

Synthesis, characterization, and thermal investigation of some transition metal complexes of benzopyran-4-one Schiff base as thermal stabilizers for rigid poly(vinyl chloride) (PVC)

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Received: 25 May 2012 / Accepted: 21 January 2013
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Abstract New metal complexes of Schiff base (PB) prepared from condensation reaction of 2-aminopyridine and 6-formyl-5,7-dihydroxy-2-methylbenzopyran-4-one with metal ions; Mn(II), Co(II), Ni(II), and Cu(II) are prepared. Different analysis tools like elemental analyses, FTIR, thermal analysis, conductivity, electronic spectra, and magnetic susceptibility measurements are all used to elucidate the structures of the newly prepared metal complexes. The free Schiff base (PB) has been examined as thermal stabilizer and co-stabilizer for rigid PVC in air, at 180 °C. Its high stabilizing efficiency is detected by its high induction period value (T_s) when compared with some of the common reference stabilizers used industrially, such as dibasic lead carbonate and calcium–zinc stearate (Ca–Zn soap). Blending Schiff base or its metal complexes with Mn(II), Co(II), Ni(II), and Cu(II) ions with the reference stabilizers in different ratios had a synergistic effect on the induction period (thermal stability). The stabilizing efficiency is attributed at least partially to the ability of the stabilizer to be incorporated in the polymeric chains, thus disrupting the chain degradation process.

Keywords Schiff bases · Transition metal complexes · PVC · Stabilizer · Induction period · Degradation

Introduction

Schiff bases (–CH=N–), play an important role in the development of coordination chemistry as they readily form stable complexes with most of the metal ions. Schiff base metal complexes have played a key role in the development of coordination chemistry, resulting in an enormous number of publications, ranging from pure synthetic work to modern physicochemical and biochemically relevant studies of metal complexes [1]. Schiff bases offer a versatile and flexible series of ligands capable of binding with various metal ions to give complexes with suitable properties for many applications [2]. In recent years, many copper, nickel, and manganese complexes of Schiff bases were prepared and characterized by several techniques [3, 4].

Poly(vinyl chloride) (PVC) is one of the most important commercial thermoplastic polymers used in our daily life, as it has a great technical and economic importance. But it still has some problems due to its poor thermal stability leading to its degradation by a dehydrochlorination reaction initiated at the labile sites present on the polymeric chains, such as branching, chloroallyl groups, end groups, oxygen-containing groups, and head-to-head structures [5], in addition to the tacticity [6]. This leads to a strong discoloration of the polymer and a deterioration of its physical and mechanical properties.

For thermal stabilization of the polymer, highly effective additives such as metallic soaps [7–11], basic compounds [12], and organotin compounds [13] have been commercially used. However, some of them are toxic and cause environmental problems, as most of them leave toxic residues during the degradation process. This has recently directed attention towards the use of organic stabilizers [14–16].

In this study, the newly prepared Mn(II), Co(II), Ni(II), and Cu(II) metal ion complexes of Schiff base prepared from condensation reaction of 2-aminopyridine and

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6-formyl-5,7-dihydroxy-2-methylbenzopyran-4-one have been prepared and characterized. In addition, Schiff base and its prepared complexes have been investigated as thermal stabilizers and co-stabilizers for rigid PVC. The complexes exhibit a higher thermal stability than that of the free Schiff base.

Experimental

Materials and reagents

All materials and solvents used in this study were chemically pure grade. They included 2-aminopyridine, 5-methoxy-2-methyl-furanobenzopyran-4-one (purchased from Memphis Company for Pharmaceutical and Chemical Industry, Cairo, Egypt), potassium dichromate ($K_2Cr_2O_7$), hydrochloric and sulfuric acid (purchased from El-Nasr Pharmaceutical Chemicals, Adwic, Egypt), and copper(II) acetate ($Cu(CH_3COO)_2 \cdot H_2O$), nickel(II) perchlorate ($Ni(ClO_4)_2 \cdot 6H_2O$), cobalt(II) acetate ($Co(CH_3COO)_2 \cdot H_2O$), and manganese(II) chloride ($MnCl_2 \cdot 4H_2O$) (purchased from Aldrich).

The commercial PVC (suspension) used in this study was additive-free, with a K value 70 and supplied by Hüls Co., dibasic lead carbonate (DBLC) (Rolite lead) from the National Lead Co., Germany was also used and Ca–Zn stearate was obtained from “Lagor-S.P.A.” Co., Italy.

The organic solvents used included ethanol, dimethyl formamide (DMF), and toluene. All these solvents were either spectroscopic pure grade solvents from BDH or purified with the recommended methods [17].

Analysis and physical measurements

Carbon, hydrogen, and nitrogen were analyzed by standard microanalysis methods at Microanalytical center, Cairo University, Giza, Egypt.

Infrared spectra ($4,000\text{--}400\text{ cm}^{-1}$) were obtained with KBr disk technique using test scan Shimadzu FTIR spectrometer. Molar conductivity of 10^{-3} M solutions of the complexes in DMF was measured on the conductivity meter ORION model 150 of 0.6 cell constant. Thermal analyses have been carried out using Shimadzu-50 Thermal Analyzer from room temperature to $1,000\text{ }^\circ\text{C}$ under heating rate of $10\text{ }^\circ\text{C min}^{-1}$. Magnetic susceptibilities of the chelates were measured at room temperature using a magnetic susceptibility Sherwood Scientific, Cambridge, England.

The electronic absorption spectra in Nujol mull were measured using UV/Vis–NIR 3101 PC Shimadzu spectrophotometer. The effective magnetic moments were calculated from the expression $\mu_{\text{eff}} = 2.828(X_M T)^{1/2}\text{ BM}$, where X_M

is the molar susceptibility corrected using Parcel’s constants for diamagnetism of all atoms in the compounds [18]. Analysis of the metal ions were carried out by dissolving 20–25 mg of the metal chelate in concentrated nitric acid followed by hydrogen peroxide, neutralizing the diluted aqueous solutions with sodium hydroxide to pH 5.5 and the metal content was determined by recommended method [19] or were determined by the mass of the complex residue after thermal decomposition.

Synthesis of the Schiff base

A 5,7-dihydroxy-6-formyl-2-methylbenzopyran-4-one was synthesized from 5-methoxy-2-methyl-furanobenzopyran-4-one as previously discussed [20]. Schiff base (SB) was prepared by addition of 2-aminopyridine (10 mmol) in 20 mL ethanol dropwise with continuous stirring to a solution of 5,7-dihydroxy-6-formyl-2-methylbenzopyran-4-one in ethanol (20 mL, 10 mmol). The mixture was stirred at room temperature for at least 30 min and then the yellow solid was obtained “mp = $210\text{ }^\circ\text{C}$, yield 95 %” and collected by filtration, washed with ethanol, and recrystallized from DMF (Scheme 1).

Synthesis of the metal complexes

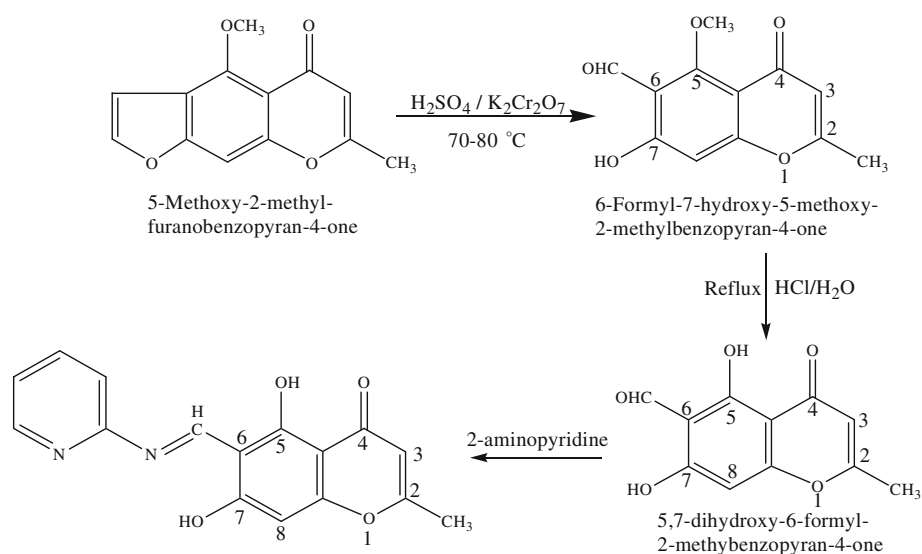
A hot ethanolic solution of the metal salt (0.068 mol L^{-1} , 10 mL) was gradually added to 10 mL solution of the ligand in (1:1) molar ratio, and the solution was stirred on a water bath for 2 h during which the metal complex precipitated. On the other hand, the precipitation of nickel complex required addition of ammonia solution dropwise to adjust the pH to 6.8. The resulting complexes “yield 70–85 %” were filtered out, washed thoroughly with successive portions of hot ethanol followed by petroleum ether until the filtrate becomes colorless. The obtained complexes were kept in a vacuum desiccator over anhydrous calcium chloride. The complexes are air stable in the solid state and soluble in DMF or DMSO.

Preparation of PVC samples

Samples of PVC for heat degradation were prepared by thoroughly mixing 1 g of PVC powder with 2 wt% of the stabilizer (or a mixed stabilizer) in a mortar and 0.2 g of the resulting fine powder was used in the investigation.

Evaluation of stabilizing efficiency

Evaluation of the stabilizing efficiency of the investigated thermal stabilizers was carried out by using Congo-red dye paper to measure the thermal stability value (T_s), i.e.,

Scheme 1 Preparation of Schiff base (PB)


the time elapsed for the detection of HCl gas evolved at 180 °C, in air [21].

Results and discussion

Characterization of the prepared complexes

In the present investigation, the newly prepared complexes of Schiff base (PB) are investigated and their structures are characterized via several analysis tools. These complexes are stable in air, non-hygroscopic and have high melting point (>300 °C), they are easily soluble in DMF and DMSO, and slightly soluble in non-polar solvents. The C, H, N, Cl, and metal contents of both theoretically calculated and measured values are in accordance with the tentative formula of the complexes. The obtained data for the complexes confirm to a (1:1) (metal:ligand) stoichiometry. The analytical and physical data of Schiff base and its complexes are shown in

Table 1. The molar conductance values of the complexes at room temperature in DMF lie in the 14–30 $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ range. These values are much lower than the values reported for the (1:1) electrolytes in the same solvents [22], indicating their non-electrolytic nature.

Infrared spectroscopy

The bonding between the ligand and metal ions can be inferred by comparing the IR spectra of the metal chelates with this of the free ligand. IR band assignments of Schiff base (PB) and its metal chelates are listed in Table 2. The IR spectra of the complexes are very similar. The characteristic bands have similar shifts [23, 24], suggesting that they have similar coordination structures.

The band at 1,658 cm^{-1} of the free Schiff base (PB) assigned to the stretching vibration of C=O group, does not show change on complexation, indicating that it does not participate in chelation.

Table 1 Analytical and physical data of the metal complexes of Schiff base (PB)

Symbol	Ligand or complex	Formula	M. W.	Yield/ %	Calc. (found)				
					% C	% H	% N	% M	% Cl
PB	(PB)	$\text{C}_{16}\text{H}_{12}\text{N}_2\text{O}_4$	296.28	95	64.86 (65.00)	4.08 (3.99)	9.46 (9.60)	–	–
Mn–PB	$[\text{Mn}(\text{PB}) \cdot \text{Cl} \cdot 3\text{H}_2\text{O}] \cdot \text{H}_2\text{O}$	$\text{C}_{16}\text{H}_{19}\text{ClMnN}_2\text{O}_8$	457.72	70	41.98 (41.94)	4.18 (4.12)	6.12 (6.15)	12.00 (12.06)	7.74 (7.60)
Co–PB	$[\text{Co}(\text{PB}) \cdot \text{OAc} \cdot 3\text{H}_2\text{O}] \cdot \text{H}_2\text{O}$	$\text{C}_{18}\text{H}_{22}\text{CoN}_2\text{O}_{10}$	485.30	74	44.55 (44.70)	4.57 (4.56)	5.77 (5.81)	12.14 (12.20)	–
Ni–PB	$[\text{Ni}(\text{PB}) \cdot \text{OH} \cdot 3\text{H}_2\text{O}] \cdot 2\text{H}_2\text{O}$	$\text{C}_{16}\text{H}_{22}\text{NiN}_2\text{O}_{10}$	461.04	85	41.68 (41.64)	4.81 (5.01)	6.08 (6.07)	12.73 (12.85)	–
Cu–PB	$[\text{Cu}(\text{PB}) \cdot \text{OAc} \cdot \text{H}_2\text{O}] \cdot 2\text{H}_2\text{O}$	$\text{C}_{18}\text{H}_{20}\text{CuN}_2\text{O}_9$	471.90	80	45.81 (45.84)	4.27 (4.26)	5.94 (5.89)	13.46 (13.50)	–

OAc acetate group

Table 2 Assignment of IR-bands of metal chelates of Schiff base (PB)

Compound	Wavenumber/cm ⁻¹						
	M:L	ν C=O	ν C=N	ν C-O	γ OH	ν M-N	ν M-O
Schiff base PB	–	1,658	1,589	1,170	954	–	–
Mn-PB	1:1	1,658	1,549	1,206	964	556	425
Co-PB	1:1	1,655	1,546	1,177	964	558	425
Ni-PB	1:1	1,656	1,542	1,180	964	512	429
Cu-PB	1:1	1,652	1,545	1,176	964	510	410

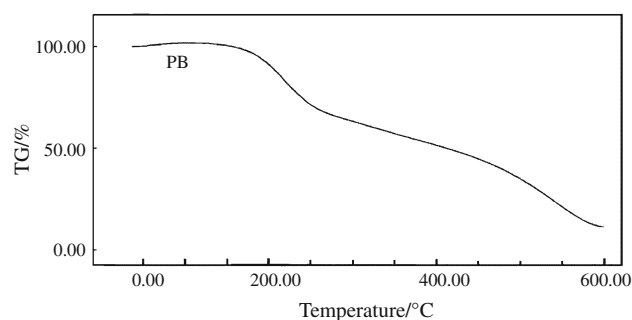
IR spectrum of Schiff base displayed a shoulder at $1,589\text{ cm}^{-1}$ which could be assigned to C=N stretching of azomethine group. The shift in this band to a lower wave number ($1,542\text{--}1,549\text{ cm}^{-1}$) indicates that the azomethine group of Schiff base (PB) is coordinated to the metal ions in all the complexes.

Schiff base (PB) contains a pyridine nucleus, the shoulders at $1,625\text{ cm}^{-1}$ could be assigned to C=N stretching of pyridine [25]. No significant change is observed in the infrared spectra of the complexes, this indicates that the C=N of the pyridine ring does not participate in the chelation.

Schiff base shows a band at $1,170\text{ cm}^{-1}$ due to the phenolic C–O stretching vibration [26], undergoes a shift towards higher wave number in the spectra of the complexes. This shift confirms the participation of oxygen in the C–O–M bond [27].

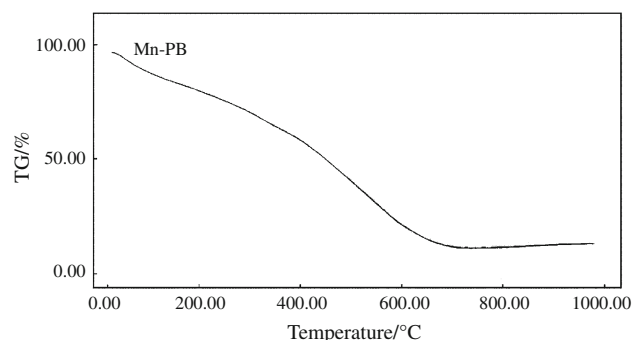
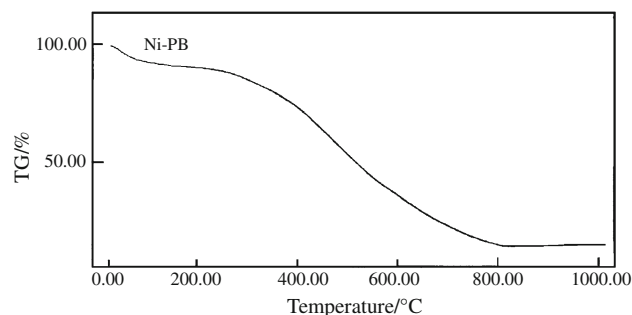
The acetate ion in aqueous solution is characterized by bands at $1,578$ and $1,411\text{ cm}^{-1}$, which are commonly assigned to antisymmetric (ν_{as}) and symmetric (ν_{sym}) stretching vibrations of the carboxylate group. These frequencies and, in particular, their difference, $\Delta\nu = \nu_{\text{as}} - \nu_{\text{sym}}$, have been used as empirical indicators of coordination modes of the acetate group. In Co–PB and Cu–PB complexes, the frequency of the vibration ν_{as} (COO) appears at $1,598\text{ cm}^{-1}$, while that characteristic of the ν_{sym} (COO), appeared at $1,397\text{ cm}^{-1}$, $\Delta\nu > 200\text{ cm}^{-1}$. According to Deacon and Phillips [28], a difference larger than 200 cm^{-1} indicates a mono-dentate coordination mode of acetate ion in these complexes.

In the low frequency region, new bands observed in the IR spectra of all chelates in the region $410\text{--}429\text{ cm}^{-1}$ may be attributed to ν M–O [29]. This band is possibly due to the bond between the metal ion and the oxygen of phenolic groups of the benzopyran-4-one ring. The new band observed at $510\text{--}558\text{ cm}^{-1}$ in the infrared spectra of the complexes may be attributed to ν M–N stretching [30].

**Fig. 1** Thermogravimetric curve, TG of PB Schiff base

This indicates that both phenolic oxygen and nitrogen of azomethine group are involved in the chelation with metal ion [31].

Broad bands at $3,360\text{--}3,386\text{ cm}^{-1}$ [32, 33] in the IR spectra of all complexes could be attributed to the OH stretching vibrations of the OH of the lattice water molecules and –OH group in position five. The weak band observed at 964 cm^{-1} in the IR spectra of the complexes may be due to the bending motion of coordinated water molecules [34].

**Fig. 2** Thermogravimetric curve, TG of Mn-PB complex**Fig. 3** Thermogravimetric curve, TG of Ni-PB complex

Thermogravimetric analysis (TG) of the metal complexes

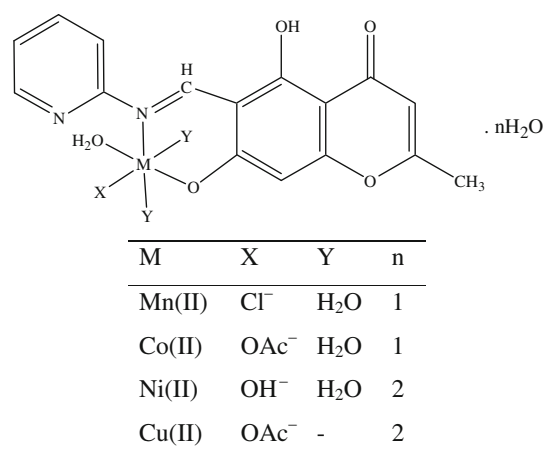
This method of analysis is used to confirm the results of elemental analyses. TG analysis was measured for PB Schiff base (Fig. 1), Mn–PB (Fig. 2), and Ni–PB complexes (Fig. 3), the heating rate was suitably controlled at $10\text{ }^{\circ}\text{C min}^{-1}$ and the mass loss was conducted from the ambient temperature up to $1,000\text{ }^{\circ}\text{C}$.

Figure 1 shows the TG of the free Schiff base, PB, as shown in this figure, the decomposition of the ligand occurs in two steps, the first one in the range of $0\text{--}300\text{ }^{\circ}\text{C}$ and the other on $300\text{--}600\text{ }^{\circ}\text{C}$. At $600\text{ }^{\circ}\text{C}$, the ligand was completely decomposed. As shown in Fig. 2, for the Mn–PB complex, the first stage of the decomposition in the range of $18\text{--}100\text{ }^{\circ}\text{C}$ with mass loss of 4.00% indicated a loss of one molecule of water of crystallization [34] (calculated 3.93%). The second decomposition stage occurs in the temperature range of $100\text{--}200\text{ }^{\circ}\text{C}$ is due to loss of three water molecules (11.61%) which is coordinated to the metal ion to fulfill its coordination center [35] (calculated 11.81%). The degradation of the ligand was observed till $600\text{ }^{\circ}\text{C}$. After this, the complex completely converts into MnO_2 and the mass becomes stable. The experimental mass value of MnO_2 (19.10%) is in a good agreement with the calculated one (18.99%). On the other hand, the TG curve of Ni–PB complex, Fig. 3, shows the first mass loss of 8.00% corresponding to the elimination of the two crystal water molecules (calculated 7.81%) occurred in the stage beginning at $27\text{ }^{\circ}\text{C}$ and ending at $100\text{ }^{\circ}\text{C}$. The second mass loss (11.57%) occurs in the temperature range of $100\text{--}320\text{ }^{\circ}\text{C}$ is due to loss of three coordinated water molecules [35] (calculated 11.72%). The decomposition of the organic part of the complex occurs till a constant mass, in which the nickel oxide residue is formed as a final product. The experimental mass percent value of NiO (16.35%) is in good agreement with the calculated one (16.20%).

The metal content percentages of these two complexes (Mn–PB and Ni–PB) are thus calculated and compared with those obtained from the metal content analytical determination [36]. The average metal percentages were found to be in good agreement with those calculated from tentative formula based on the elemental analyses.

Electronic absorption spectra, magnetic moment, and molar conductivity

The Nujol mull electronic spectrum of the free ligand (PB) shows absorption band at $29,411\text{ cm}^{-1}$ attributed to the $\pi\text{--}\pi^*$ transition within the azomethine ($\text{CH}=\text{N}$) group [37]. The bathochromic shift in this band in all spectra of the



Scheme 2 Structure of the prepared complexes

complexes is confirming the participation of nitrogen atom of azomethine group in the complexation. The band at $25,907\text{ cm}^{-1}$ in the spectra of free ligand could be assigned to an intramolecular charge transfer (CT transition) involving the whole molecule.

The magnetic moment value of Mn–PB complex is 5.9 BM corresponding to the existence of five unpaired electrons which is consistent with the octahedral structure [38]. The presence of band at $28,735\text{ cm}^{-1}$ which assigned to ${}^6\text{A}_1\text{g} \rightarrow {}^6\text{T}_1\text{g}(\text{p})$ transition indicates the octahedral geometry for this complex [39].

The magnetic moment values of high spin octahedral Co(II) complexes were reported to be in the range of $4.3\text{--}5.2\text{ BM}$ [40]. In this study, the observed magnetic moment values for Co–PB complex is 4.62 BM range which is in good agreement with high spin octahedral geometry. The electronic spectrum of Co–PB complex shows that the complex may be proposed as octahedral structure, based on the appearance of band at $18,484\text{ cm}^{-1}$ which assigned to ${}^4\text{T}_1\text{g}(\text{F}) \rightarrow {}^4\text{T}_1\text{g}(\text{P})$ transition. Also, Ni–PB complex shows magnetic moment of 3.29 BM corresponds to two unpaired

Table 3 Induction period ($T_s\text{ min}^{-1}$) of investigated compounds as thermal stabilizers for rigid PVC

Compound	Symbol	T_s/min
PVC blank	PVC	2
Dibasic lead carbonate	DBLC	9
Calcium–zinc soap	Ca–Zn soap	8
Schiff base	PB	30
Ni-complex	Ni–PB	45
Cu-complex	Cu–PB	48
Co-complex	Co–PB	42
Mn-complex	Mn–PB	38

electrons. This is consistent with high spin octahedral configuration of Ni(II) [41]. The Nujol mull electronic spectrum of this complex displays peak at 16,181 cm^{-1} . This band is expected for an octahedral geometry [42] and has been assigned to ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$.

On the other hand, the measured magnetic moment value for Cu–PB complex is in the 2.07 BM indicating the presence of one unpaired electron; this suggested the presence of copper in the oxidation state II and square planar geometry for this complex [43, 44]. The spectrum of this complex shows band with low intensity at 16,447 cm^{-1} which can be attributed to ${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_g$ transition [45].

Based on the results of elemental analysis, IR, electronic spectra, magnetic moment, molar conductance measurements, and thermogravimetric analysis, it may be concluded that Schiff bases behave as mononegative N_2O tridentate ligands, coordination occurring via the azomethine nitrogen, pyridine ring nitrogen, and the deprotonated phenolic oxygen atoms in position seven of the benzopyrane-4-one ring, as shown in Scheme 2.

Investigation of the compounds as thermal stabilizer for rigid PVC

Results of the thermal stability of rigid PVC degraded in air at 180 $^\circ\text{C}$ in presence of Schiff base (PB) (by using Congo-red dye paper method) are shown in Table 3. The results for the non-stabilized blank as well as those stabilized by both DBLC and Ca–Zn soap, used as reference stabilizers, are also given for comparison.

The results reveal that the investigated Schiff base as thermal stabilizer exhibits a greater stabilizing efficiency than the two used commercial stabilizers, as it is shown by the larger thermal stability values (T_s). The thermal stability value for the investigated stabilizer is almost three times larger than the values obtained for the reference stabilizers. The metal complexes of Schiff base (PB) exhibit greater stabilizing efficiency than Schiff base itself as shown in Table 3.

Effects of mixed stabilizers on thermal stabilization efficiency in rigid PVC

It was of interest to investigate the effect of mixing the investigated stabilizers with those used in industry on the stabilization efficiency. For this purpose, the investigated stabilizer (Schiff base) and its metal complexes were examined as co-stabilizers with the two used commercial stabilizers (Table 4). Mixing was done in the range of 0–100 % of the investigated stabilizer relative to each of the reference stabilizers. The total mixed stabilizers

Table 4 Induction period ($T_s \text{ min}^{-1}$) of mixed investigated compounds with reference stabilizers

Type of stabilizer	0 %:100 % (PB:DBLC)	25 %:75 % (PB:DBLC)	50 %:50 % (PB:DBLC)	75 %:25 % (PB:DBLC)	100 %:0 % (PB:DBLC)
PB	9	34	47	36	30
Type of stabilizer	0 %:100 % (PB:Ca–Zn soap)	25 %:75 % (PB:Ca–Zn soap)	50 %:50 % (PB:Ca–Zn soap)	75 %:25 % (PB:Ca–Zn soap)	100 %:0 % (PB:Ca–Zn soap)
PB	8	39	42	37	30
Type of stabilizer	0 %:100 % (Cu–PB:DBLC)	25 %:75 % (Cu–PB:DBLC)	50 %:50 % (Cu–PB:DBLC)	75 %:25 % (Cu–PB:DBLC)	100 %:0 % (Cu–PB:DBLC)
Cu–PB	9	54	60	50	48
Type of stabilizer	0 %:100 % (Cu–PB:Ca–Zn soap)	25 %:75 % (Cu–PB:Ca–Zn soap)	50 %:50 % (Cu–PB:Ca–Zn soap)	75 %:25 % (Cu–PB:Ca–Zn soap)	100 %:0 % (Cu–PB:Ca–Zn soap)
Cu–PB	8	52	55	52	48

concentration was kept constant at 2 mass% based on the polymer mass. The results reveal a true synergism resulting from the combination of the organic stabilizer (Schiff base, PB) with each of the reference stabilizers, irrespective to the class of which the reference stabilizer belongs to. Maximum synergism is attained at the ratio 1:1 of both the investigated stabilizers with each of the reference stabilizers. These results are in accordance with many data presented in the literature for cases where conventional stabilizers are mixed with organic stabilizers [46–53].

In order to suggest a probable mechanism which can give an explanation for the stabilizing efficiency given by the investigated organic stabilizers, a set of experiments has been performed to investigate the mode of action of this type of compounds as organic thermal stabilizers for PVC:

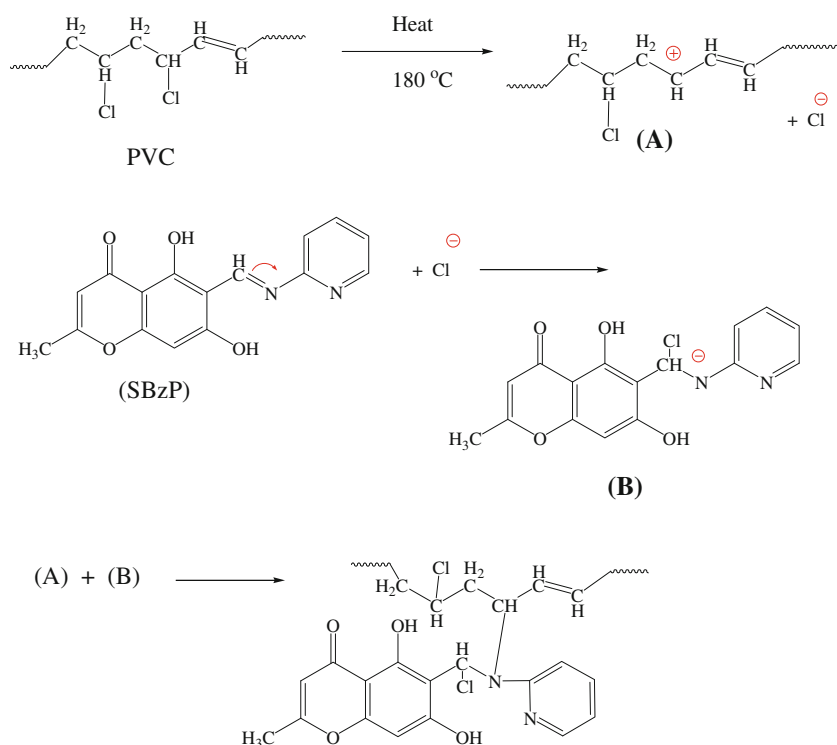
contrast to the unstabilized PVC which was found to be completely soluble in THF.

- (3) Another experimental proof for the high stabilizing efficiency of the investigated stabilizer, as compared with the reference stabilizers, is the higher T_s values of the sample stabilized with PB, relative to that of the blank sample and the samples containing either of the two used reference stabilizers as shown in Table 4.

This indicates that the stabilizer binds itself to PVC chains, and consequently it decreases the formation of conjugated double bonds on the polymeric chains.

From the aforementioned conclusions, one can suggest a probable mechanism for the stabilizing efficiency of the investigated stabilizers during the thermal degradation of PVC. The mechanism is outlined by the following equations.

Mechanism



- (1) When the organic stabilizer PB was subjected to a stream of HCl gas at 180°C in air, for 30 min. The elemental analysis of the treated sample shows the presence of chlorine (Cl % = 9 %), which indicates that PB acts as HCl absorber.
- (2) Testing the solubility of various degraded PVC stabilized with the investigated organic stabilizer at 25 and 35 min reveals the partial insolubility of the degraded samples in THF at the later stages of degradation, i.e., after the thermal stability. This is in

According to the proposed mechanism, the detached chloride anion—from PVC chain—attacks the $\text{C}=\text{N}$ double bond leaving a negative charge on the nitrogen atom which consequently block the carbocation formed on the PVC chain. This assumption was proven by the capability of the prepared Schiff base to absorb HCl gas and by the presence of nitrogen in PVC after thermal degradation in presence of the Schiff base stabilizer.

Indeed, the chloride anion is a weak base, but being the only nucleophile in the system, it can easily attack the

–C=N– double bond especially for the high sensitivity of this group to undergo acid hydrolysis. The nucleophilic attack of chloride anions—detached from PVC chains—on the unsaturated centers of some organic stabilizers has been suggested in the literature [15].

Conclusions

From these studies (elemental analyses, thermal analysis, IR spectra, electronic spectra, and magnetic moment measurements) on the prepared metal chelates, the following conclusions can be drawn concerning the chelating properties of Schiff base as well as the stereochemistry of its corresponding metal complexes. The Schiff bases behave as mononegative NO bidentate ligands, coordination occurring via the azomethine nitrogen and the deprotonated phenolic oxygen atoms in position seven of the benzopyrane-4-one ring.

A square planar structure has been proposed for Cu–PB complex, on the other hand, manganese(II), cobalt(II), and nickel(II) forms with Schiff base (PB) complexes in agreement with an octahedral environment around the metal ion.

Schiff base and its prepared complexes were investigated as both stabilizers and co-stabilizers for rigid PVC based on their greater induction period values relative to those of the reference stabilizers and the extent of discoloration which is much improved too.

Mixing the parent complexes with the two used reference stabilizers in different proportions greatly improves the induction period and also improves the extent of discoloration. The maximum synergism was obtained in the mass ratio (1:1) of the stabilizer and any of the reference stabilizer. Application of these complexes by their interaction with PVC should lead to the increased use of the inorganic complexes in biotechnology and industrial field.

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