

## Short Communications

### Synthesis and Properties of Tri- $\mu$ -hydroxo-bis[tris(pyridine)cobalt(III) Perchlorate

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Current interest in hydroxo bridged binuclear complexes of cobalt(III) prompts this note on the synthesis and some properties of the pyridine triol cation,  $[(\text{py})_3\text{Co}(\text{OH})_3\text{Co}(\text{py})_3]^{3+}$ . Triols<sup>1–7</sup> with aliphatic amines have previously been characterized and studied with respect to the kinetics of bridge-cleavage, but triols with heteroaromatic nitrogen ligands as described here have not previously been reported.

The pyridine triol,  $[(\text{py})_3\text{Co}(\text{OH})_3\text{Co}(\text{py})_3]^{3+}$ , was prepared in high yield (60%) by adding a large excess of pyridine to a concentrated aqueous solution of  $\text{mer-}[\text{Co}(\text{py})_3(\text{H}_2\text{O})_3]^{3+}$  at room temperature. The cation  $\text{mer-}[\text{Co}(\text{py})_3(\text{H}_2\text{O})_3]^{3+}$  was obtained by treating  $\text{mer-}[\text{Co}(\text{py})_3(\text{CO}_3\text{Cl})]$  with excess mercury(II) perchlorate and perchloric acid.<sup>8</sup> The triol perchlorate forms a sparingly soluble adduct with pyridine,  $[(\text{py})_3\text{Co}(\text{OH})_3\text{Co}(\text{py})_3](\text{ClO}_4)_3 \cdot (\text{py})_2 \cdot \text{H}_2\text{O}$ , and was isolated as the latter from the reaction mixture. Reprecipitation from acidic aqueous solution gave a pure salt analyzing as  $[(\text{py})_3\text{Co}(\text{OH})_3\text{Co}(\text{py})_3](\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$ .

The chemical properties of the compound provide evidence for the proposed structure. The compound reacts neutral and shows no buffer capacity in the region  $2 \leq \text{pH} \leq 10$  as determined by glass-electrode measurements. Furthermore, the visible absorption spectrum shows no dependence on  $[\text{H}^+]$  in the region  $10^{-6} \leq [\text{H}^+] \leq 6$  M. These results clearly exclude structures having terminal hydroxo groups, and thereby provide unambiguous evidence for a polynuclear structure in which all hydroxo groups act as bridging groups. Since elemental analysis shows the formula  $[\text{Co}(\text{py})_3(\text{OH})_{1\frac{1}{2}}(\text{ClO}_4)_{1\frac{1}{2}}]_n$ , the nuclearity,  $n$ , has to be even, and we propose a

binuclear structure, *i.e.*, triol. This structure seems more likely than *e.g.* a tetranuclear on the basis of recent studies on other triols of Co(III).

The triol is robust in neutral and acidic solution, as shown by spectrophotometric measurements in pure water (pH 6) and in perchloric acid (0.1–2 M) solutions. In these media the spectra change less than 1% in absorbancy within the first  $\frac{1}{2}$  h at 25°C. In more strongly acidic solutions a rapid triol-diol equilibration occurs as discussed below. This is then followed by a much slower reaction involving further hydroxy bridge cleavage which gives the monomer as the end product. The reaction with 12 M hydrochloric acid gives  $\text{mer-}[\text{Co}(\text{py})_3\text{Cl}_3]$  (yield 40%). In perchloric acid media other reactions, including reduction to cobalt(II), obscured the investigation and the stoichiometry for the cleavage reaction giving monomer was therefore not established. The triol is labile in basic aqueous solution, decomposing rapidly at  $\text{pH} \geq 8$ .

The triol in strongly acidic solution rapidly attains equilibrium with its parent diol: The complex reacts instantaneously ( $t_{\frac{1}{2}} < 20$  s at 0°C) in strong perchloric acid (9–10.5 M), giving a bluish complex. The reaction is reversible and dilution of the acidic solution with water instantaneously gives a red solution from which reformed triol can be isolated nearly quantitatively. The reaction was studied further by comparing the visible spectra in different perchloric acid media (Table 1). These spectra were measured within minutes and at 0°C to eliminate errors due to subsequent hydrolysis (see above). The spectral changes occur in the  $[\text{H}^+]$  region 9–10 M. Furthermore, the absorption curves for these media showed one isosbestic point,  $(\epsilon, \lambda)_{\text{isos}} = (90, 585)$ , suggesting

Table 1. Spectral data for  $[(\text{py})_3\text{Co}(\text{OH})_3(\text{py})_3](\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$  in different media at 0°C.

Medium	$(\epsilon, \lambda)_{\text{max}}$	$(\epsilon, \lambda)_{\text{min}}$
H <sub>2</sub> O	(183,540)	(73,465)
0.1–6.0 M HClO <sub>4</sub>	(183,540)	(73,465)
9.0 M HClO <sub>4</sub>	(160,542)	(60,467)
9.5 M HClO <sub>4</sub>	(152,543)	(57,468)
10.0 M HClO <sub>4</sub>	(134,557)	(50,470)
10.5 M HClO <sub>4</sub>	(131,557)	(49,470)

that only two species are present. We interpret these results as being due to rapid establishment of equilibrium between triol and diaqua diol,  $[(\text{py})_3\text{Co}(\text{OH})_3\text{Co}(\text{py})_3]^{3+} + \text{H}_3\text{O}^+ \rightleftharpoons [(\text{H}_2\text{O})(\text{py})_3\text{Co}(\text{OH})_2\text{Co}(\text{py})_3(\text{OH}_2)]^{4+}$ . It is seen (Table 1) that the spectra in 10.0 and 10.5 M perchloric acid are nearly identical and this shows that the equilibrium in these media is completely shifted to the right. The spectrum measured for 10.5 M is therefore that of the diaqua diol.

This type of rapid equilibration between di- and trihydroxo bridged binuclear cations has been reported recently for other Co(III) systems.<sup>1,4,5,6</sup> The equilibrium constant for the equilibrium above is clearly much less than unity (see Table 1), and in this respect the pyridine system differs from the corresponding systems with aliphatic amines for which the equilibrium constants are in the region  $1 - 20 \text{ M}^{-1}$ .<sup>6</sup>

**Experimental.** *Materials*  $[\text{Co}(\text{py})_3(\text{CO}_3)\text{Cl}]$  was prepared as described previously.<sup>9</sup> All other chemicals were of analytical grade.

*Analysis.* Co analyses were performed by atomic absorption spectrophotometry by Karen Jørgensen at the H. C. Ørsted Institute, Copenhagen. C, N, H and Cl analyses were made by the microanalytical laboratory at the same Institute.

*Spectra.* A Zeiss DMR 21 spectrophotometer was used for spectral measurements in the visible region. For the spectral data (Table 1) the absorbancy  $\epsilon$  is given in  $\text{l mol}^{-1} \text{ cm}^{-1}$  and the wavelength  $\lambda$  is given in nm.

*Preparation.* Tri- $\mu$ -hydroxo-bis[tris(pyridine)cobalt(III)] perchlorate.  $[(\text{py})_3\text{Co}(\text{OH})_3\text{Co}(\text{py})_3](\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$ .  $[\text{Co}(\text{py})_3(\text{CO}_3)\text{Cl}]$  (9.8 g, 0.025 mol) was added to 6 M perchloric acid (12.5 ml) in small portions. The complex dissolved with evolution of carbon dioxide, giving a dark blue solution. The solution was allowed to stand for 5 min in order to complete the reaction. Mercury(II) oxide (2.72 g, 0.0125 mol) was then added in small portions. The solution immediately turned purple. It was cooled in ice and then ice-cold pyridine (50 ml) was slowly added. This led to precipitation of  $\text{HgCl}_2$  which was filtered off. The solution was kept in a closed bottle for 7 days at ca. 20 °C and the resulting crystals were filtered off, washed twice with pyridine (20 ml), twice with 96 % ethanol (20 ml), and finally with ether. Drying in air gave 8.4 g (60 %) of a dipyridine adduct. Anal.  $[\text{Co}_2(\text{C}_5\text{H}_5\text{N})_6(\text{OH})_3](\text{ClO}_4)_3 \cdot (\text{C}_5\text{H}_5\text{N})_2 \cdot \text{H}_2\text{O}$ : Co, N, C, H and Cl.

The complex was purified as follows. The crude pyridine adduct (8.0 g) was dissolved in water (500 ml) and 4 M perchloric acid (4 ml) was added to the filtered solution. Saturated sodium perchlorate solution (40 ml) was then added dropwise to the solution which was then cooled in ice for  $\frac{1}{2}$  h. The precipitate was washed with 96 % ethanol and then ether.

Yield 6.6 g. The product recrystallized twice was pure. Anal.  $[\text{Co}_2(\text{C}_5\text{H}_5\text{N})_6(\text{OH})_3](\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$ : Co, C, N, H, Cl.

*Properties.* The product isolated from the reaction mixture is a pyridine adduct with 2 mol of pyridine per mol triol. This was confirmed by potentiometric titration with perchloric acid. Furthermore, the visible absorption spectrum of the pyridine adduct in perchloric acid was identical to the spectrum of the pure perchlorate salt.

The triol reacts with hydrochloric acid to give *mer*- $[\text{Co}(\text{py})_3\text{Cl}_3]$  as follows:  $[(\text{py})_3\text{Co}(\text{OH})_3\text{Co}(\text{py})_3](\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$  (0.5 g) was dissolved at 0 °C in 12 M HCl (5 ml) and cooled in ice for 2 h. Green crystals precipitated. The precipitate was filtered off and washed with water, 96 % ethanol and finally with ether. Drying in the air gave 0.16 g (40 %) *mer*- $[\text{Co}(\text{py})_3\text{Cl}_3]$  identified by comparing its infrared spectrum with that of an authentic<sup>8</sup> sample.

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