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A new anion, $[Hg_2(SCN)_7]^{3-}$: First synthesis, spectroscopic characterization and X-ray structure determination of $[Co(NH_3)_6][Hg_2(SCN)_7]$

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Abstract

The reaction of $[Co(NH_3)_6]Cl_3$ with a mixture of $HgCl_2$ and NH_4SCN in 1:2:8 molar ratio in hot aqueous medium leads to formation of a new complex salt, $[Co(NH_3)_6][Hg_2(SCN)_7]$ (**1**) in 70% yield. This hexaamminecobalt(III) complex salt has been characterized by elemental analyses, solubility measurement and spectroscopic techniques (e.g. UV/Visible, IR and ^{13}C NMR). Single crystal X-ray structure determination of **1** revealed the presence of discrete $[Co(NH_3)_6]^{3+}$ cation and a new anion, $[Hg_2(SCN)_7]^{3-}$. This is the first report of a complex salt containing the new anion. The crystal lattice of the complex salt is stabilized by electrostatic forces of attraction and N–H…N (thiocyanate) hydrogen bonding interactions.

Keywords: Cobalt(III); Coordination chemistry; Second sphere coordination; Spectroscopy; X-ray crystallography

The synthesis of hexaamminecobalt(III) salts has attracted a lot of attention because of their interesting structural chemistry [1–7]. Due to intrigue in the complex salts obtained by reacting hexaamminecobalt(III) chloride with various metal salts [8], we envisaged that octahedral hexaamminecobalt(III) complex ion should provide two triangular triammine faces with nine N–H bonds each that can act as potential hydrogen bond donors. 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 should form an intricate network of hydrogen bonds stabilizing the entire crystal lattice. 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 coordination.

We herein report our investigation of the reaction between $[Co(NH_3)_6]Cl_3$ with $(NH_4)_2[Hg(SCN)_4]$, the latter formed by reaction of $HgCl_2$ and NH_4SCN (1:4 molar ratio) in hot aqueous medium. The expected product was $[Co(NH_3)_6]Cl[Hg(SCN)_4]$ but, instead, $[Co(NH_3)_6][Hg_2 SCN)_7]$ (**1**) was obtained and this was consistent with elemental analyses and spectroscopic data [9]. A similar reaction has been carried out by reacting $[Co(NH_3)_6]Cl_3$ with $(NH_4)_2[Hg(SCN)_4]$ (prepared in aqueous medium) as well as $K_2/(NH_4)_2[Hg(SCN)_4]$ (pre-isolated) [10] in 1:2 molar ratio. The product obtained in both cases is identical to that obtained using 1:1 molar ratio as indicated by colour, melting point, elemental analyses and infrared spectra. But the yield is doubled compared to the reaction using 1:2 molar ratio. The present study provides the first reported example in the solid state of the $[Hg_2(SCN)_7]^{3-}$ anion which is topologically similar to the pyrosilicate anion,

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$Si_2O_7^{6-}$ [11]. Other in the $M_2X_7^{n-}$ class include $Cr_2O_7^{2-}$ and $Cd_2CN_7^{2-}$ [12].

Solubility measurements at room temperature show that complex salt **1** is sparingly soluble in water but hexaamminecobalt(III) chloride is soluble. The K_{sp} values for **1** and $[Co(NH_3)_6]Cl_3$ are 8.35×10^{-6} and 0.123, respectively, indicating that the $[Co(NH_3)_6]^{3+}$ cation binds (associates) much more strongly with $[Hg_2(SCN)_7]^{3-}$ compared to Cl^-.

Two transitions in the electronic spectra of hexaamminecobalt(III) complexes are observed around 470 and 340 nm (d–d transitions typical for low spin Co(III) d^6 octahedral complex) and are assigned to $^1A_{1g} \rightarrow T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$, respectively [13]. The UV–visible spectrum of the aqueous solution of complex salt **1**, shows two ligand field absorptions at $\lambda_{max} = 474$ ($\epsilon = 164.78\ mol^{-1}\ L\ cm^{-1}$) and 337 ($\epsilon = 139.32\ mol^{-1}\ L\ cm^{-1}$). The strong absorption maxima observed for the title complex salt are also in agreement with those of related salts of hexaamminecobalt(III) cation such as $[Co(NH_3)_6]Cl \cdot SeO_4 \cdot 3H_2O$ (λ_{max} 470; 340 nm) [8g], $[Co(NH_3)_6]Cl \cdot MoO_4 \cdot 3H_2O$ (λ_{max} 470; 340 nm) [8h]. $[Co(NH_3)_6]Cl_2SeCN$ (λ_{max} 474, 336), $[Co(NH_3)_6]_3Cl_4(N_3)_5$ (λ_{max} 474, 340) [8i].

Infrared spectra of the complex salt (raw powder and crystallized samples) were recorded in KBr pellets and they show typical absorption bands for coordinated ammonia ligands which are comparable with $[Co(NH_3)_6]Cl_3$ [14]. The spectrum of **1** exhibits additional strong absorption bands for the SCN group. In general the CN stretching frequencies are lower in N-bonded complexes (near or below 2050 cm^{-1}) than S-bonded complexes (near 2100 cm^{-1}). For bridging complexes (M–SCN–M) v (CN) is above 2100 cm^{-1}. The CN stretching frequencies in the case of $K_2[Hg(SCN)_4]$ [14] were observed at 2134(m), 2122(sh), 2109(s) cm^{-1} and for $Hg(SCN)_2$, where SCN is bridging at 2120 cm^{-1}. The CS stretching frequency for $K_2[Hg(SCN)_4]$ [14] was observed at 716(m) cm^{-1} with shoulders at 709 and 703 cm^{-1}. However, in the title complex salt, two bands are observed at 2107 and 2080 cm^{-1} indicating the presence of an S-bonded SCN^- group rather than one N-coordinated to mercury(II). Several workers [15] considered v (CS) as structurally diagnostic in the range 860–780 cm^{-1} for N-bonded and 720–690 cm^{-1} (rather weak) for S-bonded complexes which is rather weak and; it was observed at 715 cm^{-1} in the title complex salt **1** (S-bonded). The FTIR spectra for raw powder as well as recrystallized sample are identical as shown in Fig. 1. For complex salt **1** the ^{13}C NMR chemical shift value ($\delta = 119$) is in good agreement with that observed for $K_2[Hg(SCN)_4]$ ($\delta = 124$) [16]. No separate signals are observed for bridging and terminal thiocyanate groups.

Single crystal X-ray structure determination [17] of complex salt **1** shows that each Hg atom is coordinated by four S atoms of SCN^- ligands as shown in Fig. 2. There are two types of Hg–S bond – the bonds involving the bridging S atom are significantly longer (ca. 2.78 Å) than the rest (ca. 2.4 Å). The latter value is comparable to that found in $Hg(SCN)_2$ [18]. The topological and structural features of the $(NCS)_3$–Hg–S(CN)–Hg–$(SCN)_3$ anion are similar to those of the $(NC)_3$–Cd–C(N)–Cd–$(CN)_3$ and O_3–Si–O–Si–O_3 anions. The Cd–C(N)–Cd group is linear whereas Si–O–Si bond angle varies from 180 to 133° in various minerals depending on the cation [11]. In the new complex anion, the bridging Hg–S–Hg angle is 108°.

Similar anions have been reported in $CsA[B_2(SCN)_7]$, where **A** is Sr or Ba and **B** is Cu or Ag [19]. In these complexes, the anion has mm2 symmetry and C–S–**B**–S_{bridge} torsion angles close to 180°. **B** has nearly regular tetrahedral coordination, with no difference in the Cu–S bond

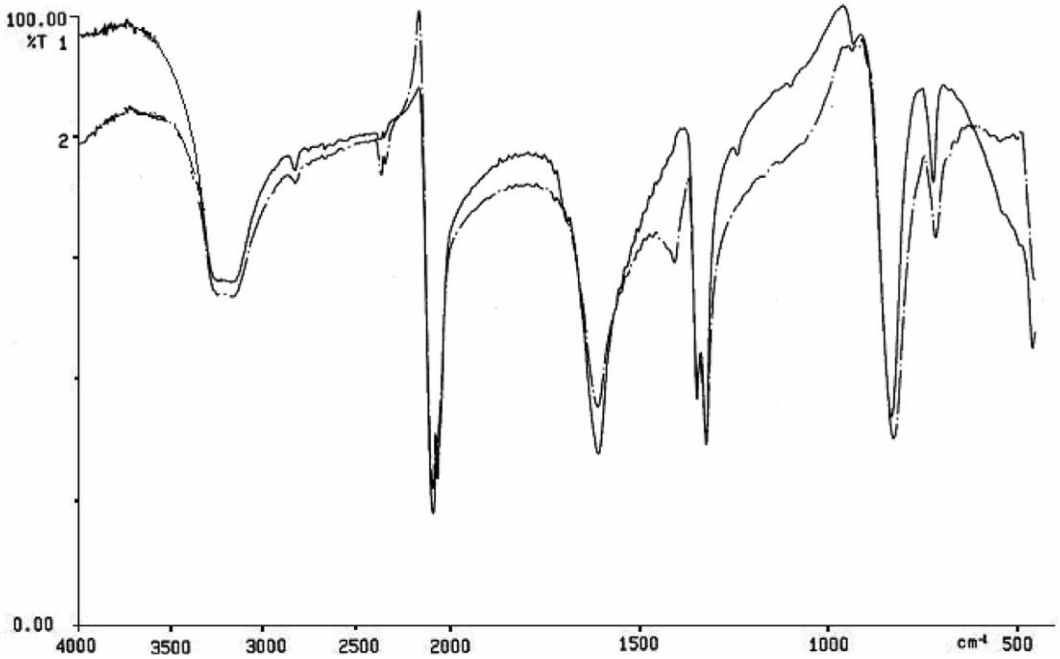

Fig. 1. Infrared spectrum of $[Co(NH_3)_6][Hg_2(SCN)_7]$: (1) raw powdered sample (solid line) (2) crystallized sample (broken line).