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The Synthesis of Salts of Polymeric Schiff Bases, and their Use in Complexation Reactions

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Salts of bridged polymeric Schiff bases were prepared with Li^+, Na^+ and K^+ cations. They are useful reagents for the synthesis of other salts with monovalent heavy metal ions (Tl^+, Cu^+, Hg_2^{2+}) or divalent alkaline earth ions (Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}) and of polymeric Schiff base complexes with transition metal ions.

Introduction

Even for monomeric Schiff bases, salts with monovalent ions or divalent ones, which are less capable for complexation like the earth alkali ions, are not well characterized [1–3]; for polymeric Schiff bases obtained from 5,5′-methylene-bis-salicylaldehyde and bridging diamines [4], they are unknown. However these salts may be useful for the preparation of complexes by replacing the cations by transition metal ions.

So far, the methods known for the preparation of monomeric Schiff base complexes [5] have also been applied for the synthesis of polymeric compounds *i.e.*

a) The Schiff base is first prepared by the reaction of the aldehyde with the amine and then complexated with the metal salt.

b) After the aldehydato-complex is obtained from the aldehyde and the metal salt, it is converted to the Schiff base complex by reaction with an amine.

c) Firstly, the amine complex of the metal is synthesized, and then reacted with the aldehyde to the Schiff base complex.

d) All components (aldehyde, diamine and metal salt) are mixed at the same time.

These methods have several disadvantages, especially for the preparation of polymeric Schiff base complexes. For b) and c), the formation depends on the stabilities of the initial complexes and on the complex equilibria from which water has to be removed; for a) and b) the polymeric Schiff base or aldehydato-complex may impose problems of solubility, and for a) and d) the generated protons have to be buffered and a complete occupation of all the complex sites within the polymeric Schiff base by metal ions may be difficult to achieve.

Via salts of the polymeric Schiff bases, these disadvantages can be avoided and the complexes are obtained by smooth reactions in a rather pure state.

Experimental

The Preparation of Alkaline Metal Salts of Polymeric Schiff Bases

The polymeric Schiff bases were prepared in a slightly modified way according to known methods [4, 6]:

5,5′-Methylene-bis-salicylaldehyde (25 mmol) obtained from salicylaldehyde and trioxane [4] is dissolved in a mixture of 150 ml DMF and 100 ml 1,2,4-trichloro-benzene. After heating to 150 °C, 25 mmol of the diamine (1,4-diaminobutane is used for the following model reactions, all kinds of other diamines can be used in a similar way), dissolved in 60 ml of benzene, is added dropwise while the reaction mixture is stirred. After refluxing till no more water separates, this is distilled off as an azeotrope with benzene, the remaining benzene is removed by a stream of argon, and the mixture is cooled down to room temperature (for the preparation of the potassium salts, the solution is concentrated to *ca.* 100 ml by evaporation under argon).

Lithium Salts

Li (50 mmol) dissolved in 100 ml absolute methanol is added at once with rapid stirring, continued for 15 minutes or more. The precipitate is sucked dry, excluding moisture completely, washed with acetone and petroleum ether, treated with petroleum ether in a Soxhlet apparatus for 24 h, and dried *in vacuo* at 95 °C. The lithium salts of polymeric Schiff bases are yellowish-white powders, stable in dry air, and insoluble in pure alcohols and DMF.

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TABLE I. Analytical Results and Thermal Stabilities of Prepared Salts and Complexes with 5,5'-Methylene-bis-salicyl-bis-1,4-butane-aldimine.

Metal ion		Mol. weight	%C	%H	%N	%M	Temp. of decomposition	
							in air (°C)	in N_2 (°C)
Li^+	calc.	320.24	71.26	5.66	8.75		260	
	exp.		64.95	5.94	6.83			
Na^+	calc.	352.34	64.77	5.15	7.95		250	
	exp.		56.40	6.20	4.29			
Be^{2+}	calc.	315.38	72.36	5.75	8.88		410	410
	exp.		67.07	5.66	7.66			
Mg^{2+}	calc.	330.67	69.01	5.48	8.47		325	330
	exp.		63.78	5.34	7.07			
Ca^{2+}	calc.	346.45	65.87	5.24	8.08		290	315
	exp.		65.54	5.84	6.51			
Sr^{2+}	calc.	393.99	57.92	4.60	7.11		285	315
	exp.		55.45	4.75	5.51			
Ba^{2+}	calc.	443.71	51.43	4.09	6.31		235	320
	exp.		56.94	4.91	4.80			
Tl^+	calc.	714.97	31.92	2.54	3.92		265	
	exp.		32.89	2.44	3.50			
Cu^+	calc.	433.45	52.65	4.18	6.46	29.31	255	
	exp.		49.90	4.07	5.42	28.06		
Hg_2^{2+}	calc.	707.54	32.25	2.56	3.96		205	205
	exp.		28.27	2.29	5.96			
Mn^{2+}	calc.	377.30	64.48	4.81	7.42	14.56	262	313
	exp.		61.17	4.89	6.48	13.84		
V^{2+}	calc.	373.37	76.39	4.77	7.42	13.52	300	300
	exp.		74.82	4.72	7.42	12.03		

In water, they hydrolyze at once to the yellow-coloured Schiff bases.

Sodium Salts

Sodium methoxide (50 mmol) dissolved in the minimum amount of absolute ethanol is added dropwise with stirring, which is continued for 15 min. The slightly yellow precipitate is sucked dry and washed with acetone, diethylether and petroleum ether, treated with diethylether in a Soxhlet apparatus for 24 h and dried *in vacuo* at 50 °C. Because of the marked tendency to hydrolyze, moisture must be avoided completely during handling the sodium salts of polymeric Schiff bases. They are yellow powders, well soluble in water-free alcohols, but insoluble in DMF. If they are exposed to air, they are slowly oxidized to orange-red products. With water, they give the free Schiff bases.

Potassium Salts

Solid potassium-tert. butoxide (50 mmol) is added to the solution, Within one minute, a viscous substance separates. The solvent is decanted and the remainder is dissolved in 50 ml methanol. When this solution is dropped into diethylether, the yellowish-white potassium salt precipitates. It is well soluble in N,N'-dialkylamides (DMF, DMA), ketones and alcohols. Because of their extreme sensitivity to moisture, it is recommended to use the potassium salts only as intermediates, which are reacted without isolation.

The Preparation of Monovalent Heavy Metal Salts of Polymeric Schiff Bases

10 mmol of the lithium salt of a polymeric Schiff base is dissolved in 100 ml of a mixture of 50% glycol, 30% acetonitrile and 20% glycol-monomethylether at 50–60 °C. 20 mmol of dry metal salt (nitrates or acetates) is added and the stirred mixture is heated on a water bath for 5 h. The precipitates are sucked dry, washed with acetonitrile and petroleum ether and dried *in vacuo* at 95 °C. Yellow Tl^+- and green Cu^+-salts have been prepared in this way. With $AgNO_3$, a salt of the polymeric Schiff base is formed too, but as yet we have not been able to isolate it in an analytically pure state. With Hg_2^{2+} heat has to be avoided because of the easy disproportionation into elemental mercury and Hg^{2+}. $Hg_2(NO_3)_2$ is added at room temperature to the solution of the lithium salt and the mixture is stirred for several hours. The precipitate is filtered off, washed with ether and petroleum-ether, and dried at room

TABLE II. Infrared Bands of Salts and Complexes with 5,5'-Methylene-bis-salicyl-bis-1,4-butane-aldimine.

free base	1630	1585	1275
Li^+	1628	1520	1309
Na^+	1621	1526	1325
Be^{2+}	1622	1535	1315
Mg^{2+}	1620	1525	1295
Ca^{2+}	1622	1523	1300
Sr^{2+}	1620	1520	1300
Ba^{2+}	1625	1525	1300
Tl^+	1621	1528	1300
Cu^+	1617	1530	1310
Hg^{2+}	1615	1590	1315
Mn^{2+}	1611	1535	1290
V^{2+}	1618	1545	1301

temperature. It is a green powder, which decomposes slowly, perceivable by the separation of finely dispersed grey mercury.

The Preparation of Earth Alkaline Salts of Polymeric Schiff Bases

10 mmol of the sodium salt of polymeric Schiff bases is dissolved in 50 ml absolute ethanol. A solution of 10 mmol of the earth alkali nitrate or acetate in methanol is added and the mixture is refluxed for 24 h. The precipitate is filtered off, treated with ethanol in a Soxhlet apparatus and dried *in vacuo* at 95 °C. Salts of Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} have been prepared by this method.

Results and Discussion

Characterization of the Polymeric Schiff Base Salts

The results of the elemental analysis of the prepared salts are summarized in Table I.

The infrared spectra of Schiff bases and their complexes include three characteristic bands, *ca.* 1630, 1585 and 1280 cm^{-1} for the free bases shifting to 1620, 1530 and 1310 cm^{-1} for the complexes [6]. The frequency values of these three bands observed for the salts of the polymeric Schiff bases are given in Table II. It is noteworthy that not only the band at 1280 cm^{-1} (attributed to the CO-vibration) shifts to *ca.* 1310 cm^{-1} as expected, but the band at 1585 cm^{-1} related to the conjugated phenyl –C=N-part of the molecule also shifts to values found for the complexes. This might indicate coordination of the N-atom even in the salts. The only exception is the Hg_2^{2+} salt, for which this band remains at 1590 cm^{-1}.

TABLE III. Hydrolytic and Molecular Sieve Behaviour of Polymeric Be^{2+}, Mg^{2+} and Ca^{2+} Schiff Base Compounds.[a]

	Be^{2+}	Mg^{2+}	Ca^{2+}
Hydrolysis	none	fast	fast
retention times (min.)			
Ar	0.49	0.46	0.40
Kr	1.14	0.59	0.56
Xe	6.37	1.93	1.83
n-pentane	1.87	0.48	0.48 (no separation)
n-hexane	3.73	0.71	
n-heptane	8.05	1.00	
cyclohexane	4.87	0.58	0.51
benzene	7.97	1.52	1.22
toluene	16.00	2.95	1.98

[a] Retention times measured in a Carlo Erba gas chromatograph Fractovap 4200 2 m column with I.D. of 2 mm filled with compounds (grain size 0.31–0.5 mm); room temperature for noble gases, otherwise 200 °C, carrier gas N_2 flow rate 30 ml/min.

However, the salts can be distinguished from the chelate complexes with regard to two properties: whereas the complexes are molecular sieves [7, 8], the salts are not; and the complexes are completely stable in water, whereas the salts hydrolyze fast and easily, except the Cu^+ compound. This can be best seen comparing the beryllium complex with the magnesium and calcium salt (Table III).

The Preparation of Transition Metal Complexes of Polymeric Schiff Bases via *their Salts*

All the salts of polymeric Schiff bases with mono- or divalent cations react with ions of transition metals to give their complexes. These reactions are smooth, fast, proceed at low temperatures, and give pure products with a complete occupation of the complex sites. Best suited are the potassium salts, which are not isolated, but kept in solution, after the potassium-tert.butoxide dissolved in a 1:2 mixture of methanol and ethanol was added to the solution of the Schiff base.

The metal salt is now added to this mixture regarding the following details:

a) water-free metal salts (chlorides, nitrates, acetates) soluble in alcohols or DMF are added at once as solids;

b) water-free metal salts insoluble in alcohols, or DMF are first dissolved in a suitable absolute, non-acid solvent and then added at once

c) metal salts containing crystal water are mixed with sodium acetate (one mol per mol water) and are then added at once as solids.

The mixture is heated to boiling point and refluxed until the liquid above the precipitated complex is nearly colourless. The complex is filtered off, treated in a Soxhlet apparatus: first 24 h with methanol, then 24 h with chloroform, dried at 95 °C, and then heated in a high vacuum at 180–200 °C.

With this method it is not only possible to synthesize the known polymeric Schiff base complexes in a better way and purer state, but one can even prepare complexes with metal ions, like Mn^{2+} and V^{2+}, not obtainable with other methods [6].

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