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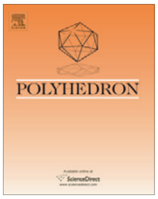

Role of hydrogen peroxide in the synthesis of nitrogen heterocycle containing cobalt complexes

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ABSTRACT

The reactions of $Co(O_2CCH_3)_2{\cdot}4H_2O$ with the sodium salt of *p*-toluene sulfonic acid (NapTS) and pyridine (py) or 4-methylpyridine (4mepy) in the presence of hydrogen peroxide in methanol led to the formation of $[Co(py)_3(H_2O)_3](pTS)_2$ or $[Co(4mepy)_2(H_2O)_4](pTS)_2{\cdot}MeOH$, respectively. The coordination polymer $[\{Co(44'bpy)(H_2O)_4\}(pTS)_2]_n$ (4,4′-bipyridine = 44′bpy) was obtained from the reaction of $Co(O_2CCH_3)_2{\cdot}4H_2O$ with 44’bpy 44′bpy in the presence of NapTS. The reaction of $Co(O_2CCH_3)_2{\cdot}4H_2O$, 2,2′-bipyridine (22′bpy) and NapTS with hydrogen peroxide resulted in the formation of the dinuclear complex $[Co_2(\mu\text{-}OH)_2(\mu\text{-}O_2CCH_3)(O_2CCH_3)_2(22'bpy)_2](pTS)$. Characterization of these complexes and the role of hydrogen peroxide in these reactions are discussed. Similar reactions with sodium sulfamate gave the mononuclear $[Co(22'bpy)_2(O_2CCH_3)]NH_2SO_3{\cdot}2H_2O$ complex and $[Co_2(\mu\text{-}OH)_2(\mu\text{-}O_2CCH_3)(O_2CCH_3)_2(22'bpy)_2](NH_2SO_3)$.

1. Introduction

Cobalt complexes are widely used as catalysts in organic reactions [1–9]. Cobalt carboxylates are commonly used for catalytic oxidation reactions [10–14]. The synthesis of binuclear [15–17] or mononuclear cobalt carboxylate complexes [17] are governed by the reaction conditions. There is the scope to prepare model cobalt complexes of peptidase enzyme [18,19] or to prepare polynuclear cobalt complexes [20–23]. In biological systems, cobalt ion containing carboxy-peptidase activities are controlled by the energy obtained from inter-conversion of ATP to ADP [24–26]. Moreover, in the ATP to ADP conversion, phosphate anions are generated which have a tetrahedral geometry. Thus, multidentate oxy-anions with a good leaving group property and having a tetrahedral geometry may be a model anion of phosphate in a bio-active metal complex. Generally, *p*-toluene sulfonate is a good leaving group and is used as a protecting group in organic chemistry [27]; it has a distorted tetrahedral geometry around the sulfur atom. Herein we present the synthesis and characterization of five cobalt complexes with the *p*-toluene sulfonate anion and show the role of hydrogen peroxide in the synthesis of these complexes.

2. Experimental

The ^1H NMR spectra were recorded on a Varian 400 MHz FT-NMR spectrometer. The FT-IR spectra were recorded using a Perkin–Elmer Spectrum One spectrometer in the range 4000–400 cm^{-1}. The UV/Vis spectra were recorded using a Perkin–Elmer Lambda 750 spectrometer.

2.1. Synthesis of complexes

*2.1.1. $[Co(H_2O)_6](pTS)_2$ (**1**)*

To a well stirred solution of pTSH (0.38 g, 2 mmol) and NaOH (0.08 g, 2 mmol) in methanol (20 ml) $Co(O_2CCH_3)_2{\cdot}4H_2O$ (0.25 g, 1 mmol) followed by pyridine (0.81 mL, 1 mmol) were added. The reaction mixture was stirred for 4 h and then kept for crystallization. Pink crystals were obtained. Yield: 41% (with respect to cobalt). IR (KBr, cm^{-1}): 3413 (br), 1670 (m), 1646 (m), 1598 (w), 1496 (w), 1451 (w), 1397 (w), 1384 (w), 1191 (s), 1127 (s), 1040 (s), 1012 (s), 845 (w), 814 (s), 708 (w), 684 (s), 568 (s). Magnetic moment (RT): 4.19 B.M. Visible (λ_{max} MeOH): 514 nm ($\varepsilon = 146\ Mol^{-1}\ cm^{-1}$).

*2.1.2. $[Co(py)_3(H_2O)_3](pTS)_2$ (**2**)*

To a solution of NaOH (0.08 g, 2 mmol) and pTSH (0.38 g, 2 mmol) in methanol (20 ml), $Co(O_2CCH_3Me)_2{\cdot}4H_2O$ (0.25 g, 1 mmol) was added and stirred for 15 min. Pyridine (0.16 mL, 2 mmol) was added to this solution, followed by the dropwise addition of hydrogen peroxide (30% v/v, 1 mL ~5 mmol). The reaction mixture was refluxed for 4 h. The resulting red solution, on standing for 48 h, led to the formation of crystals of **2**. Yield: 43% (with respect to cobalt). IR (KBr, cm^{-1}): 3408 (br), 3264 (w), 1645 (m), 1602 (m), 1488 (w), 1446 (m), 1384 (w), 1191 (s), 1127 (s), 1067 (w), 1039 (s), 1012 (s), 841 (w), 813 (m), 772 (w),

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Table 1
Crystallographic parameters of complexes **2**–**5**.

Compound	2	3	4	5
Formulae	$C_{29}H_{35}CoN_3O_9S_2$	$C_{28}H_{40}CoN_2O_{12}S_2$	$C_{72}H_{66}Co_3N_6O_{33}S_6$	$C_{33}H_{34}Co_2N_4O_{15}S$
Mol. wt.	692.65	719.67	1912.46	876.56
Crystal system	monoclinic	monoclinic	triclinic	triclinic
Space group	$C2/c$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
T (K)	296	296	296	296
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
a (Å)	15.3175(4)	7.9495(5)	14.0110(12)	10.1404(14)
b (Å)	11.4473(4)	20.0281(14)	18.3229(12)	13.408(2)
c (Å)	18.9493(7)	10.8959(7)	19.6363(12)	14.415(2)
α (°)	90.00	90.00	113.803(3)	103.674(3)
β (°)	101.009(3)	93.279(3)	90.833(3)	97.567(4)
γ (°)	90.00	90.00	110.290(3)	92.576(3)
V (Å^3)	3261.50(19)	1731.9(2)	4255.4(5)	1881.9(5)
Z	4	2	2	2
D_{calc} (Mg m^{-3})	1.411	1.380	1.493	1.547
Absorption coefficient (mm^{-1})	0.709	0.676	0.812	1.012
F(0 0 0)	1444	754	1962	900
Total number of reflections	4059	3223	14578	6105
Reflections, $I > 2\sigma(I)$	4059	2785	9944	4931
Maximum 2θ (°)	56.6	51.0	50.5	49.5
Ranges (h, k, l)	−19, 20; −15, 15; −20, 25	−9, 9; −24, 23; −13,13	−15, 16; −21, 21; −16, 23	−11, 11; −15, 15 −16, 16
Completeness to 2θ (%)	99.7	100.0	94.6	95.0
Data/restraints/parameters	4059/0/202	3223/1/214	14 578/0/1090	6105/0/508
Goodness-of-fit (GOF) (F^2)	0.823	1.067	1.394	1.499
R indices [$I > 2\sigma(I)$]	0.0353	0.0507	0.0613	0.0398
R indices (all data)	0.0531	0.0573	0.0824	0.0517
wR_2 [$I \geq 2\sigma(I)$]	0.1118	0.1357	0.1890	0.0764
wR_2 (all data)	0.1274	0.1440	0.2050	0.0793

756 (w), 684 (s), 629 (w), 568 (s), 550 (w). Elemental analysis *Anal.* Calc. for $C_{29}H_{35}N_3O_9S_2Co$: C, 50.29; H, 5.09. Found: C, 50.34; H, 5.12%. Magnetic moment (RT): 4.38 B.M. Visible ($\lambda_{\max}$ MeOH): 513 nm (ε = 79 Mol^{-1} cm^{-1}).

2.1.3. [Co(4mepy)$_2$(H$_2$O)$_4$](pTS)$_2$·MeOH (**3**)

This was prepared in a similar procedure as for **2**, but by using 4-methylpyridine instead of pyridine. IR (KBr, cm^{-1}): 3390 (br), 2927 (w), 1658 (m), 1620 (m), 1496 (w), 1428 (w), 1384 (w), 1226 (s), 1112 (m), 1164 (s), 1124 (s), 1036 (s), 1011 (s), 820 (s), 810 (m), 681 (s), 566 (s), 594 (m). Visible ($\lambda_{\max,}$ MeOH): 511 nm. Visible ($\lambda_{\max}$ solid): 505 and 464 nm. Magnetic moment (RT): 4.6 B.M. Molar conductance: 198 S cm^2 mol^{-1} in methanol.

2.1.4. [{Co(H$_2$O)$_4$(44′bpy)}(pTS)$_2$]$_n$ (**4**)

A solution of NaOH (0.08 g, 2 mmol) and pTSH (0.38 g, 2 mmol) in methanol (20 ml) was prepared. To this solution, $Co(O_2CCH_3)_2{\cdot}4H_2O$ (0.26 g, 1 mmol) followed by 44′bpy (0.156 g, 1 mmol) were added. The resulting solution was stirred for 1 h. A pink residue was formed; the residue was dissolved in methanol and water. The resulting solution, on standing for 46 h, led to a crystalline compound. Yield: 45%. IR (KBr, cm^{-1}): 3396 (br), 1651 (m), 1611 (m), 1541 (w), 1494 (w), 1418 (m), 1388 (w), 1173 (s), 1123 (s), 1066 (m), 1035 (s), 1011 (s), 856 (w), 812 (s), 685 (s), 636 (m), 562 (s). Elemental analysis *Anal.* Calc. for [$C_{24}H_{30}N_2O_{10}S_2Co$]$_n$: C, 45.79; H, 4.80. Found: C, 43.64; H, 4.26% (deviation due to end group/water of crystallization). Magnetic moment (RT): 4.20 B.M. Visible ($\lambda_{\max}$ MeOH): 512 nm (ε = 116 Mol^{-1} cm^{-1}).

2.1.5. [Co$_2$(μ-OH)$_2$(μ-O$_2$CCH$_3$)(O$_2$CCH$_3$)$_2$(22′bpy)$_2$](pTS) (**5**)

To a solution of pTSH (0.19 g, 1 mmol) and NaOH (1 mmol) in methanol (20 ml), $Co(O_2CCH_3)_2{\cdot}4H_2O$ (0.25 g, 1 mmol) followed by 22′bpy (0.16 g, 1 mmol) were added. To the reaction mixture hydrogen peroxide (30% v/v, 1 mL ~5 mmol) was added dropwise. The resulting mixture was stirred for 30 min. A dark red solution was obtained. Red crystals were obtained on standing. Yield: 38% (with respect to cobalt). IR (KBr, cm^{-1}): 3421 (br), 3081 (w), 1673 (m), 1635 (w), 1595 (s), 1527 (m), 1498 (m), 1472 (m), 1450 (m), 1426 (w), 1397 (m), 1340 (m), 1315 (m), 1224 (w), 1193 (s), 1172 (w), 1117 (s), 1071 (w), 1034 (s), 1009 (m), 915 (m), 814 (m), 778 (s), 730 (m), 707 (w), 681 (s), 658 (w), 618 (w), 564 (s), 482 (w). ^{1}H NMR (DMSO-d$_6$, 400 MHz): 9.6 (m, 2H), 8.8 (m, 4H), 8.48 (m, 2H), 8.4 (s, 1H), 8.0 (m, 4H), 7.5 (m, 4H), 7.1 (m, 4H), 2.5 (s, 3H), 2.2 (s, 3H), 1.42 (s, 6H). Visible ($\lambda_{\max}$ MeOH): 546 nm (ε = 185 Mol^{-1} cm^{-1}). LC–MS [M+]: 641.01.

The X-ray single crystal diffraction data were collected at 296 K with Mo Kα radiation (λ = 0.71073 Å) using a Bruker Nonius SMART CCD diffractometer equipped with a graphite monochromator. The SMART software was used for data collection and also for indexing the reflections and determining the unit cell parameters; the collected data were integrated using SAINT software. The structures were solved by direct methods and refined by full-matrix least-squares calculations using SHELXTL software. All the non-H atoms were refined in an anisotropic approximation against F^2 of all reflections. The H-atoms, except those attached to oxygen atoms were placed at their calculated positions and refined in the isotropic approximation; those attached to oxygen were located in the difference Fourier maps, and refined with isotropic displacement coefficients. In the crystal structures of the complexes (**2–5**), we could not locate some of the labile hydrogen atoms of the water molecules. The crystallographic parameters of the compounds are tabulated in Table 1.

3. Results and discussions

The reaction of $Co(O_2CCH_3)_2{\cdot}4H_2O$ with NapTS led to the mononuclear cobalt complex [Co(H$_2$O)$_6$](pTS)$_2$ (**1**) [28,29]. The replacement of aqua ligands from complex **1** by pyridine (py) or 4-methylpyridine (4mepy) under ordinary conditions does not take place, but the reaction of $Co(O_2CCH_3)_2{\cdot}4H_2O$ and NapTS and py or 4mepy in the presence of H_2O_2 led to mer-[Co(H$_2$O)$_3$(py)$_3$](pTS)$_2$ (**2**) or [Co(4mepy)$_2$ (H$_2$O)$_4$](pTS)$_2$·MeOH (**3**), respectively. The same reactions do not lead to the described products