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Second sphere coordination in anion binding: Synthesis, characterization, X-ray structure of tris(1,10-phenanthroline)cobalt(III)2,4-dinitrophenolate tetrahydrate, $[Co(phen)_3](dnp)_3{\cdot}4H_2O$ where dnp = 2,4-dinitrophenolate

Raj Pal Sharma [a,*], Ajnesh Singh [a], Valeria Ferretti [b,*], Paloth Venugopalan [a]

[a] *Department of Chemistry, Panjab University, Chandigarh 160014, India*
[b] *Centro di Strutturistica Diffrattometrica and Dipartimento di Chimica, University of Ferrara via L. Borsari 46, I-44100 Ferrara, Italy*

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ABSTRACT

A new cobalt(III) complex salt, $[Co(phen)_3](dnp)_3{\cdot}4H_2O$ has been synthesized in an effort to utilize $[Co(phen)_3]^{3+}$ cation as a new host for di-substituted phenolate (2,4-dinitrophenolate) anion. This cobalt (III) complex salt has been characterized by elemental analyses and spectroscopic techniques (UV/visible, IR, NMR and conductance measurements). Single crystal X-ray structure determination confirmed the composition $[Co(phen)_3](dnp)_3{\cdot}4H_2O$. A strong network of hydrogen bonding interactions C–H···O (phenolate), C–H···O (nitro) involving second sphere coordination and O–H···O hydrogen bonding interactions stabilize the crystal lattice. The formation of a complex salt of definite composition along with solubility product data suggests that $[Co(phen)_3]^{3+}$ present in $[Co(phen)_3]Cl_3$ may be used as an anion receptor for 2,4-dinitrophenolate ion.

1. Introduction

The binding of anionic species by receptor molecules through hydrogen bond donating groups is an area of interest among inorganic chemists working in the field of supramolecular chemistry because of the crucial role played by anions in medicine, biological processes, ion transport studies and catalysis [1]. Additionally, various pollutant anions (sulphates, nitrates, pertechnetate, chromate, phosphate etc.) are believed to have deleterious effects on the environment. The design and synthesis of receptor molecules that are capable to functioning as sensors for molecular recognition of charged species are a challenge for researchers because of their varied shape and size, sensitivity to pH and low charge densities as compared to cationic species [2]. Therefore, there is a great need for novel anion receptors to better characterize anion association patterns and to obtain novel binding features. A proper understanding of hydrogen bonding [3] and supramolecular synthons [4] is crucial in the design of solid-state architectures with novel interaction patterns among the functional groups [5] or their combinations. Although cationic organic anion receptors have been extensively investigated, cationic metal complexes have not received much attention.

Metal complexes of phenanthroline with cobalt(II) [6] and cobalt(III) [7] are stable and well studied. Nevertheless, much attention have been given to the kinetic studies employing $[Co(phen)_3]^{3+}$ as oxidizing agent [8]. To the best of our knowledge there is no explicit report in the literature regarding the utilization of $[co(phen)_3]^{3+}$ as binding agent (anion receptor) for nitrophenolates employing the second sphere coordination. Nitrophenolates are member of biologically and commercially important class of phenol compounds which have number of application, e.g. manufacturing drugs (e.g., acetaminophen), fungicides, insecticides, dyes and to darken leather, 2,4,6-trinitrophenol has been used in ammunitions and explosives from long time and recently their use as energetic material has been reported [9].

In our earlier studies [10], to utilize the Co(III) complexes as anion receptors, it was observed that non-covalent interactions played very crucial role in the anion binding. The cationic metal complex $[Co(phen)_3]^{3+}$ has been selected for the studies because (i) it provides 24 C–H groups which can involve in hydrogen bonding interaction with anions, (ii) stable framework on to which structural components can be assembled, (iii) presence of three unit positive charge and (iv) diamagnetic nature of complex cation is helpful to monitor the presence of organoanion by NMR studies. Thus, in continuation of our research programme to exploit cationic Co(III) complexes as anion receptors, this paper reports binding of nitrophenolate ion by complex cation $[Co(phen)_3]^{3+}$: synthesis, characterization and single crystal X-ray structure determination of $[Co(phen)_3](dnp)_3{\cdot}4H_2O$. This is the first structural report of a complex salt containing $[Co(phen)_3]^{3+}$ and nitrophenolate ion to the best of our knowledge.

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* Corresponding authors. Tel.: +91 0172 2534433; fax: +91 0172 2545074 (R.P. Sharma); tel.: +39 0532 455144; fax: +39 0532 240709 (V. Ferretti).
E-mail addresses: rpsharmapu@yahoo.co.in (R.P. Sharma), frt@unife.it (V. Ferretti).

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2. Experimental

2.1. Materials

Analytical grade reagents were used without any further purification. $[Co(phen)_3]Cl_3$ has been prepared by the reaction between $[Co(NH_3)_5Cl]Cl_2$ and 1,10-phenanthroline monohydrate according to the method described in literature [11].

2.2. Instruments and measurements

C, H, N were estimated micro analytically by automatic PERKIN ELMER 2400CHN elemental analyzer. Cobalt was determined by standard gravimetric method of estimation [12]. UV/visible spectrum was recorded using HITACHI 330 spectrometer in acetone as solvent. Infrared spectrum of the title complex salt was recorded using PERKIN ELMER spectrum RX FT-IR system using KBr pellet. ^{1}H-, ^{13}C-NMR spectra of title complex salt were run in the solvent DMSO-d_6 at 25 °C by using BRUKER AC 400 F (400 MHz) spectrophotometer. The chemical shift values are expressed as δ value (ppm) down field from tetramethylsilane as an internal standard. Conductance measurements were performed on Pico Conductivity Meter (Model CNO4091201, Lab India) in aqueous medium at 25 °C by using double distilled water.

2.3. Synthesis of $[Co(phen)_3](dnp)_3{\cdot}4H_2O$

0.5 g (0.0007 mol) of $[Co(phen)_3]Cl_3$ was dissolved in 10 ml of water. In another beaker 0.084 g (0.0021 mol) of NaOH was dissolved in a minimum amount of water and 0.39 g (0.0021) of 2,4-dinitrophenol, was added to it. The two clear solutions were mixed and resulting orange-yellow coloured precipitated product was filtered, washed with cold water and air-dried. The complex salt (mp 195 °C) is slightly soluble in water, fairly soluble in acetone and DMSO. This precipitated product when dissolved in 3:1 acetone/water mixture and allowed to evaporate slowly at room temperature, red coloured crystals started appearing after two days. These crystals were allowed to grow for one weak, collected and dried in air. These crystals were suitable for single crystal X-ray structure determination. Elemental analysis: found Co, 4.02%; C, 52.20%; H, 3.15%; N, 13.31%. Calculated for $C_{54}H_{41}CoN_{12}O_{19}$: Co, 4.83%; C, 53.11%; H, 3.36%; N, 13.77%. Solubility (25 °C) = 0.024 g/100 ml.

Table 1
Crystal data, data collection and refinement parameters of $[Co(phen)_3](dnp)_3{\cdot}4H_2O$

Empirical formula	$C_{54}H_{41}CoN_{12}O_{19}$
M_w	1220.92
Crystal system	Triclinic
Space group	$P\bar{1}$
a/ [Å]	13.5174(4)
b/ [Å]	15.1977(4)
c/ [Å]	15.8100(6)
α/ [°]	115.0411(10)
β/ [°]	91.8940(13)
γ/ [°]	113.9861(12)
V [Å^3]	2604.66(15)
Z	2
D_c [Mg m^{-3}]	1.557
μ/ [mm^{-1}]	0.423
Reflections collected	19523
Unique reflections [R_{int}]	5418 [0.0937]
Final R indices	
R_1, wR_2 [$I > 2\sigma I$]	0.0679, 0.1891 [5418]
R_1, wR_2 (all data)	0.1671, 0.1427

2.4. X-ray structure determination

Crystal data for the title complex salt were collected on a Nonius Kappa CCD diffractometer using graphite-monochromated MoKα radiation ($\lambda = 0.71069$ Å) at room temperature (295 K). Data sets were integrated with the Denzo-SMN package [13] and corrected for Lorentz-polarization effects. The structures were solved by direct methods (SIR97) [14] and refined by full-matrix least-squares methods with all non-hydrogen atoms anisotropic; hydrogen atoms were found in the Difference Fourier map and refined isotropically. The positions of the hydrogens belonging to O1w and O4w solvent water molecules were not included in the refinement. All calculations were performed using SHELXL-97 program [15] and WINGX system of programs [16]. Crystal data, data collection and refinement parameters of complex salt are presented in Table 1.

3. Results and discussion

3.1. Synthesis

Tris(1,10-phenanthroline)cobalt(III)chloride and sodium salt of 2,4-dinitrophenol could react in aqueous medium in number of ways depending upon the stoichiometric ratios of the reactants.

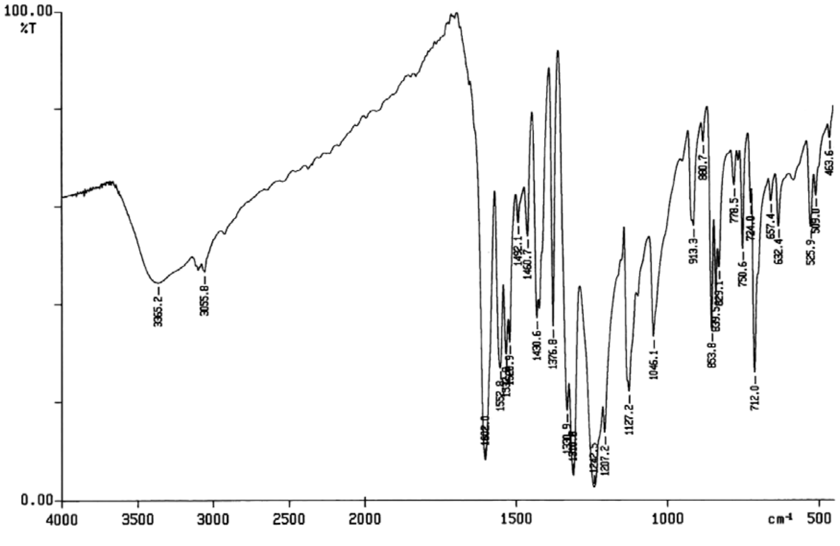

Fig. 1. FT IR spectrum of complex salt.