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Preparation and Thermal Stability of Polymeric Metal Chelates with Schiff Bases

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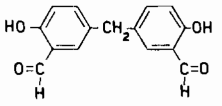
Polymeric bridged Schiff base complexes of Be^{2+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, Pd^{2+}, Pt^{2+}, Co^{2+}, Fe^{2+}, Cr^{2+}, V^{2+}, In^{3+}, Co^{3+}, Rh^{3+}, Fe^{3+}, Cr^{3+}, Ti^{4+} *and* U^{6+} *have been prepared with 5,5′-methylene-bis-salicylaldehyde and different diamines forming the base. No such complexes could be obtained with* Mn^{2+}. *Besides analytical results, the complexes are characterized by magnetic and infrared measurements. Their thermal stability was studied by a dynamic method heating the samples up to 1000 °C in dry air. For the divalent ions, stabilities increase in the order* $Co^{2+} < Zn^{2+} < Cr^{2+} < Fe^{2+} < Pd^{2+} < Cu^{2+} < Be^{2+} < Ni^{2+}$ *and for the higher valent ions* $Ti^{4+} < Fe^{3+} < Co^{3+} < Rh^{3+} < U^{6+} < Cr^{3+} < In^{3+}$.

Introduction

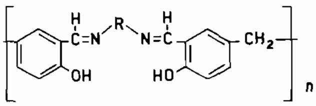
Although an extremely large number of monomeric metal complexes with various azomethine ligands is known [1], only few complexes with polymeric Schiff bases have been reported as yet. Polymeric Schiff bases are accessible since the synthesis of 5,5′-methylene-bis-salicylaldehyde (I) [2] and com-

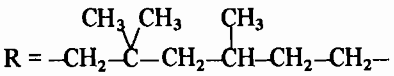


I

plexes have been prepared with such ligands for the first row transition metal ions Cr^{3+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Co^{3+}, Ni^{2+}, Cu^{2+}, Zn^{2+} [3, 4].

As we are interested in the chemical behaviour of complexes with polymeric Schiff bases, we have studied the chelate formation of the ligands II–VI with a great number of main and transition group metal ions





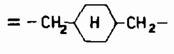
$$R = -CH_2-C(CH_3)_2-CH_2-CH(CH_3)-CH_2-CH_2-$$

II

(5,5′Sal-TMD)

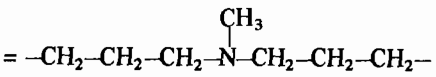
III

(5,5′Sal-IPD)



IV

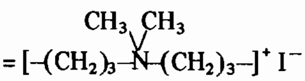
(5,5′Sal-CHD)



$$= -CH_2-CH_2-CH_2-N(CH_3)-CH_2-CH_2-CH_2-$$

V

(5,5′Sal-MeDPT)

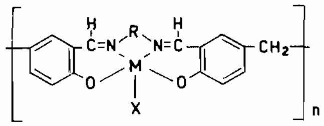


$$= [-(CH_2)_3-N(CH_3)_2-(CH_2)_3-]^+\,I^-$$

VI

(5,5′SalDiMeDPTJ)

resulting in complexes of the common type



VII

X = additional inorganic ligand

and we have investigated the thermal stability of these compounds.

TABLE I. Analytical Data and Colours of the Complexes Prepared (the theoretical values correspond to n = ∞).

Compound		X	Colour	Formula		Analyses			
Metal	Ligand					C	H	N	Metal
Ni^{2+}	II	–	green	$C_{24}H_{28}N_2NiO_2$	calc.	66.25	6.44	6.44	13.50
					found	64.29	6.48	6.24	13.47
Co^{2+}	III	–	brown	$C_{25}H_{28}CoN_2O_2$	calc.	67.12	6.26	6.26	13.19
					found	68.63	7.31	6.39	13.19
Ni^{2+}	III	–	green	$C_{25}H_{28}N_2NiO_2$	calc.	67.16	6.27	6.27	13.14
					found	64.99	6.27	5.66	12.86
Cu^{2+}	IV	–	brown	$C_{23}H_{24}CuN_2O_2$	calc.	65.16	6.57	6.61	15.00
					found	63.09	5.88	5.90	14.68
Zn^{2+}	V	–	yellow	$C_{22}H_{25}N_3O_2Zn$	calc.	61.63	5.84	9.80	15.26
					found	62.59	6.54	10.07	13.56
Cu^{2+}	V	–	brown	$C_{22}H_{25}CuN_3O_2$	calc.	61.90	5.86	9.85	14.88
					found	60.33	5.51	8.59	16.22
Ni^{2+}	V	–	green	$C_{22}H_{25}N_3NiO_2$	calc.	62.60	5.93	9.96	13.92
					found	60.79	5.66	9.49	14.35
Co^{2+}	V	–	brown	$C_{22}H_{25}CoN_3O_2$	calc.	62.57	5.93	9.95	13.97
					found	60.19	5.72	9.06	13.02
Fe^{2+}	V	–	brown	$C_{22}H_{25}FeN_3O_2$	calc.	63.03	5.97	10.03	13.33
					found	62.33	5.78	8.76	12.34
Cr^{2+}	V	–	yellow–green	$C_{22}H_{25}CrN_3O_2$	calc.	63.62	6.02	10.12	12.53
					found	61.57	6.33	9.89	13.63
Be^{2+}	V	–	yellow	$C_{22}H_{25}BeN_3O_2$	calc.	70.98	6.72	11.29	2.42
					found	69.36	6.74	10.88	
Pd^{2+}	V	–	yellow	$C_{22}H_{25}N_3O_2Pd$	calc.	56.24	5.33	8.94	22.67
					found	54.45	5.27	8.46	22.23
Pd^{2+}	III	–	olive–green	$C_{25}H_{28}N_2O_2Pd$	calc.	60.69	5.66	5.66	21.52
					found	59.92	5.50	5.39	17.95
Pd^{2+}	VI	–	rust–red	$C_{23}H_{28}JN_3O_2$	calc.	44.96	4.56	6.84	17.33
					found	44.06	4.92	6.64	17.85
Pt^{2+}	V	–	rust–brown	$C_{22}H_{25}N_3O_2Pt$	calc.	47.26	4.47	7.51	
					found	44.58	4.12	6.20	
Co^{3+}	V	Cl	brown	$C_{22}H_{25}ClCoN_3O_2$	calc.	57.71	5.46	9.18	12.88
					found	59.14	5.49	7.45	11.59
Co^{3+}	V	N_3	brown	$C_{22}H_{25}CoN_6O_2$	calc.	56.91	5.39	18.11	12.70
					found	56.35	5.47	16.41	11.32
Fe^{3+}	V	Cl	black	$C_{22}H_{25}ClFeN_3O_2$	calc.	58.10	5.50	9.25	12.29
					found	56.38	5.31	8.27	11.49
Cr^{3+}	V	Cl	yellow–green	$C_{22}H_{25}ClCrN_3O_2$	calc.	58.60	5.55	9.32	11.54
					found	56.66	6.05	8.14	11.20
Ti^{4+}	V	2 Cl	orange	$C_{22}H_{25}Cl_2N_3O_2Ti$	calc.	54.78	5.19	8.71	9.95
					found	55.92	5.64	7.55	10.39
In^{3+}	V	Cl	yellow	$C_{22}H_{25}ClInN_3O_2$	calc.	51.45	4.87	8.19	22.36
					found	51.64	4.99	8.50	21.95
Rh^{3+}	V	Cl	orange	$C_{22}H_{25}ClN_3O_2Rh$	calc.	52.68	4.98	8.38	20.51
					found	51.64	4.96	7.92	19.07
U^{6+}	V	2 O	orange	$C_{22}H_{25}N_3O_4U \cdot H_2O$	calc.	40.55	4.14	6.45	36.56
					found	41.58	3.90	5.27	35.39
Mn^{2+}	I	–	yellow	$C_{15}H_{10}MnO_4$	calc.	58.27	3.24		17.78
					found	56.76	3.26		16.97

Experimental

5,5′methylene-bis-salicylaldehyde (I) was prepared according to the literature [2a] from salicylaldehyde and trioxane.

The Schiff bases II–VI were prepared by polycondensation of I with the proper diamines in DMF. 10 mmol I were dissolved in 50 ml hot DMF, then 10 mmol of the diamine were added dropwise and the water formed was removed by azeotropic distillation with toluene. The reaction is complete after 2–5 hours. After cooling to room temperature the Schiff base was precipitated with methanol, filtered and dried *in vacuo* at 105 °C. All complexes VII were prepared by coordination of the polymeric Schiff bases II–VI to the proper metal ions in DMF with Na-acetate as buffer. The metal ions were generated by the acetates (or hydrated acetates) of Cr^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}; $FeSO_4 \cdot 7H_2O$, $Be(NO_3)_2$, $Cr(py)_3Cl_3$, $FeCl_3 \cdot 6H_2O$, $Co(NH_3)_6Cl_3$, $RhCl_3 \cdot H_2O$, $InCl_3 \cdot H_2O$, $TiCl_4$, K_2PdCl_4, K_2PtCl_4; $UO_2(NO_3)_2 \cdot 6H_2O$. 10 mmol of the ligand were dissolved in 100 ml DMF by stirring at 100 °C, then 20 mmol solid Na-acetate were added and afterwards 10 mmol of the metal compound dissolved in 100 ml DMF were dropped slowly into this mixture. Mostly, the complex precipitated within 30 min. The temperature was held at 100 °C for another 24 hours. After cooling, the solid was filtered off, washed with DMF and H_2O, treated with CH_3OH in a Soxhlet apparatus for 24 hours and dried *in vacuo* at 105 °C.

For preparation of the Ti^{4+} complexes from $TiCl_4$, complete exclusion of water is mandatory to avoid hydrolysis and the reaction temperature was held at 25 °C instead of 100 °C. The complexes of Cr^{2+}, Mn^{2+}, Fe^{2+} and Co^{2+} were prepared in an N_2-atmosphere and in O_2 and H_2O free DMF. For preparation of $Co^{3+}(N_3)$(5,5′-SalMeDPT), 10 mmol NaN_3 dissolved in a small amount of water were added to the mixture of Schiff base and Na-acetate in DMF and air was bubbled through the solution, then $Co(ac)_2 \cdot 4H_2O$ was dropped in slowly. For preparation of Mn^{2+}(5,5′Sal), 10 mmol of I and 20 mmol Na-acetate were refluxed in methanol and a solution of $Mn(ac)_2 \cdot 4H_2O$ in MeOH was added slowly. The yellow precipitate was filtered off after 4 hours, washed with H_2O and treated with MeOH in a Soxhlet apparatus for 24 hours and dried *in vacuo* at 50 °C. The yields are 50 to 70% of the theoretical expectations. All complexes are amorphous, infusible powders, which are insoluble in all customary solvents. With acids partial decomposition is observed. Colours are mostly yellow to brown, the Ni^{2+} complexes are green, the $Fe^{3+}Cl$(5,5′SalMeDPT) is black.

Infrared absorption spectra were recorded as Nujol mulls between 4000 and 200 cm^{-1} on a Perkin–Elmer spectrometer type 625; the thermogravimetric measurements were carried out on a Netzsch TG 409 E apparatus and the magnetic measurements at 293 °K with the Gouy method and $CoHg(SCN)_4$ as reference compound.

Magnetic Measurements

The magnetic susceptibilities of some of our solid complexes were measured at room temperature and the values obtained for μ_{eff} are reported in Table II. All compounds except $Cr^{2+} \cdot$5,5 SalMeDPT are high spin complexes as analogous monomeric Schiff base complexes of these metal ions [5]. The somewhat low value for $Fe^{2+} \cdot$5,5SalMeDPT may indicate some metal–metal interaction, but this would need to be confirmed by measuring the temperature dependence of the magnetism.

TABLE II. Magnetic Measurements.

Compound	μ_{eff} (B.M.)[a]
$Co^{2+} \cdot$5,5′ SalIPD	3.25
$Co^{2+} \cdot$5,5′ SalMeDPT	3.87
$Fe^{2+} \cdot$5,5′ SalMeDPT	4.03
$Fe^{3+} \cdot$5,5′ SalMeDPT	6.09
$Cr^{2+} \cdot$5,5′ SalMeDPT	2.97
$Cr^{3+} \cdot$5,5′ SalMeDPT	3.63
$Mn^{2+} \cdot$5,5′ Sal	5.29

[a] Diamagnetic corrections are considered.

Infrared Spectra

The infrared spectra of the ligands II–VI exhibit three characteristic features at *ca.* 1630, 1585 and 1275 cm^{-1}, which is in agreement with findings for monomeric Schiff bases [6]. The $\nu_{C=O}$ of the starting material I appears as a weak shoulder at 1653 cm^{-1} for II–VI as well as for the complexes, which indicates that the end groups of the polymers are carbonyl groups. On complexation, the frequency at 1630 cm^{-1} remains almost constant (downward shift of only 2–15 cm^{-1}), the band at 1585 is lowered by *ca.* 50 cm^{-1} and that at 1275 cm^{-1} is increased by 15–50 cm^{-1} (see Table III). For most of the complexes, the total disappearance of the bands of the free bases indicates an almost complete occupation of the coordination centers. Only for the Be^{2+} and Pt^{2+} complexes a weak band at 1277 cm^{-1} shows that some of them must be empty.

For $UO_2 \cdot$5,5′SalMeDPT, the characteristic UO_2 vibration (ν_{as}) was observed at 892 cm^{-1}. Of the N_3-stretching vibrations of $CoN_3 \cdot$5,5′SalMeDPT, only ν_{as} can be unequivocally assigned at 2010 cm^{-1}.

Thermal Stability

One of the aims of former preparations of polymeric Schiff base complexes was to get thermally stable compounds [2–4]. In these papers, the thermal stability was measured by static methods (time dependence of the loss of weight). We have used a dynamic method by heating about 20 mg of the sample with an increase of 10 °C per min from room temperature to 1000 °C in dry air. The loss of weight observed for the different metal complexes with ligand V is depicted in Fig. 1 and 2.

If the thermal stability is characterized by the temperature at which the first deviation from the zero line is observed, the following sequence is found for the divalent metal ions:

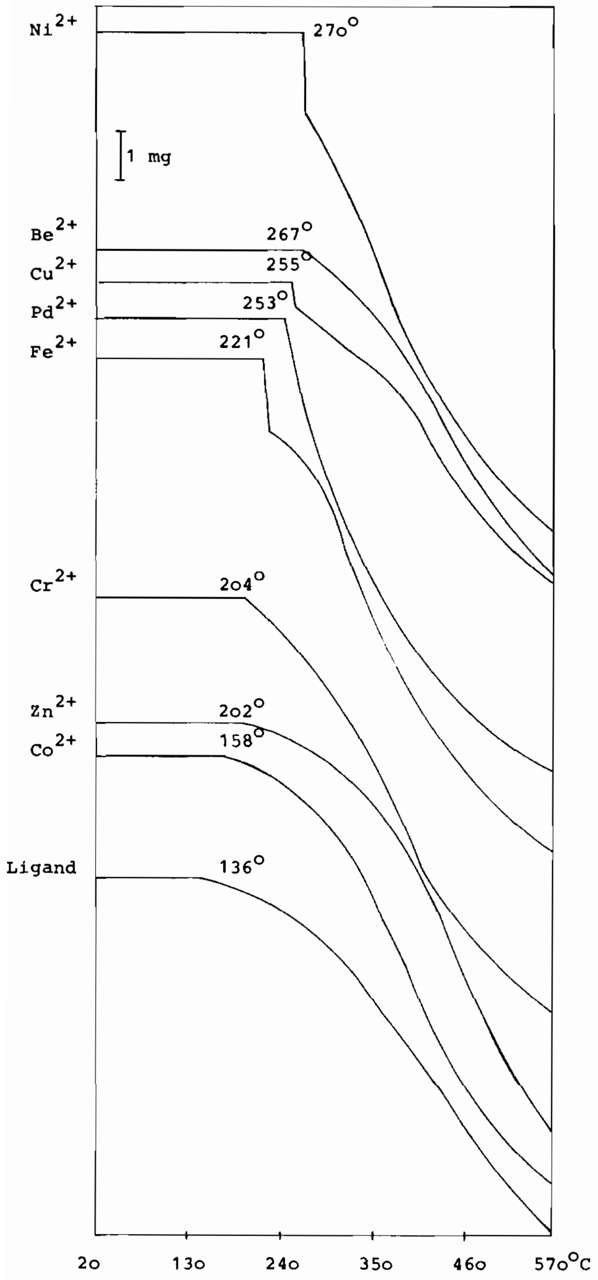


Figure 1. Loss of weight of the M^{2+} chelates with ligand V.

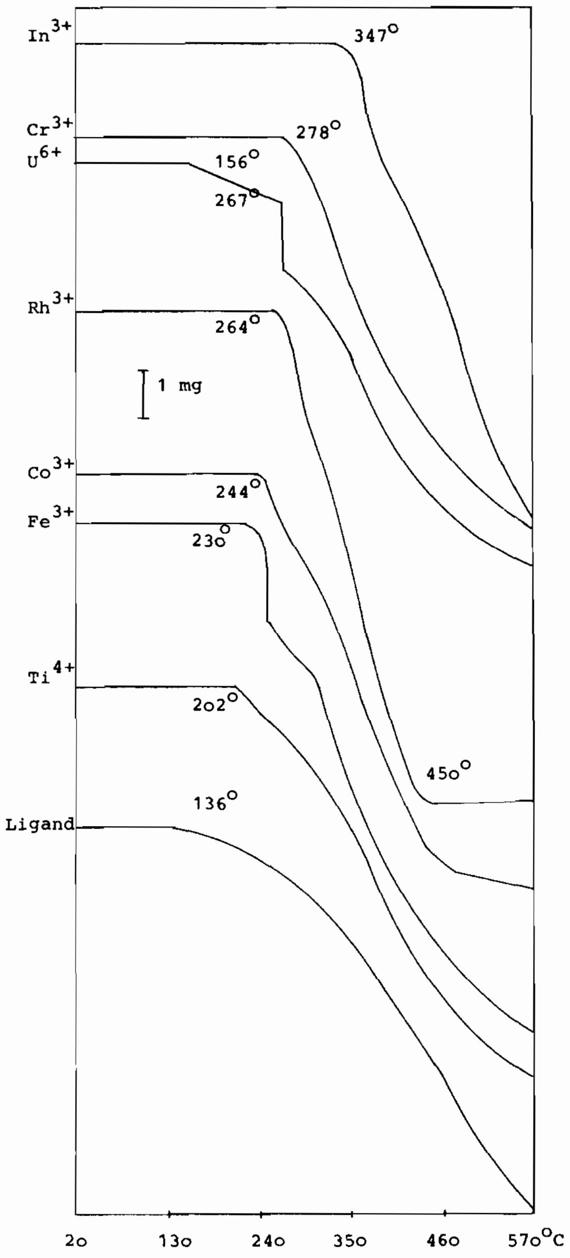


Figure 2. Loss of weight of the $M^{\geqslant 3+}$ chelates with ligand V.

$$Co^{2+} < Zn^{2+} < Cr^{2+} < Fe^{2+} < Pd^{2+} < Cu^{2+} < Be^{2+} < Ni^{2+}$$

and for the higher valent ions:

$$Ti^{4+} < Fe^{3+} < Co^{3+} < Rh^{3+} < U^{6+} < Cr^{3+} < In^{3+}.$$

For UO_2–5,5SalMeDPT·H_2O, the water molecule is released at 156 °C, and the water free complex starts decomposing at 267 °C. This higher temperature was used in the order of stabilities.

In all cases, the stability of the ligand (V) itself was considerably increased by complexation, and it should be noted that unexpectedly the complexes with the main group elements Be^{2+} and In^{3+} are amongst the most stable ones, the In^{3+}Cl·5,5SalMeDPT being the most stable. If a metal forms complexes in different oxidation states (Fe, Co, Cr), the trivalent complexes are more stable then the divalent ones.

TABLE III. Infrared Spectra (cm^{-1}).

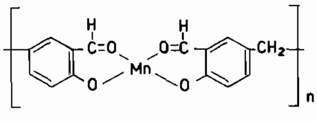
Compound			
Ni 5,5'SalTMD	1620	1539	1325
Co 5,5'SalIPD	1619	1532	1320
Ni 5,5'SalIPD	1621	1538	1323
Cu 5,5'SalCHD	1625	1535	1322
Zn 5,5'SalMeDPT	1625	1531	1305
Cu 5,5'SalMeDPT	1622	1525	1310
Ni 5,5'SalMeDPT	1622	1525	1313
Co 5,5'SalMeDPT	1628	1533	1308
Fe 5,5'SalMeDPT	1618/13	1536	1311
Cr 5,5'SalMeDPT	1615	1525	1320
Be 5,5'SalMeDPT	1621	1531/42	1310
Pd 5,5'SalMeDPT	1620	1533	1315
Pd 5,5'SalIPD	1618	1531	1311
Pd 5,5'SalDiMeDPTJ	1618	1529/31	1311
Pt 5,5'SalMeDPT	1610	1525	1309
CoCl 5,5'SalMeDPT	1625	1535	1310
$CoN_3$5,5'SalMeDPT	1625	1535	1310
FeCl 5,5'SalMeDPT	1623	1536	1308
CrCl 5,5'SalMeDPT	1616	1535	1310
$TiCl_2$ 5,5'SalMeDPT	1618	1552	1292
InCl 5,5'SalMeDPT	1628	1528	1513/05
RhCl 5,5'SalMeDPT	1627	1538	1310
UO_2 5,5'SalMeDPT	1628	1535	1280

Results and Discussion

We succeeded not only in the preparation of polymeric azomethine complexes of these metal ions already known [2 - 4] (however, with different amine bridges within the Schiff bases) but we also synthesized such complexes with some new metal ions, which seem more interesting in several aspects.

Thus, within the first row transition series, no Schiff base complexes, neither monomeric nor polymeric, were known as yet for Cr^{2+}. We had no difficulties in preparing Cr^{2+} complexes with our polymeric Schiff bases [7], and these compounds are especially effective for the intercalation of organic molecules, on which we will report separately [8]. We observed also complexation of V^{2+} by polymeric Schiff bases, but so far we were not able to get an analytically pure material.

On the other hand, we did not observe the formation of analogous Mn^{2+} complexes. When we attempted to prepare them by a template reaction, we only got the polymeric aldehyde complex.



So far no polymeric Schiff base complexes with N_3^- as additional ligand X were known. We prepared the compound $Co^{3+}(N_3)$·5,5'SalMeDPT by oxidation of Co^{2+} with O_2 (from air), when N_3^- was present too. Contrary to findings for polymeric bound Pd^{2+} [9], we did not observe reaction of the N_3 with 40 atm CO at room temperature to the isocyanato group.

Although many monomeric Schiff base complexes of Co^{3+} and Ni^{2+} are extant, those compounds are exceedingly rare for the analogous platinum metals. Thus, for Rh^{3+}, RhCl(salen)py was solely reported by West *et al.* [10], and he obtained it only under reducing conditions. From ligand V and $RhCl_3·3H_2O$ in DMF at 120°, RhCl·5,5'SalMeDPT is formed easily without adding reducing agents.

The first bridged monomeric Schiff base complexes of Pd^{2+} were reported quite recently [11]. We had no problems in obtaining these complexes with our polymeric Schiff bases and even Pt^{2+} reacted in the same way, although the present results indicate that not all sites apt for the metal ion are occupied [12].

Monomeric N-alkyl Schiff base complexes of Be^{2+} were mainly studied as a means for the analytical determination of this metal [13], but many of them are extremely sensitive to hydrolytic decomposition [14]. Complexes with alkyl substitution on both N atoms have not been prepared as yet, presumably because coordination to the very small Be^{2+} ion is hampered. Starting with $Be(NO_3)_2$, we got Be–5,5'-SalMeDPT in the water-free solvent DMF. It is likely to contain Be^{2+} in tetrahedral configuration, which becomes possible by the high flexibility of the ligand

V. Once formed, the compound is completely stable towards water.

Attempting to complex Al^{3+} with ligand V, we got a yellow compound, the infrared spectrum of which exhibited features which indicate the presence of free OH groups. Surprisingly, the reaction with $InCl_3$ yielded the very stable complex InCl·5,5'-SalMeDPT, without additional OH groups showing up in the infrared spectrum. Thus, at least a four-fold coordination of In^{3+} is assured in the complex.

For most of the complexes, the analytical and infrared spectroscopic results indicate clearly that an almost complete occupation of all the coordination centers of the polymeric Schiff bases was achieved. Only for the ions Al^{3+} V^{2+} and Pt^{2+}, which are expected to react with difficulty with Schiff bases, a varying deficiency of metal content was found, showing that this is not the case. Altogether, it is surprising that these metal ions react at all, and the ease should be noted with which polymeric Schiff base complexes can be obtained for Be^{2+}, In^{3+}, Rh^{3+} and Pd^{2+}, for which monomeric complexes of this kind are formed only with difficulty or not at all. This might be due to the insolubility of the polymeric chelates, which reduces the sensitivity against hydrolytic decomposition.

While the polymeric ligands II–IV are fourdentate in the anionic forms, and a corresponding structure of their complexes can be assumed, ligand V contains 5 base centers and thus the coordination number may be 4 or 5. Although we can give no exact proof as yet due to the extreme insolubility of the compounds, one might be able to compare these compounds with similar monomeric complexes. For the complexes of the bivalent metal ions of Mn, Co, Ni, Cu and Zn with N,N-bis(salicylidene)-N-methylpropylenetriamine five-coordination was inferred from spectroscopic and magnetic properties [15] and it was recently proven to be true for Ni^{2+} and Co^{2+} [16, 17]. Therefore, it seems appropriate to assume five-coordination for our polymeric complexes of Cr^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Pd^{2+} too. For the tri- and tervalent ions, additional ligands X^- increase the coordination number to 6 in an approximately octahedral arrangement, and for UO_2·5,5'-SalMe-DPT·H_2O it might be even higher (probably 8). On the other hand for Be^{2+} and Zn^{2+}, a tetrahedral arrangement is most likely.

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