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Isolation and Characterization of $[(Co(NH_3)_5NCS)_2$-$Hg](ClO_4)_6 \cdot H_2O$

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Introduction

The ion Hg^{2+} plays an important role in the catalyzed aquation of transition metal complexes of the type ML_5X^{2+}, where M = Co, Rh, Cr or Ru, L = amine, and X = halide or pseudo halide [4]. The mechanism of reaction is generally accepted to involve the bridged intermediate $L_5M–X–Hg^{4+}$. In those cases where $X = NCS^-$ formation constants of the intermediate have in fact been measured [5–7]. Falk and Linck [5] reported two formation constants for the reaction of $Co(NH_3)_5NCS^{2+}$ with Hg^{2+} in acidic aqueous solutions of $K_1 = 9.8 \times 10^4$ and $K_2 = 1.4 \times 10^4$ M^{-1} at 298 K. These constants are thought to correspond to the following equilibria:

$$Co(NH_3)_5NCS^{2+} + Hg^{2+} \rightleftharpoons Co(NH_3)_5NCSHg^{4+} \quad (1)$$

$$Co(NH_3)_5NCSHg^{4+} + Co(NH_3)_5NCS^{2+} \rightleftharpoons (Co(NH_3)_5NCS)_2Hg^{6+} \quad (2)$$

However, the product of eqn. (2) was not isolated and, to our knowledge, no similar 'mercury' bridged compound has yet been prepared. Our interest in the kinetics of mercury catalyzed aquation under the influence of high pressure [8] led us to reinvestigate the above system and thereby confirm the existence of this species.

Experimental

$[Co(NH_3)_5NCS](ClO_4)_2$ was prepared by established methods [5]. *Anal.* Calcd for $C_1H_{15}N_6S_1Cl_2O_8Co_1$: C, 3.0; H, 3.8; N, 21.0; Cl, 17.7. Found C, 3.3; H, 3.8; N, 21.5; Cl, 17.6. The UV/Visible spectrum shows peaks at 306 and 498 nm with extinction coefficients of 1500 and 175 M^{-1} cm^{-1}, respectively, which are in good agreement with the values reported in the literature [5, 9, 10].

$[(Co(NH_3)_5NCS)_2Hg](ClO_4)_6 \cdot H_2O$ was synthesized by the dropwise addition of a concentrated solution of $Hg(ClO_4)_2$ in dilute $HClO_4$ to a well-stirred concentrated solution of $[Co(NH_3)_5NCS](ClO_4)_2$ in water. The resulting precipitate was filtered off and then washed with a minimum amount of ice-cold water, followed by ethanol and ether. The pale orange powder was dried over P_2O_5 under vacuum for 12 hours and stored at *ca.* 250 K. *Anal.* Calcd for $C_2H_{32}N_{11}S_2Cl_6O_{25}Co_2Hg_1$: C, 1.97; H, 2.65; N, 13.78; S, 5.26. Found C, 2.29; H, 2.81; N, 13.75; S, 5.23.

The UV/Visible spectra were measured on a Zeiss DMR 10 spectrophotometer. The IR spectra were taken in Nujol and Hostaflon mulls using a Leitz spectrophotometer equipped with a LiF, NaCl or CsBr prism. The Raman spectra were recorded on a Coderg T 800 spectrophotometer. The samples were excited by a Spectra Physics 165 Kr^+ laser (647.1 nm, 300 mW) and rotated during measurement to reduce photodecomposition. A Beckman Fourier spectrometer 720 was used to record the FIR spectra.

Results and Discussion

The significance of the large valves of K_1 and K_2 quoted in the introduction is that even at relatively low concentrations, $>10^{-4}$ M, the majority of the complex ions are bound to Hg^{2+} in the form of a 1:2, Hg^{2+}: $Co(NH_3)_5NCS^{2+}$ adduct. By way of contrast it is of interest to note that Lalor and Miller [10] claim to have spectrophotometric evidence for a 2:1, Ag: $Co(NH_3)_5NCS^{2+}$ species in nitrate medium.

The IR and Raman spectra of the Hg^{2+} adduct are depicted in Fig. 1. The N–H stretching (3318, 3243 br), degenerate bending (1624), symmetric bending (1345) and rocking (836) (all in cm^{-1}) modes can be readily assigned. From a comparison of these values with those of the corresponding vibrational modes in the parent complex $Co(NH_3)_5NCS^{2+}$, the stretching modes are shifted to lower energies by *ca.* 20 cm^{-1}; the degenerate modes remain virtually unaffected; whereas the symmetrical bendings and the rocking vibrations are shifted to higher energies by *ca.* 20 and 30 cm^{-1}, respectively. The positions of the C–N, C–S stretching and the NCS bending modes are more indicative of the type of bonding exhibited by the NCS ligands and are, therefore, more characteristic of the title complex.

The C–N stretch at 2211 cm^{-1} is shifted by *ca.* 90 cm^{-1} to higher frequencies. Similar shifts in the order of 50 cm^{-1} were found for the C–N stretching mode of such bridged complexes as $[Co(NH_3)_4(NO_2)NCSAg]ClNO_3$ and $[Co(NH_3)_4(NO_2)NCSHg]Cl_3$.

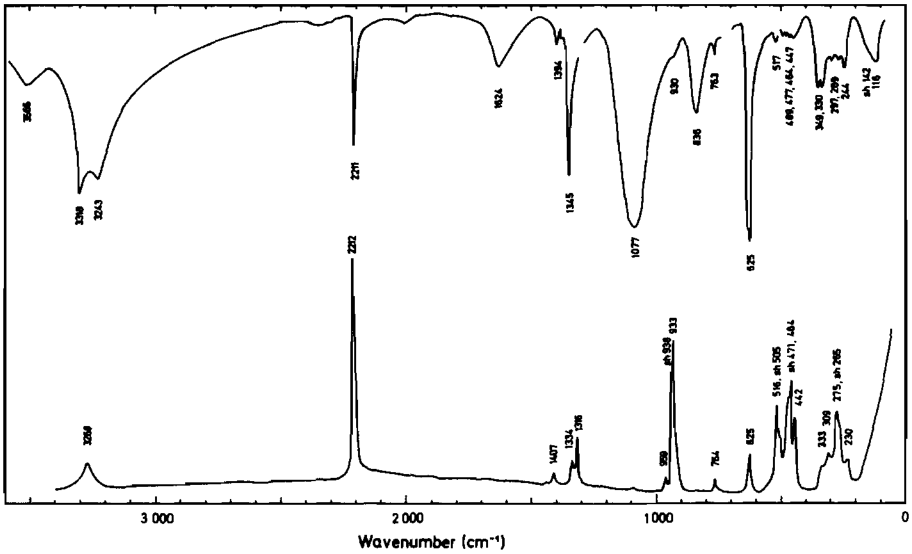

Fig. 1. IR and Raman spectrum of the powder at room temperature. Upper line: IR transmission spectrum in Hostaflon (3500–1300 cm^{-1}) and Nujol mulls (1300–80 cm^{-1}). Lower line: Raman scattering spectrum.

In the literature [12–14] the following ranges are given for the C–S stretch: 780–860 when N-bonded and 690–720 cm^{-1} for S-bonded SCN. We have assigned the peak at 763 cm^{-1} to the C–S stretching vibration, which lies between the ranges quoted above and provides further evidence of SCN bridging. When N-bonded the NCS bending mode appears as one band at *ca.* 475 cm^{-1} and as more than one band in the range 400 to 480 cm^{-1} when S-bonded [12, 14]. In this general range we found a series of bands centered at 447, 464, 477, 489 and 517 cm^{-1}. Due to the superposition of Co–N vibrations, probable low site symmetries and vibrational coupling, a definitive assignment of these bands is not possible at the moment.

The presence of Hg–S stretching vibrations is confirmed in the Raman spectrum shown in Fig. 1 by the appearance of a strong band at 275 cm^{-1} with a shoulder at 265 cm^{-1}, which are not observed in the spectrum of the parent complex. The Hg–S stretch for $Hg(SCN)_2$, which corresponds to the central fragment of the title complex, was observed as a very strong band at 270 cm^{-1} [15].

References

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