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Solid State Structural, Catalytic and Physico-chemical Elucidation of VO(IV), Pt(IV) and Ce(IV) Coordinated Compounds of Schiff Bases

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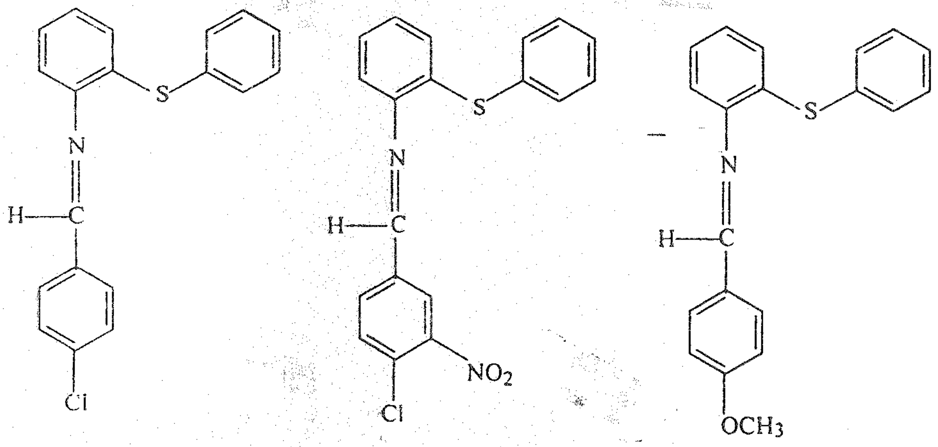
Pt(IV), VO(IV) and Ce(IV)-complexes of the Schiff bases, *viz.*, 2-(phenylthio) anilimino-4-chloro benzylidene (PACB), 2-(phenylthio) anilimino-4-chloro-3-nitro benzylidene (PACNB) and 2-(phenylthio) aniliamino-4-methoxy benzylidene (PAMB) have been synthesized and characterized by elemental analyses, molar conductance, electronic, infrared spectra, ^{1}H NMR, ESR, thermal and magnetic susceptibility measurements. Synthesized complexes have been tested for their reactivity and substitution behaviour. All the ligands behave as bidentate, coordinating through O and N atoms. The proposed geometry for the complexes is square-pyramidal. Conductivity studies reflect the semi-conducting behaviour of the complexes.

Key Words: VO(IV), Pt(IV) and Ce(IV) complexes, Schiff base, Spectral, Thermal, Conductance, Magnetic and catalytic effect.

INTRODUCTION

The coordination chemistry of VO(IV), Pt(IV) and Ce(IV) with polydentate ligands is inviting attention of researchers because of their growing applications in catalysis[1] and therapeutics[2]. Ce(IV) plays a vital role as catalyst in oxidation of alcohols in acidic medium[3], while vanadium containing compounds have their utility as insulin mimetic[4, 5] and antiamoebic agent[6], V(IV)-V(III) redox system from reactivity point of view[7] and in various homogeneous/heterogeneous catalytic processes[8] where they exhibit good synthetic potential[9]. Distortion in their geometry from trigonal-bipyramidal, octahedral to square-pyramidal has also been a subject of interest. Considering their relevance and significance, the work done is being described in the present paper which deals with VO(IV), Ce(IV) and Pt(IV) complexes with three Schiff bases, *viz.*, 2-(phenylthio) anilimino-4-chloro benzylidene (PACB), 2-(phenylthio) anilimino-4-chloro-3-nitro benzylidene (PACNB) and 2-(phenylthio)-anilimino-4-methoxy benzylidene (PAMB) (Fig. 1).



PACB PACNB PAMB

Fig. 1. Structure of Schiff bases

EXPERIMENTAL

All the used chemicals and solvents were of AnalaR grade. Satisfactory elemental analyses were done by the reported procedures[10–12]. Magnetic measurement was made by Gouy's method. Electronic spectra (in MeOH) were recorded on Perkin-Elmer Lambda-2B-spectrophotometer. IR spectra was done on Perkin-Elmer 577 spectrometer. ^{1}H NMR was recorded on Bruker Avance Series spectrometer. The conductivity has been measured by impedance spectroscopic method using HIOKI 3532-50 LCR Hitester at room temperature.

Synthesis of Schiff bases

The three Schiff bases (PACB, PACNB, PAMB) have been synthesized by adding the methanolic solution of 4-chlorobenzaldehyde/4-chloro-3-nitro-benzaldehyde/3-methoxy benzaldehyde (0.01 M) with methanolic solution of 2-(phenylthioaniline) (0.01 M) in equimolar ratio. The reaction mixtures separately were then refluxed for 5–6 h. The condensation products were filtered, thoroughly washed with ethanol and ether, recrystallised and dried *in vacuo*. The purity of the synthesized compounds was monitored by TLC using silica gel (yield 60–75%).

Preparation of metal complexes

All the metal complexes have been prepared by mixing the methanolic solution of the corresponding metal salts ($VOSO_4 \cdot 5H_2O$/ceric nitrate/Pt-sulphate) (0.01 M) to the methanolic solution of Schiff bases (PACB, PACNB, PAMB) (0.02 M) in 1 : 2 molar ratio. The resulting mixture was then refluxed for 7–8 h. A coloured product appeared on standing and cooling the above solution. The complexes were filtered, washed with ether and dried under reduced pressure over anhydrous $CaCl_2$ in a desiccator. The products were further dried in an electric oven at 50–70°C.

RESULTS AND DISCUSSION

All the metal chelates are coloured solids, stable towards air and moisture, decompose at high temperature and more or less soluble in common organic solids. The analytical data of the complexes are consistent with the proposed molecular formulae. All the metal chelates have 1 : 2 (metal : ligand) stoichiometry. The molar conductance values of the complexes (10^{-3} M) suggest their semiconducting nature[13]. The complexes have a general composition $[ML]\cdot xH_2O$.

The solution of complexes was made in methanol (99%) to check the reactivity and the substitution behaviour against ammonia, chloro, aqua, thiocyanato and hydroxy acid. Reaction was monitored by observing change in colour or precipitation.

Reaction with dilute $NH_3(aq)$: Complexes of PACB and PACNB do not react with dilute aqueous ammonia on keeping for 1 h at room temperature but complexes of PAMB react slowly. All the complexes react poorly on heating.

Reaction with dilute HCl: PAMB complexes do not react with dilute HCl even on retaining for 1 h at room temperature, but PACB and PACNB react slowly under similar conditions. On heating the complexes react appreciably.

Reaction with H_2O: PACB and PACNB complexes react slowly while of PAMB reacts rapidly on addition of slight amount of water at room temperature. All the complexes decompose on heating with water.

Reaction with dilute KSCN: All the complexes react slowly on keeping for 1 h at room temperature; however, all the complexes react to sufficient extent on heating.

Reaction with dilute NaOH: PACB-complex reacts slowly but PACNB and PAMB complexes reacts fast at room temperature (1 h). All the complexes react well on heating.

^1H NMR spectra of the ligands exhibit the following data (δ ppm): PACB, 6.72–8.10 (m, 12H, Ar-H), 8.70 (s, 1H, azomethine) and 3.25 (m, 3H, —CH_3); PACNB, 6.52–8.40 (m, 11H, Ar-H), 3.12 (m, 3H, —CH_3), 8.60 (s, 1H, azomethine); PAMB, 6.50–7.92 (m, 12H, Ar-H) 8.68 (s, 1H, azomethine). The assignments based on chemical shift and intensity pattern between ligand and complex have been compared. The coordination induced shifts $\Delta_\delta = [\delta \text{ (free ligand)} - \delta \text{ (complex)}]$ or absence of the signals in the vicinity of coordinating functions have been noted. In the complexes, the signals due to azomethine group associated pattern shift down, suggesting the withdrawal of electron density between C=N on coordination with nitrogen. The remaining other signals remains almost unchanged and unshifted in complex spectra[14–17].

A careful comparison of the ligand and complex spectra resulted in the following information regarding various groups: IR spectra of Schiff base ligands (PACB, PACNB, PAMB) give medium intensity band at above 1620 ± 15 cm^{-1} due to ν(C=N) (azomethine group). This band shifts to lower side by 30–50 cm^{-1} in the complexes, suggesting coordination through azomethine nitrogen. A shift of electron density from this group has also been noted in ^1H NMR data. The chelation of thiolic sulphur is supported by upward shift (± 20 cm^{-1}) in complexes. The appearance of broad band around 3400–3200 cm^{-1} in the spectra of complexes may be due to associated lattice water molecules. Some characteristic low intensity bands in the spectra of complexes at 900–775 and 610–550 cm^{-1} have been attributed to (M-S) and (M-N), respectively[18–20].

The electronic spectra (in methanol) of the complexes exhibited bands in the regions as follows: VO (IV), 14290–13790, 21000–19100 and 24900–24150 cm^{-1} due to $^2B_2 \rightarrow {}^2E$, $^2B_2 \rightarrow {}^2B_1$ and $^2B_2 \rightarrow {}^2A_1$.

The geometry of these neutral five-coordinated mononuclear complexes can be described in terms of a trigonal bipyramid distorted towards a tetragonal pyramid or square pyramid[21, 22].

The ESR spectra of oxovanadium(IV) (d^1;^{51}V, $I = 7/2$) complexes are not so resolved at room temperature to exhibit all the eight hyperfine lines. The calculated values of $g_{\|}$, $g_{\perp}$, g_{av} and Δ_g for all the three complexes have been given in Table-1. Here $g_{av} = 1/3\ (2g_{\perp} + g_{\|})$. The values are typical of the spectra displayed by square pyramidal VO(IV) complexes with one unpaired electron in an orbital of mostly d_{xy} character. The g_{av} values determined from the spectra are nearer to spin-only value; a slight variation may be accounted to spin orbit coupling. In square pyramidal complexes with C_{4v} symmetry, the (V═O) band is along z- and the other donor atoms (N, O) are along the x-, y-axes, an anisotropic ESR is expected exhibiting two g values ($g_z = g_{\|} < g_{\perp} = g_x = g_y$)[6, 23, 25] (Table-1).

TABLE-1
ANALYTICAL, PHYSICAL AND ESR DATA OF COMPLEXES

Complexes	Colour	m.w.	Yield (%)	Found (Calcd). (%)					ESR		
				C	H	N	M	μ_{eff}	$g_{\|}$	$g_{\perp}$	g_{av}
$VO(C_{19}H_{20}O_3NClS)\cdot 3H_2O$	Yellowish green	744	80	51.1 (51.3)	4.1 (4.5)	2.8 (3.2)	11.2 (11.4)	1.70	1.94	1.97	1.96
$Pt(C_{19}H_{20}O_3NClS)\cdot 3H_2O$	Green	572	65	39.2 (39.8)	3.1 (3.4)	2.1 (2.4)	34.1 (34.1)	1.88	1.99	1.97	1.98
$Ce(C_{19}H_{20}O_3NClS)\cdot 3H_2O$	Pale green	517	73	74.1 (74.4)	3.2 (3.8)	2.2 (2.7)	27.2 (27.1)	—	1.47	—	—
$VO(C_{19}H_{19}O_5N_2ClS)\cdot 3H_2O$	Black	489	75	45.8 (46.6)	3.2 (3.8)	5.1 (5.7)	10.6 (10.4)	1.76	1.96	1.99	1.97
$Pt(C_{19}H_{19}O_5N_2ClS)\cdot 3H_2O$	Brown	617	68	36.1 (36.9)	3.3 (3.1)	4.1 (4.5)	31.1 (31.5)	1.84	1.98	1.99	1.97
$Ce(C_{19}H_{19}O_5N_2ClS)\cdot 3H_2O$	Light brown	562	78	41.2 (40.5)	3.6 (3.4)	4.2 (4.9)	24.2 (24.9)	—	1.48	—	—
$VO(C_{20}H_{25}O_4NS)\cdot 3H_2O$	Brown	441	60	54.1 (54.3)	5.3 (5.6)	2.7 (3.1)	11.1 (11.5)	1.78	1.99	2.01	2.00
$Pt(C_{20}H_{25}O_4NS)\cdot 3H_2O$	Dark yellow	570	75	41.9 (42,1)	4.1 (4.3)	2.6 (2.4)	34.0 (34.2)	1.84	1.96	2.00	1.98
$Ce(C_{20}H_{25}O_5NS)\cdot 3H_2O$	Yellowish brown	515	65	40.1 (40.5)	4.2 (4.8)	2.9 (2.7)	27.0 (27.2)	—	1.46	—	—

Ce(IV) in the ground state $^2F_{3/2}$ is typical of many of rare earths with even electrons exhibiting relatively much smaller effect of crystal field in removing orbital degeneracy. This can be bacause of (i) their crystal field parameters are much smaller than the iron series, (ii) interatomic distances are greater, (iii) spin-orbit coupling coefficients are larger. As orbital angular momentum is retained, hence energy levels are characterized by resultant J values, instead of L and S; hence g-factors are expected to be anisotropic and may differ greatly from free spin value. Strong spin-lattice interaction resulting from strong spin-orbit coupling means that very low temperatures are needed for observation. The spectra thus show $g_{\perp}$~O and $g_{\parallel}$ very far from the free spin value[27, 28].

Pt(IV) with d^6 configuration showed its nuclear spin to be 9/2 and $g = 1.98$ which is nearly isotropic[29, 30].

The electrical conductivity of the synthesized complexes at room temperature (37°C) has been measured. The value range is $[(VO(PACNB)\cdot 3H_2O]= 1.62 \times 10^{-4}$ S cm^{-1}; $[Pt(PACNB)\cdot 3H_2O] = 2.48 \times 10^{-5}$ S cm^{-1} and $[Ce(PACNB)\cdot 3H_2O)] = 6.83 \times 10^{-4}$ S cm^{-1}. The values falls in the semi-conductor region[24].

The thermal degradation behaviour of the complexes has been studied at four temperatures (100°, 325°, 400° and 600°C). The resulting weights were measured. The remaining weight at 100°C corresponds to loss of lattice water molecules from the complexes[25, 26].

The weight measured after heating at 325°C indicates almost no change in weight of complexes suggesting them as appreciably thermally stable chelates. On further heating to 400°C, the remaining weight corresponds to loss of parts of ligand moiety almost equal to one ligand. The weight of pyrolysis product after heating at 600°C corresponds to formation of oxide. At this temperature, the ligands degrade (Table-2).

Ce (IV) complex is used in the oxidation of phenols. 6-Methoxy-1-naphthol and 4-methoxy phenol were taken as substrates, stirred under an atmosphere of molecular oxygen in an acetonitrile solution of the complex (10 mL) (Table-2). Good yield of the corresponding 4-methoxybenzoquinone and 6-methoxy-1,4-napthaquinone was obtained.

Formation constants evaluation

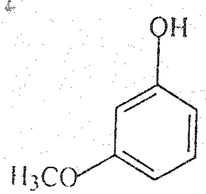
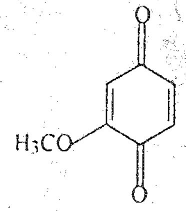
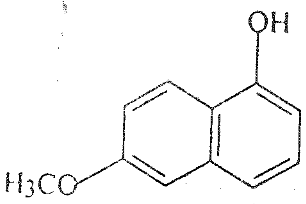
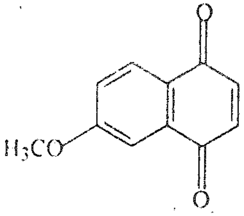
The formation constants of the compounds increases with increasing electron releasing ability of the substituents in the ring and are in the order.

$$p\text{-OCH}_3 > p\text{-CH}_3 > p\text{-H} > p\text{-Cl}$$

As the logarithmic factors of the stability constants bear a linear relationship with Hammett σ constants except *p*-Cl, a small decrease in the stability may be due to the predominance of inductive effect over the mesomeric effect of Cl group.

The NO_2 group having a very large σ value (1.27), is the *m*-directing group.

TABLE-2
THERMAL AND CATALYTIC ACTIVITY OF THE COMPLEXES

<table>
<tr><th>Complexes</th><th>Dec. temp. (°C)</th><th>% Weight loss Obs. (Calc.)</th><th>Residue comp.</th><th>% Weight found</th><th>Catalyst</th><th>Substrate</th><th>Con V_n (%)</th><th>Product</th><th>Yield (%)</th></tr>
<tr><td rowspan="2">VO(PACB)·3H_2O</td><td rowspan="2">487.02</td><td rowspan="2">72.39</td><td rowspan="2">VO_2</td><td rowspan="2">27.61</td><td rowspan="6">Ce (IV)</td><td rowspan="3"></td><td rowspan="3">66</td><td rowspan="3"></td><td rowspan="3">62</td></tr>
<tr></tr>
<tr><td rowspan="2">Pt(PACB)·3H_2O</td><td rowspan="2">597.02</td><td rowspan="2">62.41</td><td rowspan="2">PtO_2</td><td rowspan="2">37.59</td></tr>
<tr><td rowspan="3"></td><td rowspan="3">72</td><td rowspan="3"></td><td rowspan="3">65</td></tr>
<tr><td rowspan="2">Ce(PACB)·3H_2O</td><td rowspan="2">540.20</td><td rowspan="2">65.92</td><td rowspan="2">CeO_2</td><td rowspan="2">34.08</td></tr>
<tr></tr>
</table>

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