

# 一个特殊的多吡啶钴(Ⅲ)配合物

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本文介绍一五胺配合物 $[\text{Co}(\text{terpy})(\text{bpy})\text{Cl}]^{2+}$ , 三元胺是 2, 2': 6', 2''-三联吡啶, 二元胺是 2, 2'-联吡啶, 此配合物结构特殊在于分子中没有任何酸性氢。利用其考察非碱催化水解过程中发现, 该配合物的水解速率出人意料地快。这个取代反应可能是一氧化还原过程。

关键词: 特殊配合物 结构 无酸性氢 氧化还原  
分类号: O614. 81 O626. 32

## A Novel Polypyridyl Ligand Cobalt (Ⅲ) Complex

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A new pentaaminechlorocobalt (Ⅲ) complex  $[\text{Co}(\text{terpy})(\text{bpy})\text{Cl}]^{2+}$  has been synthesised which is unusual in that it is devoid of any acidic protons, and in this complex, the terpy and the bpy is 2, 2': 6', 2''-terpyridine and 2, 2'-bispyridine respectively. In an attempt to demonstrate a lack of (base-catalysed) hydrolysis, it was unexpectedly reactive but the process of substitution appears to be redox driven.

Keywords: novel complex structure no acidic proton redox

## 0 Introduction

There have been a number of studies involving 2, 2': 6', 2''-terpyridine (terpy) and its complexes with metal ion such as Ru, and Ni<sup>[1]</sup>. Some work on the bis-terpyridine-cobalt (Ⅲ) complex has been published where the focus has been on the Co (Ⅲ)/Co (Ⅱ) electron exchange reaction<sup>[2]</sup>. The base catalysed hydrolysis of a wide variety of the octahedral complexes of the kind  $[\text{Co}(\text{triamine})(\text{diamine})\text{Cl}]^{2+}$  have been studied<sup>[3]</sup> however no  $[\text{Co}(\text{Ⅲ})(\text{terpy})(\text{diamine})\text{Cl}]^{2+}$  complex has been reported to date. A commonly accepted mechanism first proposed in 1937 by Garrick<sup>[4]</sup> and taken up by Basolo and Pearson in 1956<sup>[5]</sup> requires acidic amine protons for the base catalysis. An important

收稿日期: 1999-10-15. 收修改稿日期: 1999-12-01.

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corollary was that if the pentaamine complex lacked such centres there would be no base catalysis, but this have never been directly demonstrated<sup>[6]</sup>.

Herein, we report a new  $[\text{Co}(\text{triamine})(\text{diamine})\text{Cl}]^{2+}$  complex in which the triamine is 2, 2': 6', 2''-terpyridine and the diamine is 2, 2'-bispyridine (bpy). (Fig. 1) There are no acidic protons and this complex was anticipated to hydrolyse at a rate independent of  $[\text{OH}^-]$ .

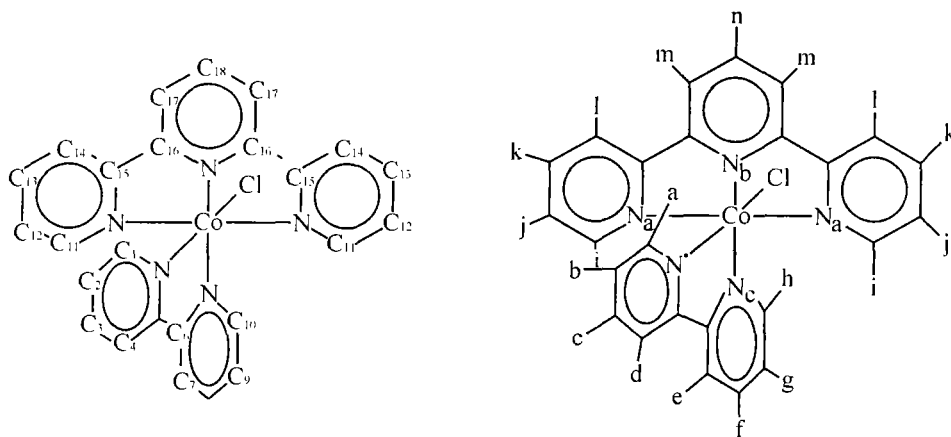


Fig. 1. Marked  $[\text{Co}(\text{terpy})(\text{bpy})\text{Cl}]^{2+}$

## 1 Experiment

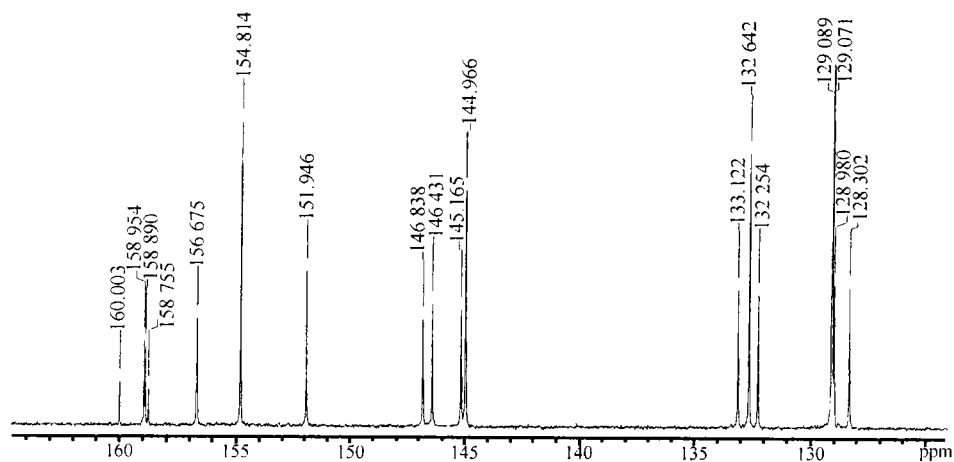
### 1.1 Synthesis of the $[\text{Co}(\text{terpy})(\text{bpy})\text{Cl}]^{2+}$

Synthesis of a  $[\text{Co}(\text{terpy})(\text{bpy})\text{Cl}]^{2+}$  complex was achieved using the procedure of Bosnich and Dwyer<sup>[7]</sup> for the  $[\text{Co}(\text{dien})(\text{en})\text{Cl}]^{2+}$  ions, on a one-fifth scale.  $[\text{Co}(\text{terpy})\text{Cl}_3]$  (1.0 g, 4.3 mmol) was suspended in 10 mL of water and 2, 2'-bispyridine (0.7 g, 4.3 mmol) was added. The mixture was stirred at room temperature until the suspension cleared, then quenched with excess HCl (5 mol  $\cdot$  L<sup>-1</sup>) and loaded onto a Dowex 50W-X2 column (H<sup>+</sup> form). Elution with HCl (2 ~ 3 mol  $\cdot$  L<sup>-1</sup>) yielded a single pink-orange band which after rotary evaporation yielded crystals from H<sub>2</sub>O/HCl/Me<sub>2</sub>CO. A perchlorate salt was also obtained (H<sub>2</sub>O/HClO<sub>4</sub>). The yield of the complex was about 40 ~ 50%.

### 1.2 Characteristics of the $[\text{Co}(\text{terpy})(\text{bpy})\text{Cl}]^{2+}$

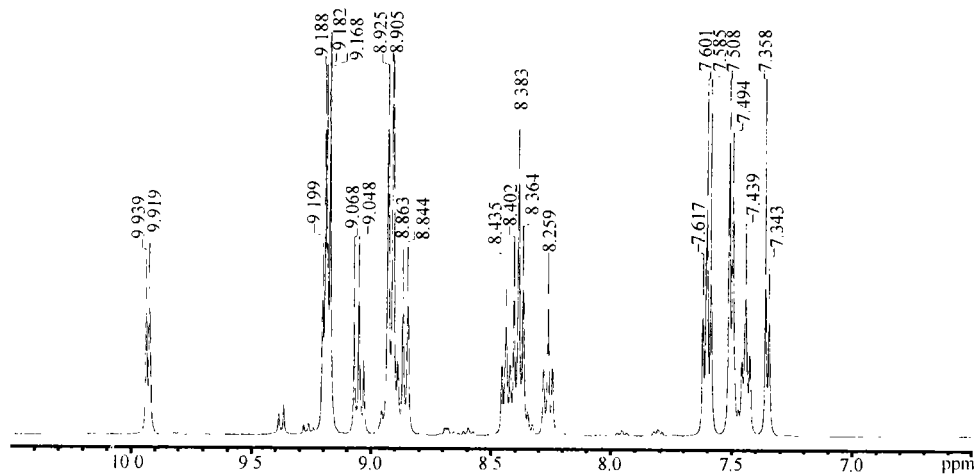
UV/visible spectra (H<sub>2</sub>O): max 456 (136.2); min 422 (99.3) / ( $\lambda/(\epsilon) = \text{nm}/(\text{mol} \cdot \text{L}^{-1} \cdot \text{cm}^{-1})$ ). The 1D and 2D NMR spectra (DQCOSY, NOESY, and HETCOR) have been used to confirm the solution structure of the complex which proved to be a single pure isomer.

The  $[\text{Co}(\text{terpy})(\text{bpy})\text{Cl}]^{2+}$  complex can exist in three isomeric forms - mer, sym-fac or un-sym-fac. The first two have a plane of symmetry while the last is asymmetric, thus for the 25 carbon atoms in the molecule, the number of lines expected in the 1D <sup>13</sup>C NMR spectrum would be 20 (5  $\times$  2C, 15  $\times$  1C), 15 (10  $\times$  2C, 5  $\times$  1C) or 25 (25  $\times$  1C), respectively. The <sup>13</sup>C NMR spectrum (Fig. 2a) shows that there are 18 resonances, the intensities of seven of them being double the others. Clearly this is a mer isomer, with 2 sets of the resonances being accidentally degenerate (the resonances are split in the spectrum of the ClO<sub>4</sub><sup>-</sup> salt in Me<sub>2</sub>SO-d<sub>6</sub>, where the expected 20 lines are

Fig. 2a  $^{13}\text{C}$  NMR spectrum of the  $[\text{Co}(\text{terpy})(\text{bpy})\text{Cl}]^{2+}$  complex

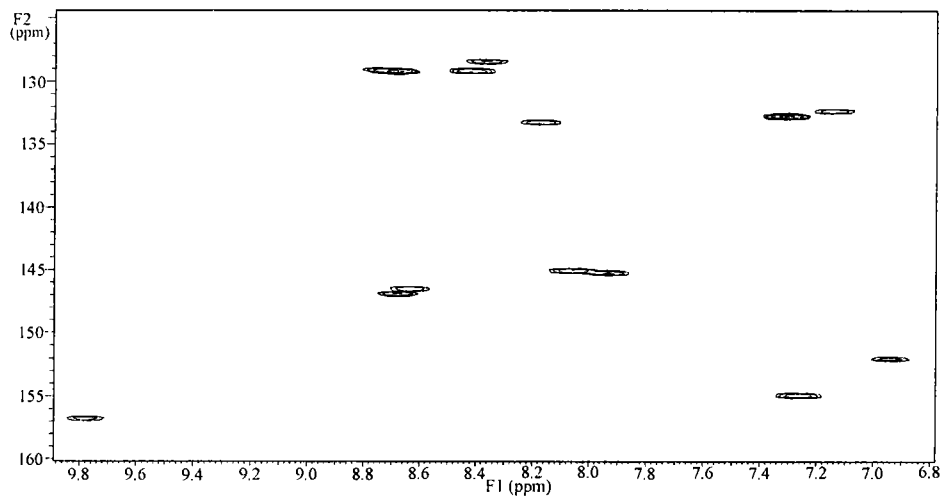
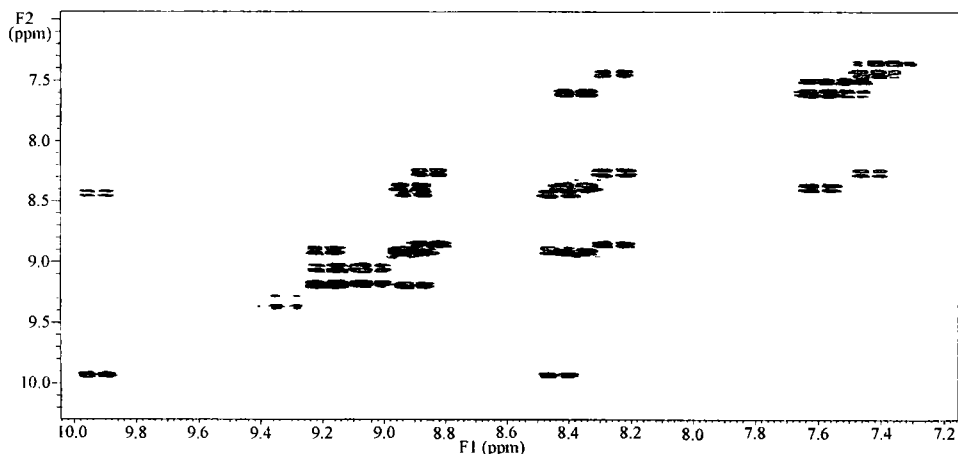
observed).

The mer symmetry is also clearly reflected in the  $^1\text{H}$  NMR spectrum. (Fig. 2b) Fourteen C-H resonances are expected and indeed observed, five of intensity 2 and nine of intensity 1, with the "outer" aromatic signals appearing as doublets and the "inner" as triplets. The shifts to higher fields for the i, j, b and a protons are consistent with deshielding by the adjacent aromatic rings. The splitting pattern, as for the  $^{13}\text{C}$  NMR spectrum, is unique to the mer configuration.

Fig. 2b  $^1\text{H}$  NMR spectrum of the  $[\text{Co}(\text{terpy})(\text{bpy})\text{Cl}]^{2+}$  complex

In the HETCOR spectrum (Fig. 2c), the fourteen carbon-proton correlations are all observed, and four uncorrelated carbon resonances at 156.2, 155.9 ppm ( $\text{C}_{15}$ ,  $\text{C}_{16}$ ), and 157.0, 155.78 ppm ( $\text{C}_5$ ,  $\text{C}_6$ ) are of course the four different quaternary carbon sites in the complex; one set is distinguished from the other through their relative intensities in the 1D spectrum (2:1; Fig. 2b and Fig. 2c).

Four groups of terpy and bpy C-H protons are defined by the DQCOSY spectrum (Fig. 2d). The resonances at 7.36, 7.45, 8.26 and 8.85 ppm represent protons a, b, c and d; 9.20, 8.90,

Fig. 2c HETCOR NMR spectrum of the  $[\text{Co}(\text{terpy})(\text{bpy})\text{Cl}]^{2+}$  complexFig. 2d DQCOSY NMR spectrum of the  $[\text{Co}(\text{terpy})(\text{bpy})\text{Cl}]^{2+}$  complex

8.44 and 9.93 ppm are for protons e, f, g and h; 7.52, 7.61, 8.40 and 8.91 ppm for protons i, j, k and l; and 9.18 and 9.05 ppm for the protons m and n (Fig. 2c and d).

These assignments were assisted through the NOESY spectrum (Fig. 2e) and by the fact the inner aromatic C-H protons are triplets, while the outer protons are doublets in the 1D spectrum. In the NOESY spectrum, based on the expected through-space correlations between the protons d and e on the bpy ring (8.85/9.20 ppm) and m and l on the terpy ring (9.18/8.91 ppm), precise assignments of all the protons in the terpy and bpy rings were possible (Fig. 2c and e). The NMR spectra are thus totally consistent with a pure mer- $[\text{Co}(\text{terpy})(\text{bpy})\text{Cl}]^{2+}$  complex.

The exclusive formation of the mer isomer is hardly surprising since either of the alternate fac forms require the tridentate terpy to fold with severe distortion, and which also results in loss of  $\pi$ -aromatic conjugation.

## 2 Results and discussion

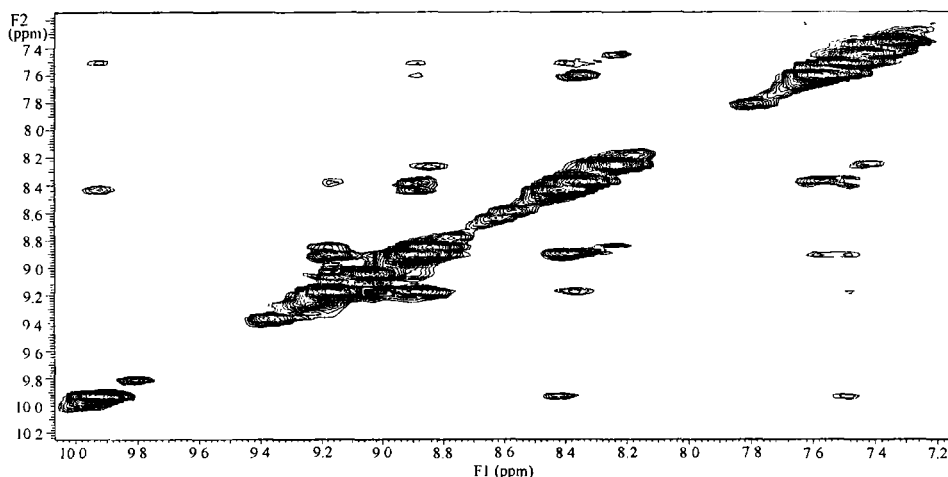


Fig. 2e NOESY NMR spectrum of the  $[\text{Co}(\text{terpy})(\text{bpy})\text{Cl}]^{2+}$  complex

The synthesis of pentaamminecobalt(Ⅲ) complexes lacking any acidic amine centres has recently been addressed. Gillard and Vagg have reported such a complex<sup>[11]</sup>, but there has been no work on its base catalysed hydrolysis. Jackson et al. have synthesised the tacn derived pentadentate ligands dmptacn and dmpmetacn, the latter complex also meeting the requirements. Both these complexes show base catalysis for substitution of  $\text{Cl}^-$ , the N-Me substate being surprisingly faster, but a special mechanism involving deprotonation at a pyridyl  $\alpha\text{-CH}_2$  has been demonstrated. It seems likely, Gillard's complex will be shown to behave similarly. The complex reported here lacks both acidic amines and acidic pyridyl methylenes, and was therefore of especial interest.

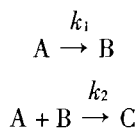
Although there is no acidic amine proton in the  $[\text{Co}(\text{terpy})(\text{bpy})\text{Cl}]^{2+}$  complex, the kinetics revealed that it was appreciably reactive in basic medium. In TES buffers<sup>[8]</sup>, (pH range 6.44 to 8.44), the apparent rate of base hydrolysis ( $k_{\text{OH}}$ ) was  $5.85 \times 10^3 \text{ mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$ , and this is little different from the complexes having acidic amine protons. For example, under identical conditions, the rates of base hydrolysis of the reported complexes  $[\text{Co}(\text{dien})(\text{bpy})\text{Cl}]^{2+}$ <sup>[9]</sup> and  $[\text{Co}(\text{dien})(\text{en})\text{Cl}]^{2+}$ <sup>[10]</sup> are  $8.7 \times 10^3$  and  $3.7 \times 10^3 \text{ mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$ , respectively.

Previous work<sup>[2]</sup> has shown the ability of the terpyridine cobalt complexes to facilitate  $\text{e}^-$  transfer processes, and the possibility of  $\text{OH}^-$  mediated  $\text{e}^-$  transfer therefore merited consideration. For example, production of Co(Ⅱ) might have been detected by the broadening of the  $^1\text{H}$  NMR spectral resonances for the three protons on the central ring in the terpyridine<sup>[2]</sup>.

The course of hydrolysis of  $[\text{Co}(\text{terpy})(\text{bpy})\text{Cl}]^{2+}$  at different pH values was progressively followed by NMR. The pH of a concentrated solution of the chloride salt in  $\text{D}_2\text{O}$  was adjusted with 0.01M NaOD gradually. The substitution began to be observed at pH 4 ~ 4.5; between 4.5 ~ 6.5, the substitution was finished quickly, and an equilibrium established between the precursor and the substituted species  $[\text{Co}(\text{terpy})(\text{bpy})\text{OH}_2]^{3+}$ . At pH = 9, the  $^{13}\text{C}$  NMR revealed only the substituted species  $[\text{Co}(\text{terpy})(\text{bp})\text{OH}]^{2+}$ . Even at pH = 12; the product spectra ( $^1\text{H}$ ,  $^{13}\text{C}$ ) were well resolved, and stable in time; there was no indication of broadened signals. The UV/visible spectra confirmed only the presence of chloro and/or hydroxo species under this range of conditions, and there was no

indication of any net redox process.

The above observations are consistent with a base-driven hydrolysis which is reversible in the lower pH region because under the conditions of the NMR experiments,  $[\text{Co}]$  is high, while the background  $[\text{Cl}^-] = 1 \text{ mol} \cdot \text{L}^{-1}$  for the buffers used. It was also clear from the spectrophotometric studies that the rate for the forward reaction was essentially linear in  $[\text{OH}^-]$ .



The clue to understanding the apparent base catalysis came from the observation of a short induction period in the absorbance - time traces for the reaction of  $[\text{Co}(\text{terpy})(\text{bpy})\text{Cl}]^{2+}$  in TES buffers. This suggested to us an autocatalytic reaction where the catalyst was a labile Co(II) species arising from  $\text{OH}^-$  induced reduction of A. Such an account can accommodate the  $[\text{OH}^-]$  dependence of the rate, in the clear absence of deprotonatable NH sites. Both experience and theoretical considerations show that the kinetic behaviour beyond the induction period approximates a single exponential function, as observed. Moreover, under such circumstances first order rate constants ( $\pm 10 \sim 20\%$ ) tend not to be as reproducible as normally ( $\pm 2\%$ ), and they are theoretically dependent upon  $[\text{reactant}]_0$ . Again, for the present system, both behavioural facts are observed.

The poor reproducibility of the rate data in the known autocatalytic  $\text{SO}_3^{2-}$  substitution reaction of *trans*- $[\text{Co}(\text{en})_2\text{Cl}_2]^+$  has been traced to trace Co(II) impurity in the reactant, and the level varies from sample to sample. Thus autocatalysed sulfite substitution arises from two sources, Co(II) in the reactant, and Co(II) produced by  $\text{SO}_3^{2-}$  reduction.

An important point to emerge from that study was the clean substitution chemistry-no Co(II) could actually be detected (and the test is sensitive), but catalysis could be demonstrated by the deliberate introduction of the catalyst, and through the complete quenching of the catalysis by sequestering with  $\text{EDTA}^-$ . Given the known sensitivity of imine and polypyridine complexes such as *trans*- $[\text{Co}(\text{phen})_2\text{Cl}_2]^+$  and *mer*- $\alpha\beta$ - $[\text{Co}(\text{picdien})\text{Cl}]^{2+}$  towards reduction by anions such as  $\text{N}_3^-$  and  $\text{OH}^-$ , ready reduction of  $[\text{Co}(\text{terpy})(\text{bpy})\text{Cl}]^{2+}$  by  $\text{OH}^-$  would not be unexpected. Indeed, the critical test for the involvement of Co(II) is quenching of the base catalysed reaction by  $\text{EDTA}^-$ , and we have now observed this. In control experiments using TES buffers at the same pH, with and without low levels of  $\text{EDTA}^-$ , the observed rates were totally different. The rate of hydrolysis was almost completely suppressed by the  $\text{EDTA}^-$ .

### 3 Conclusion

It is concluded that base does not catalyse  $\text{Cl}^-$  hydrolysis in the usual way, but rather by a redox mechanism involving Co(II) at very low levels and by a mechanism presently obscure in detail. The problem of demonstrating a lack of  $\text{OH}^-$  catalysis for non-NH containing Co(III) complexes therefore remains.

We thank the Australia Research Council for a research grant to Jackson W. G.

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