Synthesis, magnetic and spectral studies on polystyrene-anchored coordination complexes of bi-, tri-, tetra- and hexavalent metal ions with unsymmetrical dibasic tetradentate onno donor schiff base derived from 3-formylsalicylic acid, ethylenediamine and 2-hydroxy-1-naphthaldehyde

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ARTICLE INFO	**ABSTRACT**
	Polystyrene-anchored Cu(II), Zn(II), Cd(II), Ni(II), Mn(II), MoO$_2$(II), UO$_2$(II), Fe(III) and Zr(IV), complexes of unsymmetrical dibasic tetradentate ONNO donor Schiff base derived from the condensation of chloromethylated polystyrene, 3-formylsalicylic acid, ethylenediamine and 2-hydroxy-1-naphthaldehyde (PS—LH$_2$) have been synthesized. The polystyrene anchored complexes have the formulae: PS—LM (where M = Cu, Zn, Cd, Ni, MoO$_2$, UO$_2$), PS—LFeCl·DMF, PS—LMn·2DMF and PS—LZr(OH)$_2$·DMF. The polystyrene-anchored coordination compounds have been characterized by elemental analysis, IR, reflectance, ESR and magnetic susceptibility measurements. The per cent reaction conversion of polystyrene anchored Schiff base to polystyrene supported coordination compounds lies between 24.0–77.9. The coordinated dimethylformamide is completely lost on heating the complexes. The shifts of the ν(C=N)(azomethine) and ν(C—O)(phenolic) stretches have been monitored in order to find out the donor sites of the ligands. The Cu(II) complex is paramagnetic with square planar structure; the Ni(II) complex is diamagnetic with square planar structure; the Zn(II) and Cd(II) complexes are diamagnetic and have tetrahedral structure; the Mn(II) and Fe(III) complexes are paramagnetic and have octahedral structure; the MoO$_2$(II) and UO$_2$(II) complexes are diamagnetic and have octahedral structure and the Zr(IV) complex is diamagnetic and has pentagonal bipyramidal structure.

Introduction

In recent years there has been considerable interest in the synthesis and use of functionalized polymers having chelating abilities due to their practical convenience, operational flexibility and formation of coordination with high metal to polymer bond energies[1-4]. Although a large number of bidentate[5-7] and tridentate[8-20] ligands have been anchored to polymer matrix, only a few multidentate ligands like triethylenetetramine[21], tetraethylenepentamine[22], 1,4,8,11-tetraazocyclotetradecane[23], phthalocyanine[23], porphyrine[24], dithio- carbamate[25], imidazole[26], crown ethers[27], tetrathiol[28], N-phenacyl-4,4-bipyridinium bromide[29], 2,2'-[diimino-1, 2-ethanediylbis(1,2-ethanediylnitrilo- methylidyne)]diphenol[18], N,N'-ethylenebis(7-salicylialdimine-5-sodium- sulphonate)[30], N,N'-iminobis(ethylenesalicylideneimine)[31], N,N'-iminobis (propylenesalicylideneimine)[31], o-phenylenebis(salicylialdimine)[32], N,N'-diethyl- enetriaminebis(salicylialdimine)[33], N,N'-ethylenebis(5-vinylsalicylideneimine)[34], N,N'-ethylenebis(salicylideneimine)[35], N-salicylideneimine-N'(3-carboxysalicylidene- imine) ethane[36] etc. have been anchored to polymer matrix. The non-anchored Schiff base (Structure I) behave as strong field quadridentate ligand.

Experimental

Ammonium molybdate tetrahydrate (Glaxo,)); copper(II) acetate dihydrate, cadmium(II) acetate dihydrate, iron(III) chloride(anhydrous), dioxo- uranium(VI) acetate tetrahydrate,

zinc(II) acetate dihydrate, hexadecaaqua-octahydroxotetrazirconium(IV) chloride (BDH); nickel(II) acetate tetrahydrate [Fluka AG(Switzerland)]; manganese(II) acetate tetrahydrate (Sarabhai M Chemicals Co.) were used for the syntheses. Chloromethylated polystyrene, 2-hydroxy-1-naphaldehyde [Fluka AG(Switzerland)], ethylenediamine[Sarabhai M Chemicals Co], DMF, DMSO, CH$_3$COOC$_2$H$_5$, (C$_2$H$_5$)$_3$N etc. (Glaxo) were used for the syntheses. 3-Formylsalicylic acid, bis(acetylacetonato) dioxomolybdenum(VI) and hexadecaaquaocta-hydroxotetrazirconium (IV) acetate were synthesized according to the literature procedures[37-39].
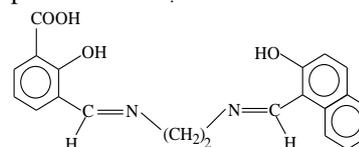
Structure I

Analysis and Physical Measurements

The metal contents and the coordinated DMF in the polystyrene supported coordination compounds were analysed as per the reported methods[40]. The coordinated DMF was determined by heating the complexes at a temperature given in parenthesis: Ni(II), Co(II), Fe(III) complexes (110° C, in vacuo), Cu(II) complex (105° C, in vacuo), Zn(II) complex (160° C, in

vacuo), Cd(II) complex (170° C, in vacuo) and U(VI) and Mo(VI) complexes (180° C, in vacuo). The IR spectra were recorded in KBr pellets on a Nicolet 5DX FTIR Spectrophotometer calibrated with polystyrene. Reflectance spectra were recorded on a Beckman DU spectrophotometer attached with a reflectance arrangement. The magnetic susceptibilities were measured at room temperature by the Gouy method using $Hg[Co(NCS)_4]$ as the calibrant[41]. The paramagnetic susceptibilities were corrected for the diamagnetism of ligand and metal atoms[42]. ESR spectra were recorded at liquid nitrogen temperature in polycrystalline solids on a Varian V4502 X-band ESR Spectrophotometer with 100 KHz modulation using diphenylpicrylhydrazide as a g-marker and monitoring the frequency with a frequency meter.

Synthesis of Schiff base

An ethanolic solution (20 ml) of 3-formylsalicylic acid (1.66 g, 10 mmol) was mixed with an ethanolic solution 2-hydroxy-1-naphthaldehyde (10 mmol) and the mixture was kept in an ice bath. To this, an ethanolic solution of ethylenediamine was added dropwise with constant stirring. The yellow coloured precipitates obtained were suction filtered, washed with ethanol and petroleum ether. The Schiff base was recrystallized from $CH_3COOC_2H_5$ and dried in vacuo. Yield = 75%. M.P. LH_2 = 217°C, Observed N% =7.52 against calcd. N% = 7.73.

Synthesis of polystyrene-anchored Schiff base PS—LH_2

PS—Cl (1.0 g) was allowed to swell in DMF (30 ml) for 45 min. To this suspension, a DMF solution (50 ml) of Schiff base (3.51 mmol) was added. Ethyl acetate (100 ml) and triethylamine (5 ml) were added, and mixture was heated under reflux for 8 h, while stirring magnetically. The colour of PS—Cl changed from white to yellow. The mixture was cooled to room temperature, suction filtered, washed several times with DMF, ethyl acetate, ethanol, methanol and acetone. It was then dried in vacuo.

General method for the synthesis of Cu(II), Zn(II), Cd(II), Mn(II), UO₂(II) and Ni(II) complexes

PS—LH_2 (0.5 g) was suspended in DMF (20 ml) for 1 h. A DMF solution (25–40 ml) of the appropriate metal salt/metal complex (1.17 mmol) was added to the above suspensions. The mixture was heated under reflux for 8 h, while stirring magnetically. The mixture was cooled to room temperature and the coloured products obtained were suction filtered, washed with DMF, ethanol, methanol and acetone. The compounds were dried in vacuo .

Synthesis of PS—FeCl·DMF

PS—LH_2 (0.5 g) was suspended in DMF (20 ml) for 1 h. A DMF solution (30 ml) of FeCl₃(anhydrous) (0.19 g, 1.17 mmol) was added to the above suspension. The mixture was heated under reflux for 8 h, while stirring magnetically and then cooled to room temperature. The brown coloured products obtained were suction filtered, washed with DMF, ethanol, methanol and petroleum ether and dried in vacuo

Synthesis of PS—LZr(OH)₂·DMF

PS—LH_2 (0.5 g) was suspended in DMF (20 ml) for 1 h. A freshly prepared DMF solution (50 ml) of zirconium(IV) acetate (2.34 mmol) was added to the above suspension. The mixture was heated under reflux for 8 h, while stirring magnetically. The cream coloured products obtained were suction filtered, washed with DMF, ethanol methanol and acetone and dried in vacuo.
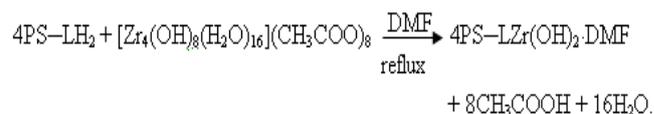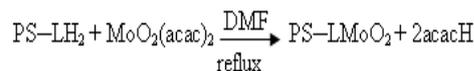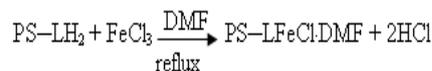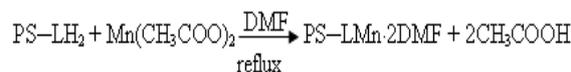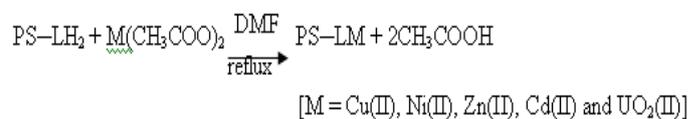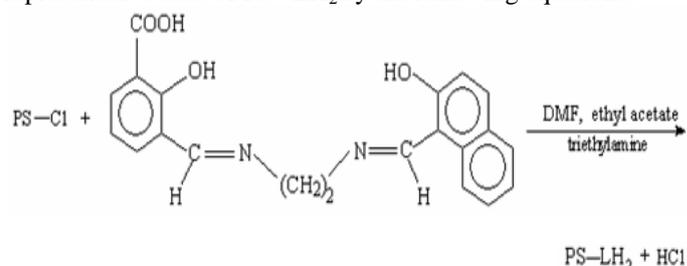
Synthesis of PS—LMoO₂

PS—LH_2 (0.5 g) was suspended in DMF (20 ml) for 1 h. A DMF solution(25 ml of bis(acetylacetonato) dioxomolybdenum (VI) (0.383 g, 1.17 mmol) was added to the above suspension. The mixture was refluxed for 8 h, while stirring magnetically. The mixture was cooled to room temperature and the yellow

coloured products obtained were suction filtered, washed with DMF, ethanol, methanol and acetone and then dried in vacuo

Results and Discussion

The reaction of chloromethylated polystyrene with LH_2 in 1:>3 molar ratio in DMF in presence of ethyl acetate (EA) and triethylamine (TEA) results in the formation of polystyrene-anchored Schiff base, PS—LH_2. PS—Cl is white, while PS—LH_2 is yellow. As the reaction between PS—Cl and LH_2 occurs, the white colour of the PS—Cl changes to yellow. This colour remains unchanged even after the prolonged washings with DMF, ethyl acetate, ethanol and petroleum ether. In the synthesis of PS—LH_2 the per cent reaction conversion was found to be 100 and there was no chlorine present in the polystyrene-anchored Schiff base. This was possible only since we repeated PS—Cl and LH_2 in ratio, 1:3. If the ratio was 1:<3, the corresponding polystyrene—anchored Schiff base always contained some unreacted —CH_2Cl group. For the synthesis of polystyrene supported complexes, PS—Cl(containing 1.17 mmol of Cl per g of resin and 2% crosslinked with divinylbenzene) was selected since a higher crosslinking than 2% hinders the reactivity and metal binding power of the polystyrene supported Schiff base. The reaction of PS—LH_2 and appropriate metal salts in 2:1 molar ratio in DMF gives polystyrene supported coordination compounds of the types: PS—LM[where M = Cu(II), Zn(II), Cd(II), Ni(II), UO₂(II)], PS—LMoO₂·DMF, PS—LFeCl·DMF and PS—LZr(OH)₂·DMF. The formation of coordination compounds may be represented by taking the representative case of PS—LH_2 by the following equations:

$$PS-LH_2 + M(CH_3COO)_2 \xrightarrow[\text{reflux}]{DMF} PS-LM + 2CH_3COOH$$

$$[M = Cu(II), Ni(II), Zn(II), Cd(II) \text{ and } UO_2(II)]$$

$$PS-LH_2 + Mn(CH_3COO)_2 \xrightarrow[\text{reflux}]{DMF} PS-LMn \cdot 2DMF + 2CH_3COOH$$

$$PS-LH_2 + FeCl_3 \xrightarrow[\text{reflux}]{DMF} PS-LFeCl \cdot DMF + 2HCl$$

$$PS-LH_2 + MoO_2(acac)_2 \xrightarrow[\text{reflux}]{DMF} PS-LMoO_2 + 2acacH$$

$$4PS-LH_2 + [Zr_4(OH)_8(H_2O)_{16}](CH_3COO)_8 \xrightarrow[\text{reflux}]{DMF} 4PS-LZr(OH)_2 \cdot DMF$$
$$+ 8CH_3COOH + 16H_2O.$$

In the synthesis of polystyrene-anchored complexes, the Schiff base: metal ratio was maintained as 1:2 and this leads to the per cent reaction conversion between 24.0–77.9 (Table 1). There is no apparent correlation between the size of the metal ions and the per cent reaction conversion. The metal binding capacity of the resins is in the range: 0.18–0.56 mmol per g of resin (Table 1). The colour of the polystyrene-anchored Schiff base is yellow, while that of polystyrene-anchored complexes are pale yellow, yellow, cream, brown, dark brown. The colours of the metal bound polymers remains unchanged even after repeated washings with DMF, ethanol, methanol and acetone. 3-

Formylsalicylic acid exhibits a broad band at 3320 cm^{-1}, a strong band at 1660 cm^{-1} and a medium intense band at 1540 cm^{-1} due to ν(OH) (intramolecular H-bonding)[43], ν(C=O) (carboxylic/aldehyde) and ν(C–O) (phenolic) stretehes respectively. These bands occur at the same energy in LH$_2$ alongwith the appearance of a strong band between 1630 cm^{-1}. The latter may be assigned to ν (C=N)(azomethine) stretch[15]. In PS–LH$_2$, the band at 1660 cm^{-1} disappears and a new strong band at 1730 cm^{-1} appears, indicating the formation of ester linkage between PS—Cl and 3-formylsalicylic acid moiety[16–18]. The polystyrene-anchored coordination compounds, except the corresponding Zr(IV) complex, do not exhibit this band. The disappearance of this band upon complexation indicates the breakdown of H-bonding followed by deprotonation of phenolic OH group and the subsequent involvement of phenolic oxygen atom towards coordination[15]. The polystyrene-anchored zirconium(IV) complex exhibits above band at 3400 cm^{-1} indicating the presence of coordinated OH groups. The negative shift of ν(C=N) stretch[44] by 10–25 cm^{-1} and the positive shift[45] of ν(C—O)(phenolic) stretch by $\leq$10 cm^{-1} of upon complexation, indicates the dibasic tetradentate ONNO donor nature of PS—LH$_2$. DMF exhibits a band at 1680 cm^{-1} due to the ν(C=O) stretch which shifts to lower energy by 10–30 cm^{-1} in the spectra of metal bound polymers indicating oxygen coordination of DMF[46]. The polystyrene-anchoredcompounds, PS—LMoO$_2$ exhibits two bands at 950 cm^{-1} and 910 cm^{-1} due to ν_{sy}(O=M=O) and ν_{asy}(O=M=O) stretches respectively[15–17,47]. These bands are in the usual ranges(892–964 cm^{-1} and 840–925 cm^{-1}) assigned for ν_{sy}(O=Mo=O) and ν_{asy}(O=Mo=O) stretches respectively, reported for the majority of dioxomolybdenum(VI) complexes[47]. The data indicate the presence of cis-MoO$_2$ structure, since a compound with a trans-MoO$_2$ moiety is expected to show only the ν_{asy}(O=Mo=O) stretch[47]. The data rule out the presence of oligomeric structure $^{..}$Mo=O$^{..}$ Mo=O$^{..}$ in which ν(Mo=O) is expected to occur at < 850 cm^{-1} [48]. PS–LUO$_2$ exhibits a strong band at 910 cm^{-1} due to the ν_{asy}(O=U=O) stretch, which occurs in the reported range(870–950 cm^{-1}) observed for the majority of dioxouranium(VI) compounds[49]. The observation of only one ν_{asy}(O=U=O) band indicates the presence of the trans-UO$_2$ structure since the ν_{sy}(O=U=O) is infrared inactive. The force constant(f$_{U-O}$) is 6.88 mdyn/Å which agrees well with those of other UO$_2$(II) complexes. The U—O bond distance(R) is 1.74 Å which is in the usual range(1.60–1.92 Å) observed for the majority of UO$_2$(II) complexes[49,50]. The oxobridged iron(III) coordination compounds usually show a band in the region:
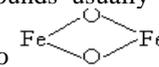
820–860 cm^{-1} due to Fe$<$O$>$Fe bridge[51]. No such band in the above region could be observed in PS–LFeCl·DMF indicating the non-participation of the phenolic oxygen atom in the bridge formation. The absence of a band in the range: 835–956 cm^{-1}, characteristic of the ν(Zr=O) stretch[52] in polystyrene-anchored zirconium(IV) coordination compound suggest the formulation of compound as PS–LZr(OH)$_2$·DMF and not as PS–LZrO(H$_2$O)·DMF. The appearance of a new band at around 1115 cm^{-1} due to the δ(Zr—OH) mode also supports the suggested formulation of polystyrene-anchored zirconium(IV) coordination compound[53].

Nujol mull electronic spectra of the polystyrene-supported coordination compounds could not be recorded, as the compounds do not form a good mull and hence the reflectance spectra of compounds were recorded. The compounds being insoluble in common solvents, the solution electronic spectra also could not be recorded. PS–LCu exhibits an asymmetric broad band at 18500 cm^{-1} which is assigned to the envelope of $^2B_{1g}\rightarrow^2A_{1g}$, $^2B_{2g}$ and ^2E_g transition for square planar arrangement of ligand around copper(II) ions[54]. PS–LNi complex exhibits a weak band at 12200 cm^{-1} (ν_1) which is assigned to a spin-forbidden $^1A_{1g}\rightarrow^3A_{2g}$ transition[55]. A strong band at 24500 cm^{-1}(ν_3) in the present compound is assigned to the $^1A_{1g}\rightarrow^1B_{1g}$ transition[56,57]. We were unable to locate the ν_2 band $^1A_{1g}\rightarrow^1A_{2g}$ transition at around 20000 cm^{-1} as it is probably merged underneath the strong ν_3 transition. Hobday et. Al[58] have also reported the presence of a single band at 23000 cm^{-1} in the spectra of square planar, Ni(salen)SnX$_2$ (where X = Cl, Br). PS–LFeCl·DMF exhibits three bands at 12100 cm^{-1}, 22200 cm^{-1} and 26700 cm^{-1} due to the $^6A_{1g}\rightarrow^4T_{1g}$(G), $^6A_{1g}\rightarrow^4T_{2g}$(G) and $^6A_{1g}\rightarrow^4A_{1g}$(G) transitions, respectively in an octahedral symmetry[59]. PS–LMn·2DMF exhibits three bands at 18450 cm^{-1}, 22990 cm^{-1} and 25240 cm^{-1} due to the $^6A_{1g}\rightarrow^4T_{1g}$(G), $^6A_{1g}\rightarrow^4T_{2g}$(G) and $^6A_{1g}\rightarrow^4A_{1g}$(G) although both Mn(II) and Fe (III) have $^6A_{1g}$ ground state, all the bands occur in Fe (III) compound at lower energy than those of Mn(II) compound. This is due to lower value of Racah parameters(B &C) in Fe (III) compound to those of Mn(II) compound.

The room temperature magnetic susceptibilities and magnetic moments of the polystyrene-anchored coordination compounds are presented in Table 2. PS—LCu exhibits magnetic moment 1.93 B.M.. This value is within the range: 1.75–2.2 B.M. reported for Cu(II) coordination compounds[60]. PS—LFeCl·DMF exhibits magnetic moment 6.00 B.M. This value is within the range: 5.8–6.02 B.M. expected for high spin magnetically dilute Fe(III) complexes[61]. PS—LMn·2DMF exhibits magnetic moment 5.90 B.M.. This value is within the range: 5.88–5.92 B.M. expected for high spin magnetically dilute Mn(II) complexes[62]. PS—LNi is diamagnetic with square planar structure[63]. The zinc(II), cadmium(II), dioxomolybdenum (VI) and dioxouranium(VI) complexes are diamagnetic as expected. A tetrahedral structure for Zn(II) and Cd(II) complexes; a square planar structure for Cu(II), Ni(II) and Co(II)polystyrene-anchored complexes; an octahedral structure for MoO$_2$(II) and UO$_2$(II) complexes and a pentagonal bipyramidal structure for Zr(IV) complex are suggested. The presence of diamagnetic large polystyrene backbone keeps the, metal centres in the polystyrene-anchored compounds considerably separated which avoids dipolar broadening. As a result, reasonably good ESR spectra were observed in polycrystalline solids in the absence of a host diamagnetic coordination compound diluent. in the EPR spectra of the present Cu(II) complex rules out the presence of M—M interaction. It has been observed that the metal ions are situated on the phenyl rings(or polystyrene) which are 6 to 7 styrene units apart when per cent reaction conversion is <100%. Thus a magnetically dilute environment around the metal ions is maintained since the path way for M—M interaction is reduced. But the polystyrene is 2% cross linked with divinylbenzene, the polymer chain may overlapped and twisted and this may bring some reactive groups closer leading to M—M interaction which was undetectable by the ESR method.

Conclusion

The mixed Schiff base can be conveniently synthesized under controlled conditions of required molar ratio of carbonyl and amine compounds. The quadridentate ligand is successfully anchored to polystyrene matrix and the polymer bound ligand is capable of acting as a chelating ligand and coordinating with a variety of metal ions. The structures of the metal bound polymers are comparable to those of the metal complexes of non–anchored ligand.

Table 1. Colour, analytical and other characterization data of polystyrene-anchored compounds[a]

S.No.	Compounds	Colour	Found(calcd)(%)		Per cent reaction conversion[b]	Metal binding capacity[c] (mmol/g of resin)
			M	DMF		
1	PS—LCu	Yellowish Green	2.6(5.12)	-	50.8	0.41
2	PS—LNi	Pale yellow	3.2(4.75)	-	67.4	0.55
3	PS—LZn	Cream	3.5(5.26)	-	66.5	0.54
4	PS—LCd	Cream	5.4(8.71)	-	62.0	0.48
5	PS—LMoO$_2$	Yellow	4.5(7.35)	-	61.2	0.47
6	PS—LUO$_2$	Yellow	9.4(16.44)	-	57.2	0.39
7	PS—LMn·2DMF	Dark brown	3.10(3.98)	8.2(10.59)	77.9	0.56
8	PS—LFeCl·DMF	Brown	1.0(4.16)	1.3(5.44)	24.0	0.18
9	PS—LZr(OH)$_2$·DMF	Cream	3.6(6.63)	2.9(5.30)	54.3	0.39

[a]Abbreviations: PS—LH = I, DMF= dimethylformamide. [b]Per cent reaction conversion(p) = (observed metal ion percentage×100)/(calculated metal ion per centage on the basis 100% reaction conversion of polystyrene-anchored ligand to polystyrene-anchored complex). [c]Metal binding capacity = [M% (observed)×10]/(atomic weight of metal).

Table 2. Infrared spectral data(cm^{-1}), magnetic susceptibility measurements and magnetic moments of the polystyrene anchored compounds

S.No.	Compounds	ν(C=N) (azomethine)	ν(C—O) (phenolic)	χ$_{dia}$ (10^{-6} cgs units)	χ$_M^{corr.}$ (10^{-6} cgs units)	Magnetic Moment B.M. [K]
1	LH$_2$	1630	1540	-	-	-
2	PS—LH$_2$	1630	1540	-	-	-
3	PS—LCu	1600	1545	−836	1594	1.93 [293]
4	PS—LNi	1605	1545	-	-	Diamagnetic
5	PS—LZn	1610	1545	-	-	Diamagnetic
6	PS—LCd	1610	1545	-	-	Diamagnetic
7	PS—LMoO$_2$	1605	1545	-	-	Diamagnetic
8	PS—LUO$_2$	1605	1550	-	-	Diamagnetic
9	PS—LMn·2DMF	1600	1545	−1093	14986	5.90 [290]
10	PS—LFeCl·DMF	1620	1545	−1161	15550	6.00 [290]
11	PS—LZr(OH)$_2$·DMF	1600	1550	-	-	Diamagnetic

References

1. Boussetta, S.; Branger, C.; Margaillan, A.; Boudenne, J.L.; Coulomb, B., React. and Funct. Polym., 68(3), (2008) 775
2. Kumar D., Gupta P.K. and. Syamal A, Indian J. Chem., 41A, (2002) 2494
3. Syamal A and Singh M.M, React. and Funct. Polym., 24, (1994) 27
4. Syamal A., Singh M.M. and Kumar D., React. Funct. Polym., 39, (1999) 27
5. Syamal A. and Singh M.M., React. Funct. Polym., 24, (1994) 27.
6. Cazaux I. and Caze C., Eur. Polym. J., 29, (1993) 1615.
7. Syamal A. and Singh M.M, Indian J. Chem., 33A,(1994), 58.
8. Syamal A. and Singh M.M., Indian J. Chem., 31A, (1992) 110.
9. Syamal A. and Singh M. M., React. Funct. Polym., 21, (1993), 45.
10. Masuda S., Kobayashi T. and Tomida T., Polymer, 34, (1993), 4562.
11. Syamal A., Kumar D., Singh A.K., Gupta P.K., Jaipal and Sharma L.K., Indian J. Chem., 41A, (2002), 1385.
12. Kumar D., Syamal A. and Singh A.K., Asian J. Chem., 16, (2004)
13. Jain V.K., Handa A., Sait S.S, Shrivastava P and Agarwal Y.K, Anal. Chim. Acta, , 4-29, (2000) 237.
14. Thamizharsi S., Reddy A.V.R. and Balasubramanium S., Eur. Polym. J., 34, (1998) 1605.
15. Kumar D., Syamal A. and Singh A.K., Indian J. Chem., 42A, (2003) 280.
16. Kumar D. Kumar, P.K. Gupta and Syamal A., Indian J. Chem., 41A, (2002) 2494.
17. Kumar D., Syamal A. and Gupta P.K., J. Indian Chem. Soc., 80, (2003) 3.
18. Syamal A. and Singh M.M., J. Polym. Mater., 9, (1992) 105.
19. Syamal A. and Singh M.M., Indian J. Chem., 32A, (1993) 42.
20. Syamal A., Ahmed S. and Bariniazi M.A, 1983, J. Indian Chem. Soc., 60, 493.
21. Syamal A. and Singh M.M., Indian J. Chem., 32A, (1993) 861.
22. Sherai H., Takemoto K. and Hojo, N. Polym. Commun., 25, (1984) 284.
23. Mori H., Shinba H., Fujimura Y. and Takegami Y., Nipon Kagaku Kaishi, (1989) 1855.
24. Szcpaniak V. and Kuezynsakii K.K., React. Funct. Polym. 3, 1985, 101.
25. Hilal H., Kim C. and Schrainer A., J. Mol. Catal., 31, (1993), 157.
26. Mathur P.N., Parashar K. and Srivastava S., Indian J. Chem., 39A, (2000), 1327.
27. Brown J., Hamerton I. and Howlin J.B., J. Appl. Polym. Sci., 72(2), (2000), 201.
28. Tomoi T., Abe O., Takasu N. and Kakiuchi, H. Makromol. Chim.,183, 1983, 2431.

29. Nishizawa N., Yokoyama T., Kimura T. and Suzuki T.M., Polyhedron, 5, (1986), 204.

30. Druta I., Avram E. and Cozan V., Eur. Polym. J., 36, (1999), 221.

31. Hassanein M. and Abdel-Hay F., El-Esawy T., Eur. Polym. J., 30(3), (1994) 335.

32. Drago R.S., Gaul J., Zombeck A. and Staub D.K., J. Amer. Chem. Soc., 102, (1980), 1033.

33. Pathak R. and Rao G.N., J. Mol. Catal. A: Chem., 130, (1998), 215.

34. Suzuki T.M. and Yokoyama T., Polyhedron, 2, (1983), 127

35. Akelah A., Abbasi M.M. and Azad M.K.H., Indian J. Chem., 25A, (1986), 923.

36. Nishikawa H. and Yamada S., Bull. Chem. Soc. Japan, 37,(1964) 8.

37. Duff J.C. and Bills E.J., J. Chem. Soc., (1932) 1987.

38. Chin C.J., McDonald J.W. and Newton W.E., Inorg. Chem., 15, (1976) 2612.

39. Syamal A. and M.R. Maurya, Indian J. Chem., 24A, (1985), 836.

40. Syamal A., Singh M.M. and Kumar D., React. Funct. Polym., 39, (1999) 27.

41. Syamal A. and Singh M.M., React. Funct. Polym., 24, (1994), 27.

42. Lewis J. and Wilkins R.G., Modern Coordination Chemistry, Interscience Publishers, New York, (1960) 412.

43. Dutta R.L. and Syamal A., Elements of Magnetochemistry 2nd Edn., Affiliated East West Press, New Delhi, (1993) 7.

44. Dean J.A., Lange's Hand Book of Chemistry, McGraw Hill, Toronto, 13th Edn.,(1985).

45. Bahad P.J., Bhave N.S. and Aswar A.S., J. Indian Chem. Soc., 77,(2000) 363.

46. Syamal A. and Kale K.S., Indian J. Chem., 19A (1980) 225.

47. Teyssi P. and Charretta J.J., Spectrochim. Acta, 19, (1963) 407.

48. Syamal A. and Maurya, M.R., Indian J. Chem., 24A, (1985) 836.

49. Syamal A. and Maurya, M.R., Coord. Chem. Rev., 95, (1989) 183.

50. Stiefsel E.I., Prog. Inorg. Chem., 22, (1977) 1.

51. Alyea E.C., Malek A. and Kazi A.I., Trans. Met. Chem., 6, (1981) 223.

52. McGlynn S.P., Smith J.H. and Neely W.C., J. Chem. Phys., 35, (1961) 105; Howkin D.J. and Grifith W.P., J. Chem. Soc., A., (1966) 472.

53. Spasibenko T.P. and Goroshchenko Y. G., Russ. J. Inorg. Chem.,14, (1969) 758.

54. Syamal A. and D. Kumar, Indian J. Chem., 24A, (1985) 62; Lever A. B. P., Inorganic Electronic Spectroscopy, (1984) 2nd Edn. (Elsevier, Amsterdam), & references there in.

55. Raman N. & Kulandaisamy A., Proc. Indian Acad. Sci., (2001) 113183;

56. Singh N. K., Singh D. K. & Singh J., Indian J. Chem., 40A, (2001) 1064.

57. Hobday D. & Smith T. D., Indian J. Chem., 9,(1971) 590.

58. Singh V. P. & Narang K. K., Synth. React. Inorg. Metal-Org. Chem., 23, (1993) 971; Bhave N. S., Bahad P. J., Sonparote P. M. & Aswar A. S., J. Indian Chem. Soc., 79, (2002)342.

59. Syamal A., Coord. Chem. Rev., 16, (1975) 309.

60. Cotton F.A. and Wilkinson G., Advanced Inorganic Chemistry, 3rd Edn. Wiley, New Delhi, (1985).

61. Syamal A. and Gupta B.K., Indian J. Chem., 33A, (1995) 495.

62. Calvin M. and Barkelew C.H., J. Amer. Chem. Soc., 68, (1964) 2273;

63. Gersman H.R. and Neiman R., J. Chem. Phys., 36, (1962) 3221.

64. Kivelson D. and Neiman R., J. Chem. Phys., 35, (1961) 149.