

Short Communication

Synthesis of *trans*-Dichloro- and *trans*-Difluorotetrakis(pyridine)-cobalt(III) Salts

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Dedicated to Jannik Bjerrum on the occasion of his 70th birthday

Only a few tetrakis(pyridine)cobalt(III) complexes have been reported in the literature. Thus the *trans*-dichloro- and *trans*-diaquatetrakis(pyridine)cobalt(III) cations^{1,2} are the only *trans* complexes which have been described until now.

The main purpose of this communication is to describe the preparation of the new classical complex, *trans*-difluorotetrakis(pyridine)cobalt(III) perchlorate whose chromium(III) analogue has proved most interesting spectroscopically³ and useful for preparative purposes.^{4,5}

Two methods are described for the preparation of *trans*-difluorotetrakis(pyridine)cobalt(III) perchlorate. One method starts from *trans*-dichlorotetrakis(pyridine)cobalt(III) chloride hexahydrate, for which an improved synthesis is also reported. This complex is treated with mercury(II) ions (added as mercury(II) acetate) in liquid hydrogen fluoride at -70°C . The second method employs the new complex aquadifluorotris(pyridine)cobalt(III) perchlorate which is heated in pyridine at 70°C . Aquadifluorotris(pyridine)cobalt(III) perchlorate itself is prepared from carbonatochlorotris(pyridine)cobalt(III) by treatment of the latter with liquid hydrogen fluoride. The configuration of the aquadifluorotris(pyridine)cobalt(III) cation is probably meridional, but we do not know whether the coordinated fluoride ions are *cis* or *trans*. However, the behaviour of the complex indicated that we are dealing with a single compound. Preliminary experiments⁶ suggest that the reaction between some other tris(pyridine)cobalt(III) complexes and

pyridine also gives *trans*-tetrakis(pyridine)cobalt(III) complexes.

The cation *trans*- $[\text{CoF}_2(\text{py})_4]^+$ behaves as a base in strongly acidic media. When the complex is formed in the anhydrous hydrogen fluoride the colour is green, becoming red when the solution is diluted with methanol. Similarly, the red perchlorate salt dissolves in 70% perchloric acid giving a green colour, and on dilution of this solution with ice-water the colour changes to red and the original compound reprecipitates. These colour changes are undoubtedly associated with a protonation reaction involving one or both of the coordinated fluorides.

Materials. Carbonatochlorotris(pyridine)cobalt(III) perchlorate was prepared according to the literature.² All other chemicals were of analytical grade.

Spectra. Absorption spectra in the 300–650 nm region, recorded using a Cary 14 spectrophotometer, were used as a check of purity and as characterization of the compounds. Data for maxima and minima are given below with the molar absorptivity ϵ in $\text{liter mol}^{-1} \text{cm}^{-1}$ and the wavelength λ in nm.

Preparations. 1. *trans*- $[\text{CoCl}_2(\text{py})_4]\text{Cl} \cdot 6\text{H}_2\text{O}$. (**CAUTION.** Personal communication from R. D. Gillard; when this synthesis is performed by the classical method, in which gaseous chlorine is employed, an explosion of severe character has sometimes resulted. The present method has been used in this laboratory at least a dozen times without ever giving rise to difficulties of this sort). Pyridine (500 ml, 6.2 mol) and methanol (750 ml) were heated under mechanical stirring in a 2 l three-necked flask. To the solution was added anhydrous cobalt(II) chloride (100 g, 0.77 mol) in small portions and the resulting blue solution was heated under reflux for 15 min. The blue solution was poured into a 4 l beaker equipped with a mechanical stirrer and cooled with dry ice and acetone. When the temperature had fallen to 10°C the red complex $\text{CoCl}_2(\text{py})_4$ began to precipitate. When the temperature had reached -40°C , liquid chlorine (30 ml, 1.33 mol) was added to the solution and the cooling bath was removed. (The liquid chlorine was condensed from a cylinder into a beaker cooled with dry ice and acetone). Over a period of ca. 30 min the temperature rose to 0°C , and the colour changed from red to a mixture of red and green. In order to prevent the temperature from increasing beyond 25°C it was necessary at this stage to cool again with the dry ice and acetone bath (alternatively

the solution could also be cooled by pouring liquid N₂ directly into it).

After the oxidation was complete the mixture was a green porridge. It was then heated to 40 °C and 4 M hydrochloric acid (2.5 l) was added gradually. When approximately 700 ml of hydrochloric acid had been added the precipitate had redissolved and on adding more hydrochloric acid the green complex began to precipitate again. After keeping the solution at -18 °C overnight it was filtered and the precipitate washed with ice-cold water and air dried. Yield 340 g (75 %). The crude *trans*-[CoCl₂(py)₄]Cl·6H₂O (160 g) was recrystallized by dissolving it in 1:1 aqueous ethanol (640 ml) preheated to 50 °C. The filtered solution was kept at -18 °C overnight and the crystals were filtered off, washed with ice-cold water and air dried. Yield 126 g. Anal. [CoCl₂(py)₄]Cl·6H₂O: Co, C, N, H, Cl. Spectral data in 0.01 M HCl: (ε, λ)_{max}: (43.1, 631), (29.8, 505), (ε, λ)_{min}: (16.5, 559), (24.1, 470).

2. *trans*-[CoF₂(py)₄]ClO₄·½H₂O. *trans*-[CoCl₂(py)₄]Cl·6H₂O (50 g, 0.1 mol) was dissolved in anhydrous hydrogen fluoride (150 ml) cooled to -70 °C with dry ice. To the green solution was added portion-wise mercury(II) acetate (48 g, 0.15 mol). After standing for 30 min, methanol (150 ml) precooled with dry ice was added when the colour changed from green to red. The solution was filtered (Whatman No. 450) and evaporated overnight in an effective hood by means of a fan (CAUTION. HF is poisonous!). During this evaporation water is taken up from the air and a reddish-purple solution containing some precipitated mercury(II) chloride remains. The complex was precipitated from this mixture by addition of 70 % perchloric acid (15 ml) followed by a saturated aqueous solution of sodium perchlorate (20 ml). It was then filtered off on a plastic Büchner funnel and washed with water.

For recrystallization the product was dissolved in 0.01 M perchloric acid (1500 ml) preheated to 60 °C. 70 % perchloric acid (40 ml) was added to the cooled, filtered solution. The reddish-purple crystals were filtered off and washed with ice-cold water. After two such recrystallizations the yield was 38 g (73 %). Anal. [CoF₂(py)₄]ClO₄·½H₂O: Co, C, N, H, Cl. Spectral data in 0.01 M HClO₄: (ε, λ)_{max}: (27.5, 567), (37.8, 479), (62.2, 371.5), (ε, λ)_{min}: (24.0, 532), (14.0, 423), (20.3, 332.5).

3. [CoF₂(H₂O)(py)₃]ClO₄. Liquid hydrogen fluoride (100 ml) was cooled in an 800 ml polyethylene beaker by addition of an excess of dry ice in small lumps and finely powdered [Co(CO₃)Cl(py)₃] (40 g, 0.102 mol) was added to the cold mixture. The carbonate complex dissolved slowly with evolution of carbon dioxide gas and formation of a reddish-purple solution. The latter was allowed to stand for 3-4 h with thorough ventilation to attain room temperature. During this time the hydrogen fluoride had almost completely evaporated and a purple

product had been formed. The last traces of hydrofluoric acid were removed by extraction with 5 % (v/v) methanol in ether (4 × 200 ml). The sample was then collected on a filter, washed with ether and sucked as dry as possible. This almost dry product was dissolved in 0.012 M perchloric acid (250 ml) and a small amount of brownish impurities and red cobalt(II) fluoride was removed by filtration. Ice-cold 70 % perchloric acid (50 ml) was then added to the filtrate with stirring and cooling in ice, when purple crystals of [CoF₂(H₂O)(py)₃]ClO₄ began to separate immediately. After cooling for one hour the precipitate was filtered off, washed with ice-cold water (3 × 40 ml) and then with 96 % ethanol (40 ml). Drying in air yielded 35.4 g (77 %) of the almost pure perchlorate. This was purified by reprecipitation from perchloric acid: 5 g was dissolved in 0.012 M perchloric acid (700 ml) at room temperature. 70 % perchloric acid (70 ml) was added to the filtered solution with stirring and cooling in ice. After cooling for one hour the precipitate was filtered off and washed as described above. The yield was 3.65 g (73 %). The sample reprecipitated three times gave a constant absorption spectrum, indicating that only one isomer was present. Anal. [CoF₂(H₂O)(py)₃]ClO₄: Co, C, N, H, F, Cl. Spectral data in 0.1 M HCl: (ε, λ)_{max}: (40.5, 520), (48.0, 381), (ε, λ)_{min}: (10.2, 443), (23.7, 344.5).

4. *trans*-[CoF₂(py)₄]ClO₄·½H₂O. Crude [CoF₂(H₂O)(py)₃]ClO₄ (4.00 g, 8.86 mmol) was added to pyridine (15 ml) in a conical flask equipped with a condenser and a calcium chloride tube. The sample dissolved to give a reddish-purple solution and on heating at 70 °C for 15 min the solution turned red owing to the formation of the cation *trans*-[CoF₂(py)₄]⁺. Cooling in ice caused precipitation of large red crystals of the perchlorate salt. To the cold solution was then added ether (40 ml) to obtain a quantitative precipitation. The product was filtered off, washed thoroughly with ether and dried in air. Yield 4.5 g. The crude product was reprecipitated once as described in Preparation 2. Drying in air yielded 2.82 g (61 %). Anal. [CoF₂(py)₄]ClO₄·½H₂O: Co, C, N, H, F, Cl. Spectral data as those given in Preparation 2.

1. Werner, A. and Feenstra, R. *Ber. Dtsch. Chem. Ges.* 39 (1906) 1543.
2. Springborg, J. and Schäffer, C. E. *Acta Chem. Scand.* 27 (1973) 3312.
3. Glerup, J., Mønsted, O. and Schäffer, C. E. *Inorg. Chem.* 15 (1976) 1399.
4. Glerup, J., Josephsen, J., Michelsen, K., Pedersen, E. and Schäffer, C. E. *Acta Chem. Scand.* 24 (1970) 247.
5. Glerup, J. and Schäffer, C. E. *Inorg. Chem.* 15 (1976) 1408.
6. Springborg, J. *Unpublished results.*

Received August 1, 1978.