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Second sphere coordination in anion binding: Synthesis, spectroscopic and X-ray structural study of $[Co(phen)_3]_2[Hg(SCN)_4]_3{\cdot}3H_2O$

Raj Pal Sharma [a,*], Ajnesh Singh [a], Paloth Venugopalan [a], Paula Brandão [b], Vítor Félix [b,*]

[a] Department of Chemistry, Panjab University, Chandigarh 160014, India
[b] Departamento de Química, CICECO, Universidade de Aveiro, Aveiro 3810-1934, Portugal

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ABSTRACT

The complex salt $[Co(phen)_3]_2[Hg(SCN)_4]_3{\cdot}3H_2O$ was synthesized by mixing the separately dissolved tris(1,10-phenanthroline)cobalt(III) chloride, mercury(II) chloride and ammonium thiocyanate in aqueous medium in 2:3:12 molar ratio. The newly synthesized complex salt was characterized by elemental analyses, spectroscopic studies (IR, ^1H, ^{13}C and ^{59}Co NMR). Single-crystal X-ray structure determination of $[Co(phen)_3]_2[Hg(SCN)_4]_3{\cdot}3H_2O$ revealed that the complex salt crystallizes in the monoclinic crystal system with space group $P2_1/n$ where $a = 12.0150(4)$, $b = 20.1916(5)$, $c = 36.1151(9)$ Å, $\beta = 94.408(2)^\circ$, $V = 8735.7(4)$ Å^3, $Z = 4$. The asymmetric unit consists of two complex cations, three anions and three lattice water molecules. Crystal lattice is stabilized by hydrogen bonding interactions of type C–H...O, C–H...N through second sphere coordination and O–H...O interactions besides the electrostatic forces of attraction. The structural studies suggest that $[Co(phen)_3]^{3+}$ is a potential anion receptor for the $[Hg(SCN)_4]^{2-}$ ion.

1. Introduction

The synthesis of transition metal based anion receptors has attracted a lot of attention because of their wide range of applications of anions in the field of biology, chemistry and environment [1–7]. In the case of metal based anion receptors, metal center can introduce the electrostatic interactions (that may be helpful in organizing the hydrogen bonding groups to optimal binding), optical, electrochemical or catalytic properties to cationic metal receptor which help in determining the anion association properties. Moreover, the second sphere coordination interactions due to the ligands coordinated to the metal center can interact with anion i.e. hetero atom N/C/O–H...X_{anion} interactions. In continuation of our extensive research programme to explore cobalt(III) complexes as anion receptors, we recently have reported the use of cationic cobalt(III) complex salts [8,9] as anion receptors for different anionic species. We envisaged that octahedral complex ion $[Co(phen)_3]^{3+}$ should provide three phenanthroline faces with eight C–H groups which can act as potential hydrogen bond donors and can interact with anions. There is also an added advantage as cobalt(III) salts are easier to synthesize in excellent yields from readily available materials, they are stable at room temperature for months and do not decay under X-ray exposure. Moreover, the cationic complex, $[Co(phen)_3]^{3+}$ fulfils all the basic criteria [10,11] to be an anion receptor, it has (i) three unit positive charge for electrostatic interaction, (ii) large number (twenty four) of C–H hydrogen bond donor groups and (iii) stable framework onto which the anionic group can be assembled.

In the present investigation the anion $[Hg(SCN)_4]^{2-}$ was selected because it has four nitrogen atoms per ion that can act as efficient proton acceptors. In the solid state, in all probabilities, these two ions, $[Co(phen)_3]^{3+}$ and $[Hg(SCN)_4]^{2-}$ should form an intricate network of hydrogen bonds stabilizing the entire crystal lattice. In our opinion, in the title complex salt, the driving force for the formation of mercury tetrathiocyanate complex is the stabilization of large cation by large counterion. We thus, envisaged that mercury tetrathiocyanate will orient itself in such a manner that four thiocyanato units will form hydrogen bonds with C–H groups originating from 1,10-phenanthroline ligands attached to the cobalt(III) center from all four sides (formed by SCN units of $[Hg(SCN)_4]^{2-}$) to give rise to intricate network. Understanding such a network of interactions for judicially chosen cations and anions could be rewarding as it can provide means of constructing complicated and novel molecular entities based on second sphere coordinations. In addition, this structural study would also enable us to evaluate the role of these weak interactions amidst the electrostatic interactions between the chosen anion and cation. Thus, this paper reports the synthesis, spectroscopic and X-ray structural study of $[Co(phen)_3]_2[Hg(SCN)_4]_3{\cdot}3H_2O$.

* Corresponding authors. Tel.: +91 0172 2534433; fax: +91 0172 2545074 (R.P. Sharma), tel.: +351 234 370 729; fax: +351 34 70 084 (V. Félix).
E-mail addresses: rpsharmapu@yahoo.co.in (R.P. Sharma), vitor.felix@ua.pt (V. Félix).

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2. Experimental

2.1. Materials

Analytical grade reagents were used without any further purification. $[Co(phen)_3]Cl_3$ was prepared by reacting $[Co(NH_3)_5Cl]Cl_2$ and 1,10-phenanthroline monohydrate according to the method described in literature [12].

2.2. Instruments and measurements

C, H and N were estimated micro analytically by automatic Perkin-Elmer 2400CHN elemental analyzer. Cobalt was determined by volumetric method of estimation [13]. Infrared spectrum of the title complex salt was recorded using Perkin-Elmer spectrum RX FT-IR system using KBr pallet. ^1H, ^{13}C and ^{59}Co NMR spectra were run in the solvent DMSO-d_6 at 25 °C by using Bruker AC 400F (400 MHz) spectrophotometer. The chemical shift values are expressed as δ value (ppm) downfield from tetramethylsilane as an internal standard.

2.3. Synthesis of $[Co(phen)_3]_2[Hg(SCN)_4]_3{\cdot}3H_2O$

Tris(1,10-phenanthroline)cobalt(III) chloride (0.5 g, 1.4 mmol) was dissolved in 10 mL of water and in another beaker 0.191 g (2.1 mmol) of mercuric chloride ($HgCl_2$) and 0.212 g (8.4 mmol) of ammonium thiocyanate were dissolved in 10 mL of water. Upon mixing the two solutions, pale yellow coloured precipitated product was obtained. The precipitated product was filtered through fine filter paper and washed with cold water and dried in air. The complex salt decomposed at 210 °C. The yield was quantitative. Single crystals suitable for single-crystal X-ray crystallography were obtained after two days by re-crystallizing the precipitated product from acetone–water mixture on slow evaporation. The crystals were separated and dried in air. The composition was established by elemental analyses. $[Co(phen)_3]_2[Hg(SCN)_3]_3{\cdot}3H_2O$. Found: (%) C, 39.20; H, 2.05; N, 13.05; Co, 4.50. Calculated; (%) C, 39.50; H, 2.11; N, 13.16; Co, 4.62.

2.4. X-ray structure determination

The X-ray data were collected on a CCD Bruker APEX II at 150(2) K using graphite monochromatized Mo-Kα radiation (λ = 0.71073 Å). The crystal was positioned at 55 mm from the CCD and the spots were measured using a counting time of 80 s. Data reduction and multi-scan absorption were carried out using the SAINT-NT from Bruker XS. The structure was solved using SHELXS-97 [14] and refined using full-matrix least squares in SHELXL-97 [14]. The C–H hydrogen atoms were included at calculated positions. The water hydrogen atoms were not located from final difference Fourier maps and therefore their atomic positions were not included in the structure refinement. Anisotropic thermal parameters were used for all non-hydrogen atoms while the hydrogen atoms were refined with isotropic parameters equivalent to 1.2 times those of the atom to which they were bounded. However, the thermal displacements of N and C of a SCN-ligand (molecule C) as well the electronic residual electronic density of 1.77 e/Å^3 located at 1.16 Å within the carbon atom suggesting that this ligand is affected by some degree of disorder degree. Several trial disorder models were tried considering the S, C and N positioned on alternative positions. Unfortunately, all the attempts had no success and then the structure refinement model presented represents the most suitable one. Furthermore, the S and C atomic positions were refined with the C–S and C–N distances constrained to 1.67 and 1.15 Å, respectively. Final *R*-values together with selected refinement details are given in Table 1.

Table 1
Crystallographic data and refinement details of $[Co(phen)_3]_2[Hg(SCN)_4]_3{\cdot}3H_2O$.

Formula	$C_{84}H_{54}Co_2Hg_3N_{24}O_3S_{12}$
M_w	2551.86
Crystal system	Monoclinic
Space group	$P2_1/n$
a/[Å]	12.0150(4)
b/[Å]	20.1916(5)
c/[Å]	36.1151(9)
β/[°]	94.408(2)
V [Å^3]	8735.7(4)
Z	4
D_c [Mg m^{-3}]	1.940
μ/[mm^{-1}]	5.979
Reflections collected	47627
Unique reflections, [R_{int}]	21415 [0.0565]
R_1, wR_2 [$I > 2\sigma I$]	0.0486, 0.1011 [13200]
R_1, wR_2 (all data)	0.0927, 0.1124

3. Results and discussion

3.1. Synthesis

When tris(1,10-phenanthroline)cobalt(III) chloride was reacted with mercuric(II) chloride and ammonium thiocyanate in 2:3:12 molar ratio in aqueous medium, the complex salt $[Co(phen)_3]_2[Hg(SCN)_4]_3{\cdot}3H_2O$ was obtained in accordance with the following equation.

$$2[Co(phen)_3]Cl_3 + 3HgCl_2 + 12NH_4SCN \rightarrow [Co(phen)_3]_2[Hg(SCN)_4]_3 + 12NH_4Cl$$

The newly formed complex salt has been characterized by elemental analyses, spectroscopic studies (FT-IR, and multinuclear NMR). The complex salt is soluble in water and acetone mixture but insoluble in other common solvents. The complex salt decomposed at 210 °C. The crystal structure of complex salt has been unambiguously established by single-crystal structure determination.

3.2. Spectroscopic characterization

Infrared spectrum of the newly synthesized complex salt has been recorded in the region 4000–400 cm^{-1} and tentative peak assignments have been made on the basis of earlier reports in literature [15–17]. IR band at 709 cm^{-1} was assigned to δ(C–H), due to out of plane motion of hydrogen atoms of heterocyclic rings and peak at 838 cm^{-1} was attributed to the δ(C=C), hydrogen atoms of central ring of the ligand. Region 1636–1400 cm^{-1} was attributed to stretching modes of >C=C< and >C=N< bonds in the title complex salt. IR signal observed at 3059 cm^{-1} showed the presence of unsaturation which was assigned to ν(=C–H) vibrations.

The characteristic IR bands due to the $[Hg(SCN)_4]^{2-}$ groups which are present as counter anions in the title complex salt were observed at 2099, 710 and 462 cm^{-1} which were assigned to ν(CN), ν(CS) and δ(SCN) vibrations. The presence of IR band at 2099 cm^{-1} indicated the presence of S-coordinated SCN^- group rather than N-coordinated [18] and also presence of band at higher frequency than for free thiocyanate indicated the presence of metal coordinated thiocyanate group. Several workers [19] considered ν(CS) as structural diagnostic in the range 860–780 cm^{-1} for N-bonded and 720–690 cm^{-1} for S-bonded complexes which is rather weak and it was observed at 715 cm^{-1} in the title complex salt (S-bonded). Similar bands were observed in case of $CoHg(SCN)_4(H_2O)_2{\cdot}2mpd$ and $CoHg(SCN)_4(H_2O)_2{\cdot}2pd$ [20] at 2140, 730, 460 and 2140, 720, 470 cm^{-1} respectively which were assigned to ν(CN), ν(CS) and δ(SCN) while in case of $CoHg(SCN)_4$ [20], bands due to ν(CN), ν(CS) and δ(SCN) were reported at 2150, 720 and 470 cm^{-1}. The FT-IR spectrum of complex salt is shown in Fig. 1.