

SHORT COMMUNICATION

THE PREPARATION AND CHARACTERISATION OF $[\text{Co}(\text{py})_4\text{C}_7\text{H}_4\text{SO}_3\text{NCl}]\text{Cl}\cdot\text{H}_2\text{O}$

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Abstract. A 1:1 complex of $[\text{Co}(\text{py})_4\text{Cl}_2]\text{Cl}$ with sodium saccharide **1** has been synthesized and characterized as *trans*- $[\text{Co}(\text{py})_4\text{C}_7\text{H}_4\text{SO}_3\text{NCl}]\text{Cl}\cdot\text{H}_2\text{O}$ by a combination of UV-Vis spectroscopy, ^1H NMR, IR, and elemental analysis.

INTRODUCTION

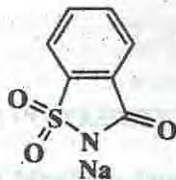
The dichlorotetrakis(pyridine)cobalt(III) complex $[\text{Co}(\text{py})_4\text{Cl}_2]\text{Cl}$ was first prepared by Werner and Feenstra in 1906 [1], and employed in the 1950's to aid in the elucidation of the $\text{S}_{\text{N}}1\text{cB}$ mechanism [2]. Chan and Hui have used it in the preparation of pentakis(alkylamine)chlorocobalt(III) complexes [3]. However, Toftlund and Pederson seem to be the first to employ it in a facile solution synthesis of chelated $[\text{CoN}_6]^{3+}$ complexes [4]. Its importance as a versatile synthetic precursor in the preparation of chelated complexes has also been shown by Purcell [5].

Other groups have utilized this complex to synthesize tris(diamine), polyamine and multidentate amine-thioether complexes [6]. Many of these syntheses involve the use of stoichiometric amounts of ligands and organic solvents such as ethanol. In this work, this complex has been used in the preparation of $[\text{Co}(\text{py})_4\text{sacCl}]\text{Cl}\cdot\text{H}_2\text{O}$ (**2**), where $\text{sac} = \text{C}_7\text{H}_4\text{SO}_3\text{N}$.

EXPERIMENTAL

NMR spectra were obtained on a Varian Gemini 300 MHz NMR instrument. ^1H NMR spectral chemical shifts are referenced to the residual solvent signals. IR spectra were recorded on a Perkin Elmer 2000 FT-IR spectrophotometer using KBr discs. Solution electronic spectra were recorded on a Shimadzu 2101 PC Spectrophotometer. Melting points were determined using a Stuart Scientific melting point SMP1 apparatus and are uncorrected.

Synthesis of $[\text{Co}(\text{py})_4\text{sacCl}]\text{Cl}\cdot\text{H}_2\text{O}$. A solution of dichlorotetrapyridinecobalt $[\text{Co}(\text{py})_4\text{Cl}_2]\text{Cl}$ (1.0457 g, 2.171 mmol) in 30.0 mL of water was added slowly with stirring, to a warm solution of **1** (1.0472 g, 4.342 mmol) in 20.0 mL water. The temperature of the dark green solution was maintained at about 40 °C for 10 minutes. The dark green solution turned to light green and the resulting precipitate was filtered off and washed thrice with 5.0 mL portions of ice cold water and dried. A fine light green



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solid was isolated, mp 150.9° [yield: 1.4886 g (60%)]. Anal. calc. for $\text{CoC}_{27}\text{H}_{26}\text{N}_3\text{Cl}_2\text{O}_4\text{S}$: C = 50.00%; H = 4.05%; N = 10.83%; Co = 9.12%; Cl = 10.97%. Found: C = 49.49%; H = 3.94%; N = 11.21%; Co = 9.12%; Cl = 11.21%.

RESULTS AND DISCUSSION

The UV-Vis spectrum of the isolated complex in ethanol gave two signals, see Figure 1 which assigned as follows: The signal at $\lambda_{\text{max}} = 628 \text{ nm}$ ($\epsilon = 43$) is probably a spin-allowed absorption corresponding to the transition: ${}^1A_{1g} \rightarrow {}^1T_{2g}$, and the band with $\lambda_{\text{max}} = 515 \text{ nm}$ ($\epsilon = 30$) to the crystal field (d-d) transition: ${}^1A_{1g} \rightarrow {}^1T_{1g}$.

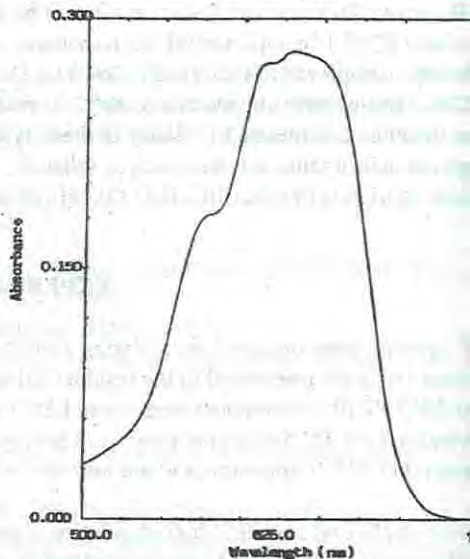
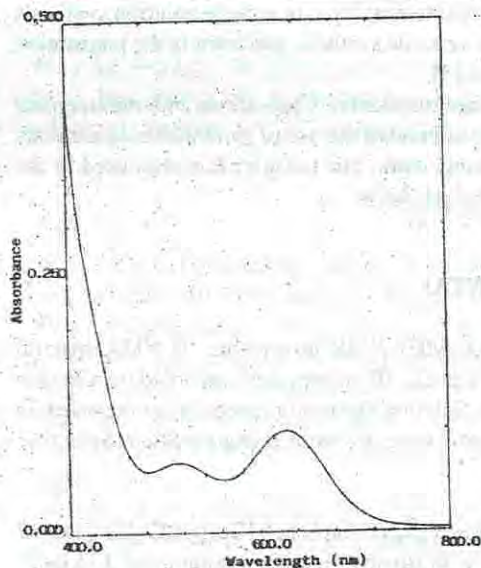


Figure 1. Absorption spectrum of the fresh solution of $[\text{Co}(\text{py})_4\text{sacCl}]\text{Cl}\cdot\text{H}_2\text{O}$.

Figure 2. Absorption spectrum of aged solution of $[\text{Co}(\text{py})_4\text{sacCl}]\text{Cl}\cdot\text{H}_2\text{O}$.

A broad band at 296 nm, $\epsilon = 10,500$ (not shown), is undoubtedly charge transfer as can be seen from its high ϵ value. A shoulder at $\lambda = 375$ nm is probably due to a spin-forbidden transition: ${}^1A_{1g} \rightarrow {}^3T_{2g}$. The ϵ values are higher than expected for rigorous Q_h symmetry suggesting that the symmetry of the postulated *trans*-[Co(py)₄sacCl]Cl complex is C_{4v} . A *cis*-complex might be expected to have even higher ϵ values.

After standing for two days, the green ethanol solution changed to a blue solution. When its spectrum was re-run, the broad absorption bands which are characteristic of six coordination were replaced by a multi-band pattern characteristic of tetrahedral coordination [14], see Figure 2. This behaviour is similar to that reported by Becker *et al.* [15], for tetrakis(cyclohexylisocyanide) bis(triphenylarsine)cobalt(II) perchlorate.

The ${}^{13}\text{C}$ NMR of **2** in CDCl_3 showed ten signals. The DEPT spectrum showed the presence of seven protonated methine carbons in agreement with the postulated structure. The ${}^{13}\text{C}$ NMR signal assignments are given in Table 1. The carbonyl signal at δ 172.6 is slightly shifted upfield compared to the signal of the carbonyl carbon of the sodium saccharide which is at δ 175.6. This shift is consistent with the saccharide being coordinated to the cobalt metal centre.

The ${}^1\text{H}$ NMR spectrum showed seven signals. The signals at δ 7.37 (t, $J = 6.9$, 8H β), 8.03 (br t, $J = 7.5$, 4H γ) and 8.37 (br d, $J = 5.6$, 8H α) were assigned to the protons of the pyridine ligands, whereas, the three signals at δ 7.52 (m, 2H, H-3, H-4), 7.72 (m, 1H, H-2) and 7.79 (m, 1H, H-5) were ascribed to the saccharide ligand protons.

The slightly broad signal upfield at δ 2.80 was assigned to the water molecule which is present as lattice water [16]. When the sample was run in D_2O , the broad signal observed at δ 2.80 in CDCl_3 was no longer there, but instead a broad signal was observed at δ 4.78 ascribed to the suspended droplets of HDO [16].

The IR spectrum showed an OH absorption band at 3420 cm^{-1} . A band at 1637 cm^{-1} corresponds to the C = O stretching. The strong N - H stretching absorption at 2900 cm^{-1} in the spectrum of the

Table 1. ${}^{13}\text{C}$ NMR spectral data of the complex *trans*-[Co(py)₄sacCl]Cl.H₂O.

Carbon No.	δ (ppm)	
	CDCl_3	D_2O
7	172.6	-
α	157.6	157.6
6	141.0	-
γ	140.7	140.7
5	133.9	134.0
2	133.5	133.5
1	126.1	126.1
β	125.5	125.6
4	123.8	123.9
3	120.6	120.6

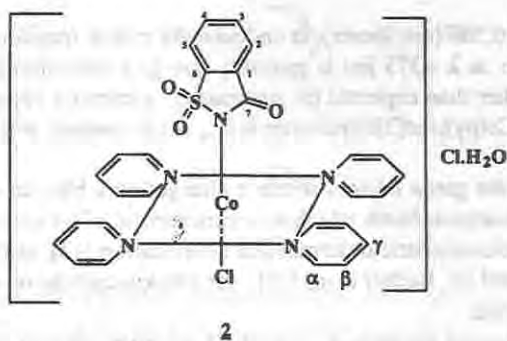


Figure 3. Suggested structure of *trans*-[Co(py)₄sacCl]Cl.H₂O.

free saccharin is absent in the spectrum of the complex, consistent with loss of a proton coordination of the saccharin anion through nitrogen.

ACKNOWLEDGEMENTS

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