; this band, attributed to ν_{C-O},[10] is shifted more than $\nu_{C=N}$ presumably because the O atoms are more strongly bonded. A band at ~1280 cm^{-1} attributed to O–H deformation vibrations[5] is present in both ligands and adducts.

In the spectra in CsI a strong band around 300 cm^{-1} is present in all adducts with $ZnCl_2$; this band is not present in the spectra of the ligands and is attributed to Zn–Cl stretching modes.[11–12]

Mass spectra of the compounds are not informative. We decided, then, to use CIMS with ammonia as reactant gas because of the soft ionizations conditions. There is no evidence of adduct molecular peaks, but we do find, in any case, peaks with the typical pattern of the zinc atom, or generated by mass loss 127 (I) and 35 (Cl). In the mass spectra of compound **6**, for example, we find signals at *m/z* $(ZnI_2 \cdot L{-}I)^+$, 359 $(ZnI_2 \cdot L{-}2I)^+$, 192 $(HO{-}C_6H_5{-}CH{=}N(CH_2)_4{-}NH_2)^+$, 383 $(HO{-}C_6H_5{-}CH{=}N(CH_2)_4NH_2)_4NH_2 \cdot ZnI)^+$ and, as base peak *m/z* 122 $(HO{-}C_6H_5{-}CH{=}NH_2)^+$. In



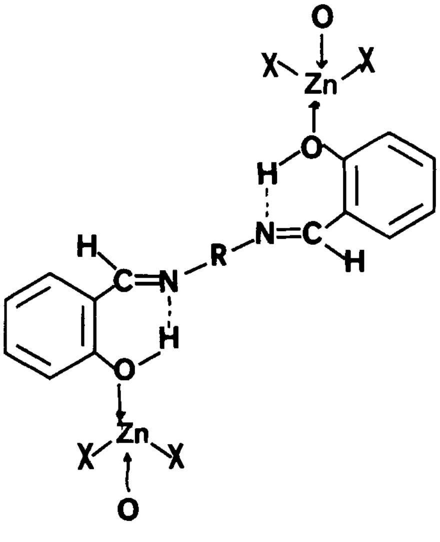
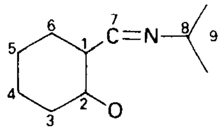
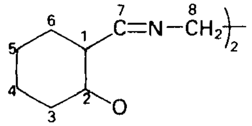
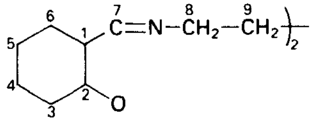
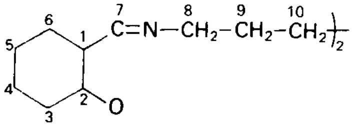


TABLE II

^{13}C chemical shifts (ppm) in deuterated DMSO for ligands and adducts.

	Carbon 1	2	3	4	5	6	7	8	9	10
	118.96	161.19	116.70	132.29	118.60	131.85	163.53	58.97	23.99	
1	122.41	168.45	113.85	136.38	118.49	134.56	170.08	61.49	23.89	
2	122.60	166.11	113.63	136.53	119.59	135.46	168.35	61.69	20.30	
	118.68	160.82	116.56	132.51	118.68	131.78	167.12	58.75		
3	119.48	166.82[a]	115.46	134.78	119.48	133.46	169.24	58.26		
4	119.12	165.51[a]	116.48	134.34	119.12	133.31	168.58	58.75		
	119.21	161.26	116.78	132.51	118.53	131.78	166.02	57.73	28.02	
5	122.26	165.43	117.43	136.60	120.80	133.60	168.51	57.65	24.43	
6	121.37	[b]	[b]	136.01	[b]	133.30	167.47	56.48	23.47	
	118.75	161.19	116.79	132.36	118.53	131.78	165.95	58.17	30.29	26.26
7	122.2	168.5[c]	117.4	136.6	119.6	133.68	168.5[c]	58.09	26.78	25.31
8	122.12	169.4[c]	117.21	136.53	119.56	134.26	169.4[c]	58.17	26.56	25.09

[a] Broad peaks. [b] Uncertain attribution. [c] Only one broad peak for C 2 and 7.

the spectra of compound **1** we find m/z 389 $(ZnCl_2 \cdot L{-}HCl{-}Cl)^+$, and, although the peak at m/z 122 is still present, the base peak is now at m/z 164 $(L + 1)^+$.

Due to the low solubility of the complexes, no spectra of these compounds in solution can be obtained. In DMSO they are prevailingly dissociated but, with ^1H and ^{13}C nmr, after excess ZnX_2 is added to the nmr tube, we have obtained signals due to the adducts as well as the free ligand. We believe that compounds **1** and **3** are the more stable; in fact, in contrast to the ^1H nmr spectra of all the other compounds, we observe signals due to the adducts, with only a slight excess of $ZnCl_2$.

In the same way, we obtain ^{13}C spectra that allow a clear assignment of the peaks (Table II) on the basis of ^{13}C shifts in μ-Oxo-bis(disalicylideneiminato) complexes.[13] If there is doubt about some of the values reported, this is because of the loss of resolution upon addition of ZnX_2.

In view of the above discussion, it appears that these aducts may have a tetraedral structure at the zinc atom with the Schiff bases coordinated though oxygen atoms (III and IV). A conformation like this is evident in addition complexes of zinc iodide with two different β-ketoimmines,[14] and has been further confirmed by X-ray studies.[15] We cannot however, exclude a polymeric structure, such as IV especially when the methylenic chain is longer. In order to properly clarify these points X-ray structural characterizations are in progress.

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