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Novel nanohybrids of cobalt(III) Schiff base complexes and clay: Synthesis and structural determinations



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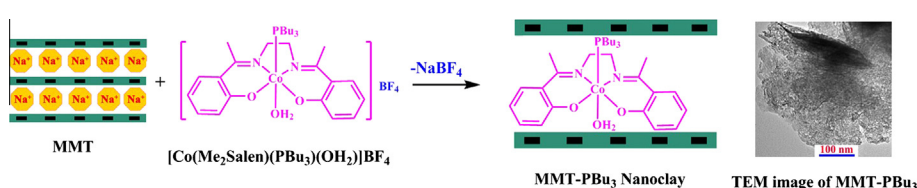
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HIGHLIGHTS

- Novel cobalt Schiff base complexes were prepared and their structures were confirmed by different techniques.
- The X-ray crystallography results show that they are hexacoordinated in the solid state.
- Nanohybrid of the above complexes and MMT clay were prepared via ion-exchange method.
- FT-IR, TGA/DTG, XRD, SEM, EDX and TEM were used for the characterization of these materials.
- SEM and TEM show the resulting hybrid nanomaterials have layer structures.

GRAPHICAL ABSTRACT



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ABSTRACT

The $[\text{Co}(\text{Me}_2\text{Salen})(\text{PBu}_3)(\text{OH}_2)]\text{BF}_4$ and $[\text{Co}(\text{Me}_2\text{Salen})(\text{PPh}_3)(\text{Sol})]\text{BF}_4$ complexes were synthesized and characterized by FT-IR, UV-Vis, ^1H NMR spectroscopy and elemental analysis techniques. The coordination geometry of $[\text{Co}(\text{Me}_2\text{Salen})(\text{PPh}_3)(\text{H}_2\text{O})]\text{BF}_4$ was determined by X-ray crystallography. It has been found that the complex is containing $[\text{Co}(\text{Me}_2\text{Salen})(\text{PPh}_3)(\text{H}_2\text{O})]\text{BF}_4$ and $[\text{Co}(\text{Me}_2\text{Salen})(\text{PPh}_3)(\text{EtOH})]\text{BF}_4$ hexacoordinate species in the solid state. Cobalt atom exhibits a distorted octahedral geometry and the Me_2Salen ligand has the N2O2 coordinated environment in the equatorial plane. The $[\text{Co}(\text{Me}_2\text{Salen})(\text{PPh}_3)(\text{H}_2\text{O})]\text{BF}_4$ complex shows a dimeric structure via hydrogen bonding between the phenolate oxygen and hydrogens of coordinated H_2O molecule. These complexes were incorporated into Montmorillonite-K10 nanoclay. The modified clays were identified by FT-IR, XRD, EDX, TGA/DTA, SEM and TEM techniques. According to the XRD results of the new nanohybrid materials, the Schiff base complexes are intercalated in the interlayer spaces of the clay. SEM and TEM micrographs show that the resulting hybrid nanomaterials have layer structures. Also, TGA/DTG results show that the intercalation reaction was taken place successfully.

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Introduction

During the past few years, terms like nanomaterials, nanocomposites and nanosystems have become designer. In fact anything with 'nano' attached to it has nearly a magical effect – not so much on performance as on expectations. There exceptional size-dependent properties make these materials superior and indispensable as they show unusual physical, chemical and biological properties [1,2]. Along with the different nanomaterials, nanoclays compose a multitalented area of exploration [3–6]. Due to its large value of aspect ratio, diameters in nanometer range, and thermal resistance, clay minerals have many attentions in recent years [7]. Sodium Montmorillonite (MMT) is the most commonly used clay owing to its natural abundance, high aspect ratio and high cationic exchange capacity (about 80–120 meq/100 g) [8–10].

Cobalt Schiff base complexes have been studied extensively. They are investigated as models for the Cobalamine (B_{12}) coenzymes [11] classified as an oxygen carrier [12]. They applied as a catalyst for the preparative oxygenation of phenols [13] and amines [14]. Cobalt(III) salen catalytic activity has been investigated. The catalytically active species contains Co(III) oxidation state [15].

Cobalt(III) Schiff base complexes with formula of $[CoL(PR_3)(OH_2)]^+$ (where L = tetradentate N₂O₂ Schiff bases) show that these types of complexes are in equilibrium with phosphines and amines to form $[CoL(PR_3)_2]^+$ and $[CoL(PR_3)(amine)]^+$ [16–25], but there is not any information about their structure. So to extension the studies on the structure of these type of complexes, Me₂Salen (bis(2-hydroxyacetophenone)ethylenediamine) Schiff base was prepared by the condensation of 2-hydroxyacetophenone within 1,2-ethylenediamine. The tertiary phosphine cobalt(III) complexes of synthesized ligand were prepared in methanol solvent (Scheme 1). The prepared complexes were identified by FT-IR, ¹H NMR, UV–Vis spectroscopy and elemental analysis. The coordination geometry of $[Co(Me_2Salen)(PPh_3)_2]BF_4$ was determined by X-ray crystallography. The synthesized complexes were incorporated into Montmorillonite K-10 nanoclay. The modified clay was identified and studied via FT-IR, XRD, TG/DTA, SEM, EDX and TEM.

Experimental

Materials

All of the chemicals and solvents used for synthesis were of commercially available reagent grade and they were used without purification. Montmorillonite K-10 (MMT) with cation-exchange capacity of 119 meq/100 g was provided by Aldrich.

Characterizations

Fourier transform infrared (FT-IR) spectra were recorded as KBr discs on a FT-IR JASCO-680 spectrophotometer in the 4000–400 cm^{-1} . The elemental analysis was determined on a CHN–O–Heraeus elemental analyzer. UV–Vis spectra were recorded on a JASCO V-570 spectrophotometer in the 190–900 nm. The ¹H NMR spectra were recorded in CDCl₃ on DPX-400 MHz FT-NMR. The

X-ray single crystal structure analysis was obtained by using Bruker smart Apex II-2009 CCD area detector diffractometer. The X-ray diffraction (XRD) was recorded on high resolution X-Ray diffractometer system model PANalytical X'PRO MRD PW3040. Transmission electron microscopy (TEM) studies were performed using Zeiss Libra[®]120 TEM system. The thermal stability of specimens was tested using PERKIN ELMER TGA7 1991 thermogravimetric analyzer from ambient temperature to 900 °C at a heating rate of 20 °C/min under nitrogen gas. Scanning electron microscopy (SEM) was recorded on QUANTA FEG 650 2012 SEM system. Energy Dispersive X-ray Analysis (EDX) (EDAX Falcon System) was conducted to analyze the presence of elements in the specimens that have been sputtered with carbon black.

Synthesis of Schiff base ligands

The Schiff base ligand, H₂Me₂Salen, was prepared according to the literature [26] by condensation between 1,2-ethylenediamine and 2-hydroxyacetophenone (1:2 mole ratio) in methanol and recrystallized by dichloromethane/methanol mixed solvent through the partial evaporation of dichloromethane.

Synthesis of metal Schiff base complexes

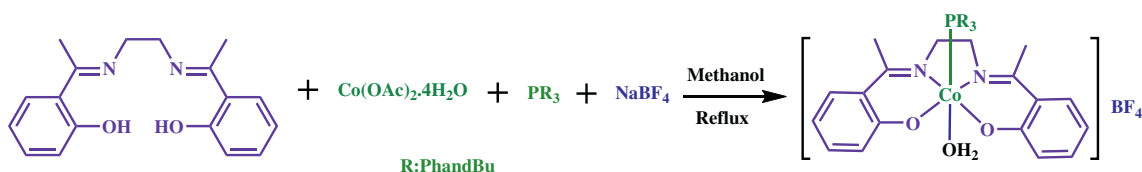
The general procedure for synthesis of $[Co(Me_2Salen)(PBu_3)(H_2O)]BF_4$, $[Co(Me_2Salen)(PPh_3)(H_2O)]BF_4$ complexes is as follows: an appropriate amount of cobalt(II)acetatetetrahydrate (0.249 g, 1.0 mmol), phosphine (1.0 mmol) were added to a methanolic solution (40 mL) of H₂Me₂Salen (0.296 g, 1.0 mmol). The reaction was refluxed for 1 h. The formed Co(II) complex was oxidized by blowing air into the solution for 2 h, then it was filtered. To the filtrate, an appropriate amount of sodium tetrafluoroborate (.110 g, 1.0 mmol) was added. The green crystals formed after 48 h. The crystals filtered off, washed with methanol and recrystallized from 2:1 ratio of methanol/ethanol and dried in vacuum at 65 °C.

$[Co(Me_2Salen)(PBu_3)(OH_2)]BF_4$ Yield (75%). Anal. calc. for C₃₀H₄₇N₂O₃PF₄Co: C, 60.89; H, 8.01; N, 4.73%. Found; C, 61.35; H, 8.12; N, 4.85%. FT-IR (KBr cm^{-1}) ν_{max} 2956, 2921, 2863 (C–H), 1597 (C=N), 1439 (C=C), 1085 (BF₄⁻). ¹H NMR (CDCl₃, δ , ppm): 0.70–0.80 (t, 9H, CH₃), 1.15–1.31 (m, 18H, CH₂), 2.70 (s, 6H, CH₃), 3.90–4.10 (d, 4H, CH₂), 6.59–7.67 (m, 8H, Aromatic). UV–Vis, λ_{max} (nm) (Ethanol): 636 (780), 397 (5700), 336 (5600).

$1/2[Co(Me_2Salen)(PPh_3)(CH_3CH_2OH)]BF_4 \cdot 1/2[Co(Me_2Salen)(PPh_3)(H_2O)]BF_4$ Yield (80%). Anal. calc. for C₃₇H₃₇N₂O₃PF₄BCo: C, 60.51; H, 5.08; N, 3.81%. Found; C, 61.44; H, 5.17; N, 3.83%. FT-IR (KBr cm^{-1}) ν_{max} 3058 (C–H), 1592 (C=N), 1438 (C=C), 1086 (BF₄⁻). ¹H NMR (CDCl₃, δ , ppm): 2.30 (s, 3H, CH₃, ethanol), 2.70 (s, 6H, CH₃), 3.50–4.30 (m, 6H, CH₂, ethanol and bridge ethylene), 6.42–7.52 (m, 23H, Aromatic). UV–Vis, λ_{max} (nm) (Ethanol): 724 (1100), 405 (5700), 337 (10,000).

Synthesis of intercalation compounds

The 0.75 g of MMT was added to an ethanol solution containing $[Co(Me_2Salen)(PBu_3)(H_2O)]BF_4$ or $[Co(Me_2Salen)(PPh_3)(H_2O)]BF_4$ (0.075 g) complexes. The reaction mixture was refluxed for 24 h



Scheme 1. The structure of Schiff base and its complexes.

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