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Complexation properties and synthesis of a novel Schiff base with triphenylene nucleus

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1. Introduction

Investigation on metal organic complexes represents one of the most active areas of material science and chemical research. Major advances have been made in these materials due to their interesting properties and potential in various applications, e.g., electrical conductivity, magnetism, host guest chemistry, ion exchange, catalysis, nonlinear optics, etc. [1–3]. Synthesis of new Schiff bases and their metal complexes are still the aim of many recent investigations. Schiff bases have played an important role in the development of coordination chemistry as they readily form stable complexes with most of the transition metals. They show interesting properties, e.g., their ability to reversibly bind oxygen [4], catalytic activity in hydrogenation of olefins [5], transfer of an amino group [6], photochromic properties [7] and complexing ability towards toxic metals [8].

The Schiff base ligands with sulphur and nitrogen donor atoms in their structures act as good chelating agents for the transition and non-transition metal ions [9–12]. Coordination of such compounds with metal ions, such as copper, nickel and iron, often enhance their activities [13], as has been reported for pathogenic fungi [14]. There is a continuing interest in metal complexes of Schiff bases. Because of the presence of both hard nitrogen or oxygen and soft sulphur donor atoms in the backbones of these ligands, they readily coordinate with a wide range of transition metal ions yielding stable and intensely coloured metal complexes, some of which have

ABSTRACT

We presented the synthesis of a novel Schiff base and its complexation properties with some transition metal ions in this work. For this, the 2,3,4,6,7,10,11 hexahydroxytriphenylene (HHTP) as starting material was synthesized according to known procedure. Moreover, the 2-((2-chloroethylimino)methyl) phenol material was prepared with reaction of salicylaldehyde and 2-chloroethylamine hydrochloride. To give the 2,3,4,6,7,10,11-hexakis(salicyliminoethoxy)triphenylene (HSE-TP) as a novel Schiff base, the HHTP were treated with 2-((2-chloroethylimino)methyl)phenol in acetone media. Complexation properties of this Schiff base were investigated towards Ni(II), Cu(II), Co(II), Zn(II), Pd(II) and Cd(II) as transition metals. The structures of these new compounds (ligand and complexes) were characterized with FT-IR, magnetic susceptibility measurement, thermal methods (TGA), ¹H NMR and elemental analyses.

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been shown to exhibit interesting physical and chemical properties [15] and potentially useful biological activities [16]. Schiff bases [17] were still regarded as one of the most potential group of chelators for facile preparations of metalloorganic hybrid materials. In the past two decades, the properties of Schiff base metal complexes stimulated much interest for their noteworthy contributions to single molecule-based magnetism, material science [18], catalysis of many reactions like carbonylation, hydroformylation, oxidation, reduction and epoxidation [19], their industrial applications [20], complexing ability towards some toxic metals [21]. The interest in Schiff base compounds as analytical reagents is increasing since they enable simple and unexpensive determinations of different organic and inorganic substances [22]. The high affinity for the chelation of the Schiff bases towards the transition metal ions is utilized in preparing their solid complexes.

Metal acetates are considered to be the most convenient substrates for complexation with Schiff bases due to their solubility in alcohols and to their being the salts of a weak acid. The application of metal nitrates or chlorides is possible when the ligand solution is first treated with sodium or potassium hydroxide, acetate or alcoholate in order to convert the neutral ligands into their respective phenolates [23].

Triphenylene with a disc structure was first described in 1935 [24]. Chandrasekhar et al. [25] reported that a disc-shaped molecule is able to organize into a liquid-crystalline structure. Now, triphenylene derivatives, especially symmetrically substituted hexaethers, have developed into an important class of discotic liquid crystalline structures. These fascinating discogens may find commercial applications in quasi-one-dimensional conductors, [26] photoconductors, [27] and light-emitting diodes [28]. Many

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efforts have been directed toward triphenylene-related areas during the past two decades [29,30].

2. Experimental

2.1. Materials and methods

In the coordination chemistry, generally, it has been used many compounds with Schiff base group as ligand, whereas the Schiff bases with triphenylene nucleus have not been studied until now, according to our knowledge. Therefore, we synthesized to a new Schiff base with triphenylene nucleus using the 2-((2-chloroethylimino)methyl)phenol and HHTP compounds and observed its complexation properties towards some transition metals ions. In addition, the characteristic properties, FT-IR and TGA/DTA results of these complexes were presented and evaluated in this study.

All starting materials and reagents used were of standard analytical grade from Fluka, Merck as well as from Aldrich and used without further purification. Melting points were measured using a Buchi B-540 melting point apparatus. ¹H NMR spectra were recorded on a Varian 400 MHz spectrometer at room temperature. Thermal gravimetric analysis (TGA) was carried out with Seteram thermogravimetric analyzer. The sample weight was 15–17 mg. Analysis was performed from 40 °C to 900 °C at



Fig. 3. ¹H NMR spectrum of HSE-TP 4.

336 **Table 1**

Elemental analysis, magnetic and physical properties of the Compounds.

Compounds	Formula	μ_{eff} (BM)	Colour	m.p. (°C)	Yield (%)	Found (Calcd.) (%)		
[HSE-TP]	C72H66N6O12	-	Red	Oil	60	71.63 (63.76)	6.96 (6.93)	5.51 (5.48)	-
[HSE-TP Co ₆]	$C_{84}H_{90}N_6O_{30}Co_6$	1.82	Brown-green	182	65	50.01 (49.96)	4.17 (4.14)	4.50 (4.43)	17.53 (17.46)
[HSE-TP Cu ₆]	$C_{84}H_{90}N_6O_{30}Co_6$	1.76	Green	150 ^b	70	49.43 (49.40)	4.11 (4.08)	4.44 (4.40)	18.65 (18.60)
[HSE-TP Ni ₆]	C84H90N6O30Ni6	2.86	Brown	155	63	50.05 (49.97)	4.17 (4.13)	4.50 (4.53)	17.47 (17.43)
[HSE-TP Zn ₆]	$C_{84}H_{90}N_6O_{30}Zn_6$	_a	Yellow	225	60	49.07 (49.02)	4.09 (4.04)	4.41 (4.46)	19.09 (18.99)
[HSE-TP Pd ₆]	$C_{84}H_{90}N_6O_{30}Pd_6$	_a	Brown	320 ^b	65	43.83 (43.80)	3.65 (3.68)	3.94 (3.89)	27.74 (27.69)
[HSE-TP Cd ₆]	$C_{84}H_{90}N_6O_{30}Cd_6$	_ ^a	Light yellow	230	68	43.15 (43.12)	3.59 (3.56)	3.88 (3.92)	28.85 (28.78)

^a Diamagnetic complex.

^b Decomposition.



Scheme 1. Synthesis of HTTP: (a) (CH₃)₂SO₄, EtOH (95%) and 50% KOH; (b) anhyd. FeCl₃ and H₂SO₄; (c) BBr₃, CH₂Cl₂ and refluxing.

heating rate of 10 °C/min in argon atmosphere with a gas flow rate of 20 mL/min. The elemental analysis for the ligand and the bridged complexes were carried out at on a Hewlett-Packard 185 analyzer. FT-IR spectra were recorded using a Mattson-1000 FT-IR using KBr pellets. Magnetic susceptibilities of metal complexes were determined using a Sheerwood Scientific MX Gouy magnetic susceptibility apparatus carried out using the Gouy method with Hg[Co(SCN)₄] as calibrant. The effective magnetic moments, μ_{eff} , per metal atom was calculated from the expression: $\mu_{eff} = 2.84(\chi_M)^{1/2}$, where χ_M is the molar susceptibility.

2.2. Synthesis of 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP) 2

2,3,6,7,10,11-hexamethoxytriphenylene 1 (HMTP) was prepared according to the reported procedure [31]. To give compound 2 (HHTP), a suspension of HMTP (2.0 g, 4.9 mmol) in 100.0 mL of dry CH₂Cl₂ was prepared and this suspension was cooled in alcohol bath to -20 °C. A solution of boron tribromide (8.6 g, 34.3 mmol) in dichloromethane was slowly added to this suspension. The mixture was refluxed for 24 h. The reaction solution was left stirring overnight. A part of the ice (50.0 g) was added to the combined organic extract. After waiting a while, extract washed with water (3 × 100 mL), dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure to afford the desired pure product. Yield; 80%, FT-IR (KBr); 3440 cm⁻¹ (OH), ¹H NMR (DMSO-d₆): δ = 7.58 (s, 6H, Ar-*H*), 9.26 (6H, Ar-*OH*) (Fig. 1).

2.3. Synthesis of (E)-2-(2-chloropropylidenamino)phenol (CPAP) 3

A solution of salicylaldehyde (10.0 mmol, 0.85 mL) in methanol (20.0 mL) was added dropwise at 30 °C to a solution of 2chloroethylamine hydrochloride (1.16 g, 10.0 mmol) in methanol (20.0 mL) over a period of 1 h. After stirring for an additional 30 min, a solution of triethylamine (10.0 mmol, 1.4 mL) in methanol (10.0 mL) was added dropwise in 20 min. The reaction mixture was stirred and gently heated for 30 min with constant stirring. During this period, the yellow precipitate was formed and filtered. This precipitate was extracted with ethylacetate $(3 \times 50 \text{ mL})$ and the organic phase was washed with water (100 mL). The combined organic extracts were dried over Na₂SO₄, filtrated, and concentrated under reduced pressure and dried in vacuum. The obtained yellowish residue was recrystalized from a mixture of hot ethanol and diethylether (1:2). Yield; 85%, FT-IR (KBr); 1693 cm⁻¹ (C=N), ¹H NMR (CDCl₃): δ = 3.80 (t, 2H, NCH₂CH₂, J = 5.4 Hz), 3.91 (t, 2H, NCH₂CH₂, J=5.4 Hz), 6.88–6.98 (m, 2H, Ar-H), 7.26–7.35 (m, 2H, Ar-H), 8.38 (s, 1H, CH = N), 13.0 (s, 1H, Ar-OH) (Fig. 2).

2.4. Synthesis of 2,3,4,6,7,10,11-hexakis(salicyliminoethoxy)triphenylene (HSE-TP) 4

A mixture of HHTP (0.48 g, 1.5 mmol) and K_2CO_3 (1.1 g, 8.0 mmol) in 50 mL of acetone was refluxed for 2 h. A solution of CPAP (2.2 g, 8 mmol, exceedingly 25%) in acetone was added to the



Scheme 2. Synthesis of CPAP 3.



Scheme 3. Synthesis of HSE-TP and its complexation with some transition metals.

mixture and refluxed for 60 h. The reaction was monitored by TLC. The resulting solution was allowed to warm up to room temperature. At the end of the reaction, the reaction mixture was filtered and the organic layer was removed under reduced pressure. The observed solid product was dissolved in CHCl₃ and washed twice with water. The combined organic phase was dried over Na₂SO₄ and the material obtained such as oil. Yield; 60%, FT-IR (KBr); 1690 cm⁻¹ (C=N), ¹H NMR (CDCl₃): δ = 3.80 (t, 12H, NCH₂CH₂, *J* = 5.4 Hz), 3.92 (t, 12H, NCH₂CH₂, *J* = 5.4 Hz), 6.87–7.00 (m, 12H, Ar-H), 7.25–7.37 (m, 12H, Ar-H), 8.38 (s, 6H, Ar-H), 8.47(s, 6H, CH=N) (Fig. 3).

2.5. Preparation of Cu(II), Zn(II), Co(II), Ni(II), Cd(II) and Pd(II) complexes

The copper (II) complex of HSE-TP: 1.0 mmol (1.2 g) of HSE-TP dissolved in 20 mL of ethanol was mixed for 6 h at 80 °C with a solution of 6.0 mmol (1.2 g) of copper acetate monohydrate $(Cu(CH_3COO)_2 \cdot H_2O)$ in 20 ml of ethanol. Then, the excess of solvent was removed under reduced pressure. The mixture was cooled and added to 20 mL of water upon it. The obtained precipitate was filtrated, washed with portions of water and dried under vacuo. Zn(II), Co(II), Ni(II), Cd(II) and Pd(II) complexes of the HSE-TP were prepared according to above described procedure and for these complexes, Zn(CH_3COO)_2 \cdot 2H_2O, Co(CH_3COO)_2 \cdot 4H_2O, Ni(CH_3COO)_2 \cdot 4H_2O, Cd(CH_3COO)_2 \cdot 2H_2O, Pd(CH_3COO)_2 \cdot 3H_2O salts were used. Elemental analysis results, magnetic and physical properties of the synthesized these complexes were summarized in Table 1.

3. Result and discussion

3.1. Synthesis of HSE-TP ligand

For the synthesis of HSE-TP ligand 4, we used CPAP 3 and HHTP 2 compounds as shown in Scheme 3. HHTP 2 used as starting material was synthesized by demethylation of 2,3,6,7,10,11-hexamethoxytriphenylene 1 (HMTP) (Scheme 1). To our knowledge, two methods to synthesis 2,3,6,7,10,11hexamethoxytriphenylene 1: electrochemical trimerization of veratrol on a platinum electrode [32] and oxidative trimerization [33]. Only small amount of 1 was obtained each time by the former method. Hence, the modified of method of Boden et all. was used to prepare 1 in a 86% yield; anhydr. FeCl₃ and more concentrated sulfuric acid were employed instead of FeCl₃.6H₂O. CPAP 3 used in synthesis of HSE-TP was prepared using salicylaldehyde, 2chloroethylamine hydrochloride and Et₃N in methanol media and depicted in Scheme 2. Finally, HSE-TP ligand 4 was synthesized using HHTP 2 and CPAP 3 compounds, K₂CO₃ in acetone. These compounds were characterized with ¹H NMR, FT-IR and elemental analysis. Figs. 1–3 show ¹H NMR spectrums of HHTP, CPAP and HSE-TP, respectively. The formation of HHTP was confirmed by the disappearance of the OCH_3 in HMTP and the appearance of the phenolic-OH at 9.26 ppm (Fig. 1). As seen Fig. 2, the synthesis of CPAP was confirmed by the appearance of imine protons (CH=N) at 8.38 ppm and the disappearance of aldehyde protons belong to salicylaldehyde. In addition, the ¹H NMR spectrum of HSE-TP prepared with HHTP and CPAP was depicted in Fig. 3. This spectrum confirmed to formation of HSE-TP due to the disappearance of the phenolic-OH in HHTP. The HSE-TP prepared in the way have been and Pd(II) of HSE-TP

presented in Table 1.

3.2.1. FT-IR spectra

stretching modes [34].

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Compound	ν (OH)	ν (CH _(alip))	ν(C=N)	ν (CH _(arom))	$v(C=C_{(arom)})$	ν (C–O–C)
HSE-TP	3440	2930	1690	2881 _(as) 1484 _(s)	1607	1260
HSE-TP(Co) ₆	3393	2985	1635	2910 _(as) 1480 _(s)	1595	1245
HSE-TP(Cu) ₆	3395	2980	1634	2923 _(as) 1478 _(s)	1587	1210
HSE-TP(Ni)6	3380	3038	1623	2938 _(as) 1476 _(s)	1538	1223
HSE-TP(Zn) ₆	3384	3069	1630	2892 _(as) 1480 _(s)	1540	1207
HSE-TP(Pd) ₆	3436	3070	1638	2938 _(as) 1453 _(s)	1607	1253
HSE-TP(Cd) ₆	3430	3060	1630	2930 _(as) 1461 _(s)	1546	1292

Characteristic FT-IR bands (cm⁻¹) of the synthesized complexes^a.

^a KBr pellet—w: wagging vibration, as: asymmetric streching vibration.

obtained in nearly quantitative yield and high purity and used as a ligand in the following complexation reaction.

All of the complexes were prepared to react of the selected metal

cations with HSE-TP ligand in ethanol media. Characterization of

these HSE-TP/metal complexes was realized by elemental analysis,

TGA/DTA, FT-IR. The physical properties of all complexes were also

Characteristic FT-IR bands of the HSE-TP and its metal com-

plexes were presented in Table 2. As seen Table 2, the vibrations

of the phenolic-OH and imine C=N groups belong to HSE-TP compound have been observed at 3400 and 1690 cm^{-1} , respectively. After the complexation reactions, the imine C=N bands are shifted

to lower frequencies (1635, 1634, 1623, 1630, 1638, 1630 cm⁻¹ for

Co(II), Cu(II), Ni(II), Zn(II), Pd(II), Cd(II), respectively) in the com-

plexes indicating that it has been affected upon coordination to

the metal ions and reduced intensity of these bands. Moreover,

the strong bands centered at 3380-3446 cm⁻¹ in the complexes

assigned to coordinated water. Also, the bands in the 554-532

and 464–479 cm⁻¹ range can be attributed to the M–N and M–O

3.2. Complexation studies with Cu(II), Zn(II), Co(II), Ni(II), Cd(II)

3.2.2. Magnetic moments studies

As is known, magnetic susceptibility measurements provide information regarding the geometric structure of the complexes. Magnetic susceptibility was determined using a magnetic susceptibility balance. The magnetic moment data of the solid-state complexes at room temperature are reported in Table 1. The magnetic susceptibility measurements show that the Co(II), Cu(II) and Ni(II) complexes are paramagnetic at ambient temperature, with the exception of the Cd(II), Pd (II) and Zn(II) complexes. The nickel(II) complex is paramagnetic with magnetic susceptibility value of 2.86 BM, which fits the two-spin value, 2.83 BM [10]. The result for the Ni(II) complex fits the d^8 metal ion in an tetrahedral structure. The magnetic susceptibility values of Co(II) and Cu(II) complexes are 1.82 and 1.76 BM, respectively. This values for Co(II) and Cu(II) complexes are consistent with expected spin-only magnetic moment of an S = 1/2 (1.73 BM), Cu(II) d⁹ system and Co (II) d⁷ system. These data proved that the Co (II) and Cu (II) complexes are in a square-planer and tetrahedral structure, respectively. The structures of the obtained complexes are presented in Scheme 3.

3.2.3. Thermal gravimetric analysis

The thermal analysis of HSE-TP ligand and its metal complexes were recorded in argon atmosphere from $40 \,^{\circ}$ C to $900 \,^{\circ}$ C. The correlations between the different decomposition steps of the compounds with the corresponding weight losses are discussed in terms of the proposed formula of the compounds. The thermal behaviours of the obtained complexes are summarized in Table 3. The results show good agreement with the formula suggested from the analytical data (Table 1).

Metal oxide residue

Compounds	TG range (°C)	Weight loss found (Calcd.) (%)	Fragments
HSE-TP(Co) ₆	40-300°C	21.80 (22.95)	Moisture, 6 H ₂ O (coord.), CO ₂ , CH ₄
	350-850°C	50.15 (52.35)	Loss of ligand leaving
			Metal oxide residue
HSE-TP(Cu) ₆	40-275 °C	5.15 (5.33)	Moisture, 6 H ₂ O (coord.)
	300-750 °C	70.12 (71.34)	CH ₄ , CO ₂ , loss of ligand leaving
			Metal oxide residue
HSE-TP(Ni)6	40-200°C	5.22 (5.36)	Moisture, 6 H ₂ O (coord.)
	250-500 °C	46.80 (45.20)	CH ₄ , CO ₂ , loss of C ₃₀ H ₃₀ O ₆ N ₆ leaving
	500-750 °C	26.46 (27.11)	Loss of C ₇ H ₅ leaving
			Metal oxide residue
HSE-TP(Zn) ₆	40-225 °C	5.75 (5.25)	moisture, 6 H ₂ O (coord.)
	225-325 °C	27.78 (28.90)	CO ₂ , N ₂ , C ₂ H ₄ , CH ₄
	325-500 °C	16.13(15.46)	C ₁₈ H ₆ O ₆ group leaving
	500-750°C	26.87 (26.45)	
			C ₇ H ₅ group leaving
			Metal oxide residue
HSE-TP(Pd) ₆	40-275 °C	31.23 (30.52)	Moisture, 6 H ₂ O (coord.), N ₂ ,C ₂ H ₄ , CO ₂ , CH ₄
	300-450 °C	14.05 (13.82)	C ₁₈ H ₆ O ₆ group leaving
	500-700 °C	23.12 (23.87)	C7H5 group leaving
			Metal oxide residue
HSE-TP(Cd) ₆	40-325 °C	29.45 (30.06)	Moisture, 6 H ₂ O (coord.), N ₂ ,C ₂ H ₄ , CO ₂ , CH ₄
	350–500 °C	12.48 (13.60)	C ₁₈ H ₆ O ₆ group leaving
	550-800°C	24.15 (23.37)	C ₇ H ₅ group leaving

The HSE-TP ligand is thermally decomposed only two successive decomposition step. The mass loss of within the temperature range 150–300 °C may be attributed to the loss of N₂ and ethyl groups (C₂H₄). At the second decomposition step, triphenylene (C₁₈H₆O₆) and salicylaldehyde (C₇H₅) groups lefts from the main structure at 350–750 °C [35].

The TGA results of Co(II) and Cu(II) complexes show a two decomposition steps within the temperature range of 40–850 °C and 40–750 °C for Co(II) and Cu(II) complexes, respectively. For the Co(II) complex, at 40–300 °C, moisture, coordinated water and CO₂ leaves from complex structure. Moreover, the loss of ligand molecules was observed within 350–850 °C. As seen Table 2. for the Cu(II) complex, these losses take place within 40–275 °C and 300–750 °C temperatures.

The decomposition steps of Ni(II), Pd(II) and Cd(II) complexes are almost the same and have three decomposition steps. For the Ni(II), Pd(II) and Cd(II) complexes, the decomposition within 40–750 °C, 40–700 °C and 40–800 °C temperature ranges is due to the loss of moisture, coordinated water, CH₄, CO₂, C₃₀H₃₀O₆N₆ (triphenylene and ethyl groups) and C₇H₅ from main structure.

As seen Table 3, the Zn(II) complex shows four decomposition steps within 40–750 °C temperature range. The first step (40–225 °C) is due to the loss of moisture, coordinated water from main structure. At the second decomposition step, CO_2 , N_2 , C_2H_4 , CH_4 left from the residue structure at 225–325 °C. $C_{18}H_6O_6$ and C_7H_5 groups leave from structure at 325–500 °C and 500–750 °C, respectively.

The total weigh losses was theoretically calculated and compared with experimentally. The estimated mass losses for all complexes were presented in Table 3 and observed to good agreement with the formulae suggested from the analytical data.

4. Conclusion

The design and synthesis of a novel Schiff base ligand and their use in preparing selected some transition metal complexes have been demonstrated in this report. HSE-TP as a new ligand was prepared using HHTP 2 and CPAP 3 compounds. The structures of these compounds were confirmed with ¹H NMR technique. HSE-TP's metal complexes were synthesized in ethanol media and in presence of the metal acetate salts. The physical properties, elemental analysis and magnetic susceptibility of these complexes were investigated. The magnetic data for complexes showed that Cd(II), Pd (II) and Zn(II) complexes were diamagnetic and Ni(II), Co(II) and Cu (II) complexes were paramagnetic. Moreover, Ni(II), Co(II) and Cu (II) complexes demonstrated well agreement with the d⁸, d⁹ and d⁷ metal ion in an tetrahedral, square-planer and tetrahedral structure, respectively. It may be possible to try to test these Schiff base complexes as antibacterial, antitubercular, antifungal and anticoagulant activity. In other words, further studies on the complexation reactions and catalytic activity of the prepared complexes on model reactions will be carried out soon.

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