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Synthesis and characterization of a trinuclear cobalt complex with acetate as bridge and O-Phenylenediamine as terminal ligand

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ABSTRACT

A trinuclear cobalt complex $[\text{Co}_3(\text{CH}_3\text{COO})_6(\text{O-Phenylenediamine})_2]$ has been synthesized from the reaction of cobalt acetate with O-Phenylenediamine in DMF. The complex was characterized by element analysis, melting point, UV/visible ¹HNMR and FT-IR spectroscopic methods. Analytical and spectroscopic data indicate that the structure of $[\text{Co}_3(\text{CH}_3\text{COO})_6(\text{O-Phenylenediamine})_2]$ consist of trinuclear cobalt unit, coordinated by two terminal ligand O-Phenylenediamine groups, and six CH_3COO^- groups featuring another kinds of bonding mode. © 2012 Trade Science Inc. - INDIA

KEYWORDS

Cobalt;
O-Phenylenediamine;
Trinuclear;
¹HNMR;
IR;
UV;
Element analysis.

INTRODUCTION

Multinuclear complexes of transition metal ions attract a lot of attention due to their catalytic activity^[1-4] utility in modeling the multimetal active sites of metalloproteins^[2] and potential use in nanoscience^[4]. Polynuclear transition metal complexes with bridging carboxyl ligands have unusual structure and demonstrate unique chemical and physical properties^[5]. Polynuclear systems with bridging ligands are among the best to create conditions for the exchange interactions between paramagnetic centers. 3d transition metal (M) complexes are of special importance in this context: high electron-density delocalisation in M-OCO-M moieties generates good exchange channels in them^[5,6]. Cyclic trinuclear cobalt complexes form an important class^[7] as they have been found to show some catalytic activity in the epoxidation of olefins^[2,8] and in the au-

toxidation of hydrocarbons^[9]. The linear, trinuclear mixed valence ($\text{Co}^{\text{III}}-\text{Co}^{\text{II}}-\text{Co}^{\text{III}}$) complexes are known since. Werner reported a series of such complexes obtained by partial oxidation of the mixtures of cobalt (II) salts and ethylenediamine [The chemistry of transition metal carboxylate complexes has attracted much attention and a variety of cobalt carboxylate complexes have been prepared over the past few decades mainly because of the design and synthesis of molecular based magnets^[11-16]. Carboxyl is often used as a ligand to design polynuclear complexes with interesting magnetizing properties^[17] previously, numerous trinuclear carboxylate complexes have been reported^[18] such as: $[\text{Co}_3(\text{CH}_3\text{COO})_8](\text{Et}_4\text{N})_2$, $[\text{Mn}_3(\text{CH}_3\text{COO})_8](\text{Et}_4\text{N})_2$ ^[19], $[\text{Mn}_3(\text{CH}_3\text{COO})_6(\text{bpy})_2]$ ^[20], $[\text{Mn}_3(\text{CH}_3\text{COO})_2(\text{bpc})_2(\text{py})_4(\text{H}_2\text{O})_2] \cdot 0.5\text{H}_2\text{O}$ ^[21] and $[\text{Co}_3(\text{CH}_3\text{COO})_6(\text{phen})_2]$ ^[22]. Herein we report the synthesis and characterization of new trinuclear complex

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$[\text{Co}_3(\text{CH}_3\text{COO})_6(\text{O-Phenylenediamine})_2]$.

EXPERIMENTAL

Materials

UV-VIS. The electronic spectra were recorded on a PERKIN ELMER UV-VIS spectrophotometer using DMF as solvent. The UV-VIS spectra were performed in department of chemistry, islamic azad university, Firoozabad branch.

IR. Infrared spectra were recorded on a FT-IR BURKER TENSOR27 infrared spectrophotometer as KBr discs in the rang of $400\text{-}4000\text{Cm}^{-1}$. The FT-IR spectra were performed in department of chemistry, islamic azad university, Firoozabad branch.

NMR. ^1H NMR spectra were recorded on DPX.300 MHz from BRUKER Company in $\text{DMSO-}d_6$ solutions with TMS as internal standard at ambient temperature. The ^1H NMR spectra were performed in department of chemistry, Islamic azad university, Zanjan branch.

Elemental analysis. The elemental analysis were performed in the department of chemistry, college of science, Shiraz university on LECO CHNS 932.

Reagents. $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, O-phenylenediamine and the solvents were purchased from MERK Company.

Method

To a stirred solution of $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (2.04mmol, 0.508g) in DMF was added a solution of O-phenylenediamine (1.36mmol, 147g) in DMF. The result solution was allowed to stir and hot and then diethylether was added and then a dark bloody solid obtained. The reaction mixture was filtered off and washed with DMF, followed by acetone and then diethylether. The solid was dried in laboratory area. Data for $[\text{Co}_3(\text{CH}_3\text{COO})_6(\text{O-Phenylenediamine})_2]$: yield: 0.29g (56.8%).

-m.p. 296°C .

-UV (DMF), $\lambda_{\text{max}}(\epsilon)$: 234 nm, 435nm.

-IR: (KBr) $\nu_{\text{Cm}^{-1}}$: 3382(N-H), 2910(C-H), 1658(N-H), 1561(asy COO^-), 1416(sy COO^-), 1375(C-H), 1268(C-N), 1170, 1110, 1100, 755, 667, 620.

- ^1H NMR(TMS) δ ppm: 1.7 (s, 18H, methyl), 6.9-6.4 ((w, 8H, amine), 8.1-7.2 (m, 8H, phenyl).

-Anal. Calc. for $\text{C}_{24}\text{H}_{30}\text{Co}_3\text{N}_4\text{O}_{12}$: C, 38.56; H, 4.58; N, 7.49. Found :C, 39.19; H, 4.71; N, 7.68%.

RESULT AND DISCUSSION

While attempting to synthesize a trinuclear metal (II) complexes which bind acetates in the manner proposed, for the low valent metal cobalt (II), we obtained the title compound $[\text{Co}_3(\text{CH}_3\text{COO})_6(\text{O-phenylenediamine})_2]$, and its structure shown in figure. The structure of synthesized complex in figure, consist of a trinuclear array of $\text{Co}(\text{CH}_3\text{COO})_3\text{Co}(\text{CH}_3\text{COO})_3\text{Co}$ unit. The central cobalt is coordinated octahedrally by six acetate oxygen atoms, while two terminal cobalts are 5-coordinate and are capped by O-phenylenediamine ligands. The resulting data are consistent with the molecular formula as $\text{Co}_3(\text{CH}_3\text{COO})_6(\text{O-phenylenediamine})_2$.

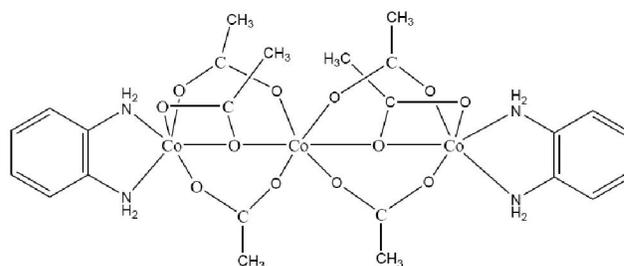


Figure 1 : The structure of $[\text{Co}_3(\text{CH}_3\text{COO})_6(\text{O-Phenylenediamine})_2]$

The infrared spectroscopy exhibits two characteristic bands at 1561Cm^{-1} and 1416Cm^{-1} due to asymmetric stretching vibration COO^- and symmetric stretching vibration COO^- all bridging acetates respectively. The difference in frequency, $\Delta(\nu_{\text{as}}(\text{COO}^-) - \nu_{\text{s}}(\text{COO}^-))$, is 145Cm^{-1} (163Cm^{-1} for free acetate ion), indicating the presence of deprotonated carboxylate group coordinated to metal as a bridge ligand. This compound resolved in water very weak, that's way we believe that its not ionic and the acetate ion must be as a ligand in complex. The IR spectroscopy also indicate that O-phenylenediamine exist in compound. A medium peak in 3382Cm^{-1} and a peak in 1658Cm^{-1} occurred due to Stretching and bending vibration of N-H (primary amines) bond respectively, and a peak (as shoulder) in 1520Cm^{-1} due to stretching vibration of C-C in aromatic chain. The IR spectrum of the O-phenylenediamine exhibits a band at 1320Cm^{-1} due to C-N bond,

which are shifted to the lower frequencies 1268 Cm^{-1} in the spectra of the cobalt complex. The decrease in the frequency indicate a decrease in the C-N bond order due to the coordination of the nitrogen to the cobalt. These peaks in 3382 Cm^{-1} , 1658 Cm^{-1} , 1520 Cm^{-1} and 1268 Cm^{-1} all of them indicate that O-phenylenediamine exist in our complex and coordinated to the cobalt ion.

Also the peaks in 2910 Cm^{-1} and 1375 Cm^{-1} depend on stratching and bending vibration of C-H bond respectively. As well as several others peaks in this IR spectroscopy had seen, that is reported in experimental part.

The $^1\text{H NMR}$ spectrum of the complex in DMSO as solvent displays an intense and sharp singlet peak at 1.7 ppm may be assigned to the methyle hydrogens in acetate bridge. Also a wide peak at 6.4-6.9 ppm range observed due to N-H hydrogens in O-phenylenediamine, which nitrogen atom linked to the benzen chain. We believe, this peak width occurred due to quadrupole widen, that N-H absorption consist of a wide range from 6.4 to 6.9 ppm. In this spectrum also observed multiple peaks at 7.1-8.6 ppm, which can be demonstrate aromatic hydrogens.

The electron spectra of the terminal ligand and their complex show an intense band at 234 nm (42735 Cm^{-1}) related to O-phenylenediamine charge transfer transition. Also the UV-Visible spectroscopy observed an absorption at 435 nm (22988 Cm^{-1}), this absorption band in visible region are assigned to $d \rightarrow d$ transition.

The complex melting point measured 296°C . this point go to mind that one of causes of this complex high melting point (296°C) is stability of synthesized compound, that can be indicate in this complex is formed chelate ring.

The element analyses is in good agreement with those calculated for the proposed formula of synthesized complex. The calculate data of CHN analyses

TABLE 1 : The element analyses data

Elements (%)	Element analysis (CHN)	
	theory	experiment
Carbon	38.56	39.19
Nitrogen	7.49	7.68
Hydrogen	4.58	4.71

Above results confirm the suggested formula for this complex.

and found data are reported in table, that indicate we have a trinuclear cobalt complex with six acetate and two O-phenylenediamine as terminal ligand ($\text{C}_{24}\text{H}_{30}\text{Co}_3\text{N}_4\text{O}_{12}$).

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