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Polymer Complexes, Part XXI. Stereochemical Changes of Metal Chelates of Poly(5-vinylsalicylidene-2-benzothiazoline)

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Summary. Poly(5-vinylsalicylidene-2-benzothiazoline) homopolymer (*PVSB*H_2) and polymer complexes of 5-vinylsalicylidene-2-benzothiazoline with a number of divalent transition metals have been prepared and characterized using spectral (^{1}H NMR and ^{13}C-NMR, IR, UV-VIS) and magnetic measurements. The data suggest that the Co(II), Ni(II), Fe(II) and Mn(II) polymer complexes are octahedral dimers, while the rest are monomeric with square planar tetrahedral geometries.

Keywords. Homopolymer; Polymer complexes; Electronic spectra; Infrared spectra; Electron spin resonance.

Polymere Komplexe, 21. Mitt.: Stereochemische Änderungen in Metallchelaten von Poly(5-vinylsalicyliden-2-benzothiazolinen)

Zusammenfassung. Es wurden homopolymere Poly(5-vinylsalicyliden-2-benzothiazolin)-(*PVSB*H_2) und polymere 5-Vinylsalicyliden-2-benzothiazolin-Komplexe mit einer Reihe von zweiwertigen Metallen hergestellt und mittels spektroskopischer (^{1}H- und ^{13}C-NMR, IR, UV-VIS) und magnetischer Messungen charakterisiert. Die Daten erlauben den Schluß, daß es sich bei den Co(II)-, Ni(II)-, Fe(II)- und Mn(II)-Polymerkomplexen um oktahedrale Dimere handelt, während der Rest monomere Strukturen mit planar-tetrahedraler Geometrie zeigt.

Introduction

Metal complexes of polymers are of interest for a variety of reasons [1]. We have been interested in the chelating properties of polymers containing mixed donor atom sets [2]. Increasing interest in synthesis and reactivity of polymeric metal complexes of poly(5-vinylsalicylidene-2-benzothiazoline) (*PVSB*H_2) arises due to their use against many diseases, antifungial activity and employment in industry [1–5]. It has recently been observed that some drugs have increased activity administered as polymeric metal complexes [6]. In this paper, polymer complexes of 5-vinyl-

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salicylidene-2-benzothiazoline with some transition metal salts were prepared and characterized.

Experimental Part

Salicylaldehyde (Aldrich) was degassed, twice distilled on a vacuum line, and stored over anhydrous Na_2SO_4. Paraformaldehyde and 2-aminobenzenthiol (Merck) were used without further purification and 2,2-azobisisobutyronitrile (*AIBN*, Eastman Kodak) was purified by recrystalization from *E*tOH [7].

5-Vinylsalicylidene-2-benzothiazoline

5-Vinylsalicylidene-2-benzothiazoline (*VSB*H_2) monomer was prepared as reported previously [1–3, 6]. Equimolar amounts of 5-vinylsalicylaldehyde and 2-aminobenzenthiol in *E*tOH were stirred for 24 h to give 5-vinylsalicylidene-2-benzothiazoline monomer (M.w. ca. 229) (Found: C 68.1, H 4.8, N 6.1, S 14.0. Calculated for $C_{13}H_{11}NSO$: C 67.9, H 4.8, N 6.0, S 13.8%).

Polymer Complexes

Polymer complexes of *VSB*H_2 with Cu(II), Ni(II), Co(II), Fe(II), Mn(II), Zn(II), Pd(II) and UO_2^{2+} were prepared by dissolving equimolar amounts of *VSB*H_2 and the metal salt in *DMF* with 0.1 *w/v AIBN* (*AIBN* = 2,2-azobisisobutyronitrile) as initiator. The mixture was boiled under reflux for 6 h and the resulting polymer complexes precipitated by pouring into a large excess of distilled H_2O containing dilute HCl to remove contaminating metal salts. The polymer complexes were filtered off, washed with H_2O and dried in vacuo at 40 °C for several days. The homopolymer and its metal polymer complexes were analyzed for C, H, N and S by microanalytical techniques at Cairo University, Egypt. Metal contents in the polymer complexes were estimated by standard methods [8].

All physical measurements were carried out as previously reported [6, 9].

Results and Discussion

The analytical and physical data for the polymer complexes, all of which are-stable, intensely coloured and insoluble in common organic solvents, are listed in Table 1. This insolubility prevented molecular weight and molar conductance determination.

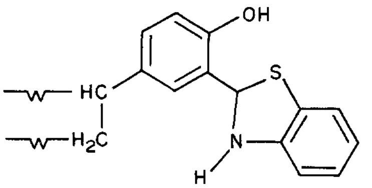
The NMR spectrum of *PVSB*H_2 homopolymer exhibits signals in the 6.4–7.2 ppm region (aromatic protons), plus signals at 11.9, 4.5, and 7.8 ppm assigned to OH, NH, and H–C=N protons, respectively. Signals at 162.2 and 150.4 ppm in the ^{13}C NMR spectrum of *PVSB*H_2 are assigned to OH and H–C=N.

The IR spectrum of *PVSB*H_2 (Table 1) shows a broad strong band in the 3300–2850 cm^{-1} region which may be assigned to ν(OH) and/or ν(NH). A strong band at 1675 cm^{-1} is attributed to N–H deformation vibrations, while the absence of ν(SH) (2500–2660 cm^{-1}) and ν(C=N) (1600–1660 cm^{-1}) are indicative of the benzothiazoline structure. Two bands of medium intensity at 1580 and 1530 cm^{-1} can be assigned to the thiazolines ring vibration. Therefore, we conclude that the homopolymer exists in the benzothiazoline form (1) rather than the Schiff base form. In all the polymer complexes ν(NH) is absent and a strong, sharp band at $1600 \pm 10\,cm^{-1}$ ascribed to ν (C=N) is observed.

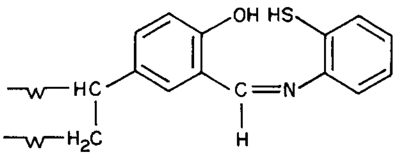
In *PVSB*H_2-uranyl acetate, *PVSB*H_2–$PdCl_2$ and *PVSB*H_2–$CdCl_2$, the *PVSB*H_2 appears to be monobasic and bidentate, coordinating via the azomethine nitrogen

Table 1. Analytical and IR data for the complexes derived from $VSBH_2$

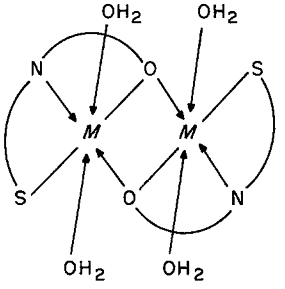
Polymer complex	Found (calcd.) %						IR bands (cm^{-1})				
	C	H	N	S	Metal	H_2O	$\nu S{-}H$	$\nu M{-}S$	$\nu M{-}N$	$\nu M{-}O$	$\nu C{-}O$
$[Mn(VSBH_2{-}2H)\cdot 2H_2O]_n$	48.9 (49.1)	4.2 (4.1)	4.2 (4.4)	9.8) (10.1)	17.1 (17.3)	11.2 (11.3)	–	335	477	531	1570
$[Ni(VSBH_2{-}2H)\cdot 2H_2O]_n$	48.4 (48.5)	3.4 (4.0)	4.4 (4.4)	9.7 (9.9)	18.4 (18.3)	11.1 (11.2)	–	395	475	530	1580
$[Co(VSBH_2{-}2H)\cdot 2H_2O]_n$	48.5 (48.5)	4.1 (4.0)	4.2 (4.4)	10.0 (9.9)	18.4 (18.3)	11.4 (11.2)	–	360	470	525	1575
$[Fe(VSBH_2{-}2H)\cdot 2H_2O]_n$	49.0 (48.9)	4.1 (4.1)	4.3 (4.4)	9.8 (10.0)	17.7 (17.2)	11.5 (11.3)	–	350	480	535	1568
$[Cu(VSBH_2{-}2H)\cdot 2H_2O]_n$	50.5 (50.6)	3.7 (3.6)	4.4 (4.4)	10.3 (10.4)	20.2 (20.6)	2.9 (2.8)	–	375	465	518	1555
$[Zn(VSBH_2{-}2H)\cdot 2H_2O]_n$	50.4 (50.2)	3.4 (3.2)	4.2 (4.2)	10.5 (10.3)	21.0 (21.1)	6.0 (5.8)	–	360	462	515	1305
$[Cd(VSBH_2{-}H)_2]_n$	54.9 (54.9)	3.5 (3.5)	4.6 (4.2)	11.2 (11.3)	20.0 (19.8)	–	2575	–	465	515	1553
$[Pd(VSBH_2{-}H)_2]_n$	55.7 (55.6)	3.7 (3.6)	4.8 (5.0)	11.1 (11.4)	9.0 (8.9)	–	2575	–	460	510	1300
$[UO_2(VSBH_2{-}H)_2]_n$	43.0 (43.1)	2.5 (2.5)	4.0 (3.9)	8.6 (8.8)	33.3 (32.9)	–	2576	–	540	460	1302



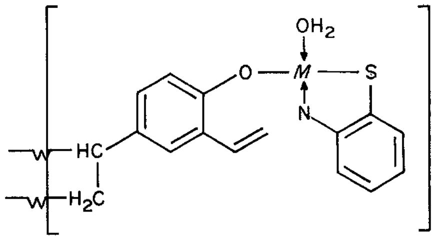
Cyclic form
(1)



Schiff base form
(2)



$M = \text{Fe}^{\text{II}}, \text{Mn}^{\text{II}}, \text{Co}^{\text{II}}$ or Ni^{II}
(3)



$M = \text{Cu}^{\text{II}}$ or Zn^{II}
(4)

and phenolic oxygen atoms. This behaviour is supported by the following evidence: (i) the disappearance of ν(OH) and the appearance of a band at 1300–1305 cm^{-1} assigned to ν(C–O) indicate the involvement of phenolic oxygen in bonding; (ii) a strong band at $1605 \pm 5\ \text{cm}^{-1}$ ascribed to ν(C=N) is observed; (iii) ν(SH) (2575 cm^{-1}) is unshifted, suggesting that the sulphur is not coordinated, and (iv) ν(M–O) and ν (M–N) are observed in the 460–515 and 465–540 cm^{-1} region respectively. The ν_3 mode of the UO_2^{2+} entity appears at 935 cm^{-1}.

The IR spectra of *PVSB*H_2–CuCl_2, *PVSB*H_2–CoCl_2, *PVSB*H_2–NiCl_2, *PVSB*H_2–MnCl_2, *PVSB*H_2–FeCl_2, and *PVSB*H_2–ZnCl_2 reveal the presence of coordinated water molecules, with a sharp band at ca. 3410 cm^{-1} and two weaker bands at ca. 850 and 705 cm^{-1}, assigned to OH stretching, rocking and wagging vibrations [10]. The homopolymer is apparently dibasic and tridentate, coordinating via the ν(C–O), ν(C–S) and ν(C=N) groups. This mode of complexation is suggested by the following evidence: (i) both the ν(OH) peaks (ca. 3300 cm^{-1}) and ν(SH) peak (ca. 2575 cm^{-1}) of the free homopolymer are absent indicating deprotonation of the phenolic and thiolic protons on complexation [11], (ii) the participation of phenolic oxygen and thiolic sulphur in coordination to the metal ion is further supported by an upward shift in ν(C–O) by 20–30 cm^{-1} and a downfield shift in ν(C–S) by 10–15 cm^{-1} in all the polymer complexes, (iii) the large shift of phenolic ν(C–O) to higher energy by ca. 30 cm^{-1} in the case of the cobalt(II), iron(II), nickel(II) and manganese(II) polymer complexes indicates the presence of phenoxo bridges [12], (iv) the lowering of ν(C=N) by ca. 15 cm^{-1} shows the participation of azomethine nitrogen atom in complexation, and (v) new bands at

Table 2. Electronic spectral bands, assignments and ligand field parameters for the polymer complexes

Polymer complex	Band position cm^{-1}	Assignment	Dq cm^{-1}	B cm^{-1}	B	ν_2/ν_1	μ_{eff}. B.M.	Geometry
$[Mn(VSBH_2\text{-}2H)\cdot 2H_2O]_n$[a]	8440		844.3	–	–	–	2.23	octahedral
	26100							
	32000							
$[Ni(VSBH_2\text{-}2H)\cdot 2H_2O]_n$	9530	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)(\nu_1)$	952.5	966	0.92	1.7	3.16	octahedral
	16400	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)(\nu_2)$						
	27000	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)(\nu_3)$						
$[Co(VSBH_2\text{-}2H)\cdot 2H_2O]_n$	8700	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)(\nu_1)$	869.3	819.4	0.84	1.97	4.16	octahedral
	17000	$^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)(\nu_2)$						
	21300	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)(\nu_3)$						
$[Fe(VSBH_2\text{-}2H)\cdot 2H_2O]_n$	10000	$^5T_{1g} \rightarrow {}^5E_g$	995.7				5.23	octahedral
$[Cu(VSBH_2\text{-}2H)\cdot H_2O]_n$	17500	$^2B_{1g} \rightarrow {}^2E_g$ $\rightarrow {}^2A_{1g}$	174.6				1.96	sq. planar
	26400	charge transfer						
$[Pd(VSBH_2\text{-}H)]_n$	26000	$^1A_{1g} \rightarrow {}^1A_{1g}$ $\rightarrow {}^1B_{1g}$ $\rightarrow {}^2E_g$				1.19		sq. planar
$[UO_2(VSBH_2\text{-}H)_2]_n$	20500	$^1\Sigma^+_g \rightarrow {}^3\Pi\mu$						

[a] Owing to very weak absorptions, the spectrum could not be assigned with certainty

510–535, 460–480 and 335–395 cm^{-1}, which do not correspond to any peak in the $PVSBH_2$ homopolymer spectrum, may be attributed to $\nu(M\text{–}O)$, $\nu(M\text{–}N)$ and $\nu(M\text{–}S)$, respectively [6, 10]. The far IR data confirm the absence of coordinated chloride.

Deprotonation is also confirmed by the observed liberation of hydrogen chloride or ethanoic acid during complexation; this was confirmed by *pH*-metric techniques, spot tests [2], and the characteristic odours.

The magnetic moments of all complexes were determined at room temperature, the values and suggested geometries are given in Table 2. The magnetic moment of the Mn(II) polymer complex is slightly lower than the spin-only value of 5.90–6.01 B.M., for high-spin octahedral configuration, possibly due to magnetic exchange or small traces of manganese(III) species [13]. The magnetic moment of $PVSBH_2\text{–}CuCl_2$ shows the presence of one unpaired electron.

The electronic spectra data are given in Table 2. It is concluded that the five coordinate polymeric metal complexes of the general formula $[M(PVSBH_2\text{–}2H)\cdot 2H_2O]_n$ (M = Ni, Co, Mn or Fe) are dimetallic with octahedral geometry (structure **3**) while the rest are monomeric and square or tetrahedral (structure **4**).

The ESR spectrum of $PVSBH_2$-copper(II) was recorded. Analysis of the spectrum gave $g_{\parallel} = 2.2342$ and $g_{\perp} = 2.0943$. These parameters were substituted into the expression, $g_{av} = [(g_{\parallel}^2 + 2g_{\perp}^2)/3]^{1/2}$ to calculate $g_{av}(2.143)$. It is clear that $g_{av} > g_{\perp} > 2.04$, characteristic of axial symmetry, which is in agreement with the square planar structure suggested by the electronic spectrum.

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