Synthesis, structure and fluxionality of Co(III) complexes containing chelated sulfate

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ABSTRACT

The syntheses and characterisation of the complexes [Co(pmea)(O$_2$SO$_2$)]ClO$_4$ and [Co(pmap)(O$_2$SO$_2$)]ClO$_4$ (pmea = bis((2-pyridyl)methyl)-2-((2-pyridyl)ethyl)amine; pmap = bis(2-(2-pyridyl)ethyl)(2-pyridylmethyl)amine), containing chelating sulfato ligands, are reported. These were prepared by oxidation of a solution containing CoSO$_4$·7H$_2$O and the tripodal tetraamine ligand with either (NH$_4$)$_2$[Ce(O$_2$NO)$_6$] (pmea) or Oxone (2KHSO$_5$·KHSO$_4$·K$_2$SO$_4$; pmap), and their structures were confirmed by X-ray crystallography. [Co(pmap)(O$_2$SO$_2$)]ClO$_4$ crystallised as the 6-isomer from aqueous NaClO$_4$ solution, while [Co(pmea)(O$_2$SO$_2$)]ClO$_4$ was obtained as a mixture of the 5- and 6-isomers, with both isomers being able to be resolved in the X-ray structure. Comparison of the IR spectra of [Co(pmap)(O$_2$SO$_2$)]ClO$_4$ and [Co(pmap)(O$_2$CO)]ClO$_4$ allowed assignment of IR bands due to the chelated sulfato ligand. Fluxionality in [Co(pmea)(O$_2$SO$_2$)]ClO$_4$ was resolved using ^{1}H VT-NMR, and was found to result from 'flapping' of the pyridylethyl arm of the pmea ligand between two possible conformations.

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1. Introduction

The coordination chemistry of oxoanion ligands has long been a significant area of study in inorganic chemistry [1]. Cobalt complexes of these ligands are numerous and indeed, Bernhardt and Lawrance's contention that "Practically every known oxoanion has been introduced into the Co coordination sphere during the last century" is no exaggeration [2]. Of the myriad known oxoanions, phosphate, sulfate, nitrate, and carbonate in particular, together with their protonated and alkylated derivatives, have been incorporated into a huge number of transition metal complexes of differing geometries, nuclearities and reactivities [3]. We have been particularly interested in Co(III) complexes containing both a tripodal tetraamine ligand [4,5] and either a carbonato or phosphato ligand, and we have shown that, amongst other things, the Co(III) mediated hydrolysis of phosphate esters is

mechanistically complex [6], Co(III) complexes containing a chelated carbonato ligand can be rendered essentially stable in acidic aqueous solution on judicious choice of the ancillary ligand [7,8], and that Co(III) complexes containing the chelated hydrogenphosphato and hydrogencarbonato ligands can be prepared and structurally characterized [9,10]. While there are numerous Co(III) complexes containing phosphato and carbonato ligands [2], the same is not true of the sulfato ligand. Like other oxoanion ligands, the sulfato ligand can display a number of bonding modes in Co(III) complexes (for example, monodentate [11,12], and bridging monodentate [13,14]), of which the chelate is surprisingly rare. For many years, it was believed that "[Co(en)$_2$(O$_2$SO$_2$)]X" (X = Br$^-$, ClO$_4$$^-$) [15] contained a chelated sulfato ligand, until this was shown to be the dimeric complex {[Co(en)$_2$(OS(O)$_2$O)]$_2$}$^{2+}$, containing bridging monodentate sulfato ligands [14]. The first structurally characterised Co(III) complex containing a chelated sulfato ligand was reported in 1991 [16], and since this time, there have only been two further examples detailed [17,18]. In this paper, we report results of our investigations of the syntheses of Co(III) complexes containing chelated sulfato ligands. We show that the strong

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oxidants Oxone and $(NH_4)_2[Ce(O_2NO)_6]$ are required in these syntheses, and we outline our efforts to prepare complexes containing a chelated hydrogensulfato ligand. We also detail the fluxional behaviour of the $[Co(pmea)(O_2SO_2)]^+$ cation in MeCN solution.

2. Experimental

2.1. General

All materials were used as received and all reactions were carried out under aerobic conditions. The tripodal tetraamine ligands bis((2-pyridyl)methyl)-2-((2-pyridyl)ethyl)amine (pmea) and bis(2-(2-pyridyl)ethyl)(2-pyridylmethyl)amine (pmap) were prepared according to literature procedures [19]. ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer, High-Resolution mass spectra were recorded on a Bruker micrO-TOF-Q II mass spectrometer in positive electrospray ionization (ESI) mode and IR spectra were obtained using a Nicolet iS10 spectrophotometer, equipped with a SMART iTR ATR attachment.

2.2. Synthesis of [Co(pmea)(O₂SO₂)]ClO₄

A solution of $CoSO_4 \cdot 7H_2O$ (1.136 g, 4.041 × 10^{-3} mol) in water (24 mL) was added to a solution of pmea (1.228 g, 4.034 × 10^{-3} mol) in methanol (24 mL). To the resulting solution was then added, with stirring, a solution of $(NH_4)_2[Ce(O_2NO)_6]$ (4.431 g, 8.082 × 10^{-3} mol) dissolved in water (10 mL). The dark solution instantly precipitated a pale brown solid, which slowly turned pink/red over 2–3 h. Stirring was continued for 24 h, after which time the mixture was filtered through celite, and the deep wine-red filtrate was diluted with water and loaded on to a Sephadex SP-C25 cation exchange column. Elution with aqueous $NaClO_4$ (0.1 M) removed a pink/red band that contained the desired product. On taking the solution to low volume (rotevap) pink crystals were obtained. These were removed by filtration, washed with 2 × 5 mL of ice-cold water, 2 × 5 mL of acetone, and air-dried. (0.38 g, 17%) ^1H NMR (400 MHz, D_2O): δ 8.96 (d, 1H), 8.89 (d, 1H), 8.82 (d, 1H), 8.69 (d, 1H), 8.22 (m, 3H), 8.09 (m, 1H), 7.95 (m, 2H), 7.85 (t, 1H), 7.75 (m, 6H), 7.33 (m, 2H), 5.45 (d, 2H), 5.45 (d, 1H), 4.50 (d, 1H), 3.87 (m, 1H), 3.53 (m, 1H). ^{13}C NMR (100 MHz, D_2O): δ 163.5, 162.1, 160.2, 159.1, 152.0, 151.4, 150.8, 150. 2, 149.5, 142.3, 141.5, 141.2, 141.1, 127.8, 127.6, 126.8, 126.5, 125.9, 124.5, 123.8, 122.3, 68.8, 67.7, 59.3, 57.3, 33.3, 32.0.

2.3. Synthesis of [Co(pmap)(O₂SO₂)]ClO₄

To a solution of pmap (1.25 g, 3.93 × 10^{-3} mol) in methanol (24 mL) was added a solution of $CoSO_4 \cdot 7H_2O$ (1.14 g, 4.01 × 10^{-3}-mol) in water (24 mL). To this was added a suspension of Oxone ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) (5.03 g, 8.18 × 10^{-3} mol) in water (10 mL) which resulted in a suspension in which the supernatant was dark red/purple. The mixture was stirred for 90 min at room temperature, filtered through celite, and the filtrate diluted to 1 L and loaded onto a Sephadex SP-C25 column. Elution with aqueous $NaClO_4$ (0.1 M) gave a pink band, which was collected and reduced in volume (rotevap). Removal of approximately half of the solvent resulted in the formation of small purple crystals. Evaporation was stopped at this stage, and the solution was cooled on ice. The purple crystals were removed by filtration, washed with a small volume of ice-cold water, and dried in a vacuum desiccator. (0.134 g, 6%). ^1H NMR (400 MHz, CD_3CN) δ 9.22 (d, 1H), 8.72 (d, 1H), 8.12 (td, 1H), 8.01 (tdd, 2H), 7.80 (m, 2H), 7.73 (d, 1H), 7.63 (t, 2H), 7.35 (t, 2H), 5.13 (d, 1H), 4.33 (d, 1H), 4.04 (ddd, 1H), 3.45 (m, 2H), 3.05 (dd, 1H), 2.94 (dt, 1H), 2.79 (m, 2H), 2.65 (m, 1H) ^1H NMR (400 MHz, D_2O) δ 9.00 (d, 1H), 8.82 (d, 1H), 8.18 (t, 1H), 8.04 (m, 2H), 7.81 (m, 3H), 7.71 (d, 2H), 7.38 (m, 2H), 5.14 (d, 1H), 4,38 (d, 1H), 3.92 (t, 1H), 3.56 (m, 2H), 3.12 (d, 1H), 2.89 (d, 2H), 2.75 (d, 2H) ^{13}C NMR (100 MHz, CD_3CN): δ 163.6, 162.5, 160.1, 153.7, 151.8, 150.9, 142.0, 141.43, 141.41, 127.9, 127.2, 126.6, 125.9, 124.8, 123.9, 67.7, 56.9, 55.6, 33.7, 32.0. UV/vis (H_2O) λ_{max} 517 nm.

2.4. X-ray structures of [Co(pmea)(O₂SO₂)]ClO₄ and [Co(pmap)(O₂SO₂)]ClO₄

X-ray quality crystals of $[Co(pmea)(O_2SO_2)]ClO_4$ and $[Co(pmap)(O_2SO_2)]ClO_4$ were obtained by crystallisation from aqueous $NaClO_4$ solution. X-ray data for these complexes were collected on a Rigaku Oxford Diffraction XtaLAB-Synergy-S single crystal diffractometer with a PILATUS 200 K hybrid pixel array detector using Cu Kα radiation (λ = 1.54184 Å). The data were processed with the SHELX [20] and Olex2 [21] software packages. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were inserted at calculated positions and refined with a riding model or without restrictions.

3. Results and discussion

3.1. Synthesis and characterisation of [Co(pmea)(O₂SO₂)]ClO₄ and [Co(pmap)(O₂SO₂)]ClO₄

The syntheses of both $[Co(pmea)(O_2SO_2)]ClO_4$ and $[Co(pmap)(O_2SO_2)]ClO_4$ involved oxidation of a Co(II) precursor in the presence of the tetradentate N_4 ligand (Fig. 1).

We have previously found aerial oxidation of similar mixtures to be somewhat capricious – indeed, a H_2O/MeOH solution of Co(II) and tepa (tepa = tris((2-pyridyl)ethyl)amine) does not undergo aerial oxidation – and PbO_2 has been our preferred oxi-

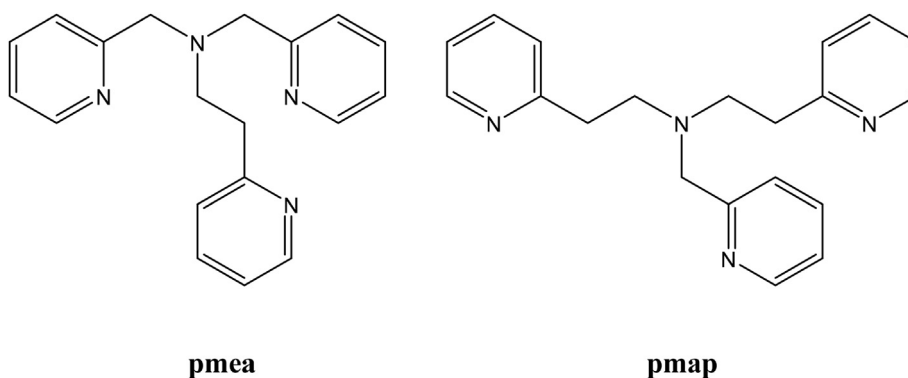**pmea**   **pmap**

Fig. 1. Structures of the pmea and pmap ligands.

dant in these types of systems. However, this reagent results in the formation of by-products which bind irreversibly to the Sephadex cation exchange resin used for product purification and we have therefore been interested in finding alternative oxidants. We have now found that both $(NH_4)_2[Ce(O_2NO)_6]$ and Oxone ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) can be used to oxidise a solution containing $CoSO_4 \cdot 7H_2O$ and the N_4 ligand (pmea or pmap) to obtain the Co(III) sulfato complexes. The former oxidant has been used previously to prepare Co(III) complexes, albeit rarely, [22] while the latter is often used in combination with Co(II) salts to oxidise and/or degrade organic substrates [23,24]. The complexes crystallised from the aqueous $NaClO_4$ eluent following column chromatography using Sephadex SP-C25 cation exchange resin. The positive ion ESI-MS of $[Co(pmea)(O_2SO_2)]ClO_4$ shows a base peak at m/z 459.0549, which corresponds to the $[Co(pmea)(O_2SO_2)]^+$ ion (m/z 459.0532, 3.7 ppm). None of the few other peaks in the spectrum display greater than 5% of the intensity of the base peak. The corresponding spectrum of $[Co(pmap)(O_2SO_2)]ClO_4$ shows a base peak at m/z 473.0684, which was assigned to the $[Co(pmap)(O_2SO_2)]^+$ cation (m/z 473.0688, 0.8 ppm). The only other peak of significant intensity in the spectrum was observed at m/z 422.1143, consistent with $[Co(pmap)(O_2CH)]^+$; formate ion is used to calibrate the spectrometer, and is presumably scavenged very efficiently by the $[Co(pmap)]^{2+}$ fragment. No infrared data have been reported for any of the three extant structurally characterised Co(III) complexes containing chelated sulfate. Barraclough and Tobe detailed IR data for the complex they believed to be $[Co(en)_2(O_2SO_2)]Br$ (bands at 1211 cm^{-1}, 1176 cm^{-1} and 1075 cm^{-1} were ascribed to the chelated sulfate ligand), but, as stated above, this was later shown to be the dimeric complex $\{[Co(en)_2(OS(O)_2O)]_2\}^{2+}$, containing bridging monodentate sulfato ligands. Comparison of the IR spectra of $[Co(pmap)(O_2CO)]ClO_4$ and $[Co(pmap)(O_2SO_2)]ClO_4$ allows us to tentatively assign bands at 1271 cm^{-1} (s), 1162 cm^{-1} (s), 918 cm^{-1} (m), 899 cm^{-1} (m) and 659 cm^{-1} (m), which are present only in the spectrum of the latter, to the chelated sulfato ligands. Analogous bands at 1268 cm^{-1} (m), 1163 cm^{-1} (m), 909 cm^{-1} (m), 894 cm^{-1} (m) and

662 cm^{-1} (m) are present in the IR spectrum of $[Co(pmea)(O_2SO_2)]ClO_4$.

3.2. X-ray crystal structures of $[Co(pmea)O_2SO_2]ClO_4$ and $[Co(pmap)O_2SO_2]ClO_4$

Both $[Co(pmea)(O_2SO_2)]ClO_4$ and $[Co(pmap)(O_2SO_2)]ClO_4$ crystallised from aqueous $NaClO_4$ solution in the monoclinic crystal system, the former in the $P2_1/c$ space group, and the latter in the $P2_1$ space group. Refinement of the latter as a 2-component inversion twin was necessary, and data collection and refinement details are given in Table 1. Two crystallographically independent enantiomeric forms of the $[Co(pmap)(O_2SO_2)]^+$ cation are present in the structure of $[Co(pmap)(O_2SO_2)]ClO_4$ while the structure of $[Co(pmea)(O_2SO_2)]ClO_4$ shows an 85:15 co-crystallisation of the 6- and 5- geometric isomers; these are named for the positioning of a 6-membered, and 5-membered chelate ring, respectively, in the same plane as the four-membered chelate ring [7].

Both complexes have a Co(III) ion coordinated to all four N atoms of the tetradentate tripodal ligand, and two O atoms of a chelating sulfato ligand in a distorted octahedral geometry. The crystal structures confirm that the 6-isomer of $[Co(pmea)(O_2SO_2)]ClO_4$ (Fig. 2) predominates over the 5-isomer in the isomeric mixture, and $[Co(pmap)(O_2SO_2)]ClO_4$ (Fig. 3) crystallises solely as the 6-isomer.

The Co–N bonds in the pmea complex are shorter on average than those in the pmap complex (1.933 Å versus 1.959 Å, respectively), probably reflecting the greater number of 5-membered chelate rings in the former, with the attendant greater rigidity imposed by these. A similar trend was found in the structurally similar $[Co(pmea)O_2CO]^+$ and $[Co(pmap)O_2CO]^+$ cations [7]. The chelated sulfato ligand is bonded slightly asymmetrically in both complexes, with the S–O bonds involving the coordinated O atoms significantly longer than those to the terminal O atoms in all cases. While the dimensions of the sulfato chelate rings are substantially similar to those found in the three previously structurally characterised $[(N)_4Co(O_2SO_2)]^+$ chelates, the complexes reported here

Table 1
Crystal data and structure refinement details for $[Co(pmea)(O_2SO_2)]ClO_4$ and $[Co(pmap)(O_2SO_2)]ClO_4$.

Empirical formula	$C_{19}H_{20}ClCoN_4O_8S$ ($[Co(pmea)(O_2SO_2)]ClO_4$)	$C_{20}H_{22}ClCoN_4O_8S$ ($[Co(pmap)(O_2SO_2)]ClO_4$)
Formula weight	558.83	572.85
Temperature	107(9) K	109.60(16) K
Wavelength	1.54184 Å	1.54184 Å
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1$
Unit cell dimensions	a = 14.7054(3) Å	a = 8.53793(12) Å
	b = 8.87930(10) Å	b = 26.6620(3) Å
	c = 17.6350(3) Å	c = 10.30544(15) Å
	β = 114.636(2)°	β = 107.803(2)°
Volume	2093.06(7) Å^3	2233.58(5) Å^3
Z	4	4
Density (calculated)	1.773 Mg/m^3	1.704 Mg/m^3
Absorption coefficient	9.069 mm^{-1}	8.515 mm^{-1}
F(0 0 0)	1144	1176
Crystal size	0.22 × 0.12 × 0.08 mm^3	0.078 × 0.048 × 0.031 mm^3
Theta range for data collection	5.696–67.706°	5.599–67.733°
Index ranges	$-17 \leq h \leq 17, -10 \leq k \leq 10, -21 \leq l \leq 15$	$10 \leq h \leq 10, -32 \leq k \leq 32, -12 \leq l \leq 11$
Reflections collected	25,076	27,194
Independent reflections	3800 [R(int) = 0.0320]	7953 [R(int) = 0.0744]
Completeness to theta = 67.684°	99.9%	99.7%
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.43442	0.823 and 0.579
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	3800/6/321	7947/1/634
Goodness-of-fit on F^2	1.072	1.094
Final R indices [I > 2sigma(I)]	$R1$ = 0.0295, w$R2$ = 0.0728	$R1$ = 0.0447, w$R2$ = 0.1081
R indices (all data)	$R1$ = 0.0301, w$R2$ = 0.0731	$R1$ = 0.0501, w$R2$ = 0.1129
Absolute structure parameter		0.083(4)
Largest diff. peak and hole	0.46 and −0.41 e.Å^{-3}	0.62 and −0.83 e.Å^{-3}

Fig. 2. View of the 6-isomer of the [Co(pmea)(O$_2$SO$_2$)]$^+$ cation. Selected bond lengths (Å) and angles (°) Co(1)–N(4) 1.9115(18); Co(1)–O(2) 1.9260(14); Co(1)–N(3) 1.9281(17); Co(1)–O(1) 1.9316(14); Co(1)–N(1) 1.9466(19); Co(1)–N(2) 1.9451(17); S(1)–O(3) 1.4403(15); S(1)–O(4) 1.4420(16); S(1)–O(2) 1.5310(14); S(1)–O(1) 1.5326(15); N(4)–Co(1)–O(2) 89.14(7); N(4)–Co(1)–N(3) 172.51(7); O(2)–Co(1)–N(3) 88.53(7); N(4)–Co(1)–O(1) 93.15(7); O(2)–Co(1)–O(1) 73.85(6); N(3)–Co(1)–O(1) 93.05(7); N(4)–Co(1)–N(1) 85.37(8); O(2)–Co(1)–N(1) 91.46(8); N(3)–Co(1)–N(1) 85.37(8); O(1)–Co(1)–N(1) 165.27(8); N(4)–Co(1)–N(2) 91.65(7); O(2)–Co(1)–N(2) 171.41(6); N(3)–Co(1)–N(2) 91.71(7); O(1)–Co(1)–N(2) 97.57(7); N(1)–Co(1)–N(2) 97.12(8); O(3)–S(1)–O(4) 113.89(9); O(3)–S(1)–O(2) 111.11(9); O(4)–S(1)–O(2) 110.44(9); O(3)–S(1)–O(1) 111.33(9); O(4)–S(1)–O(1) 110.72(9); O(2)–S(1)–O(1) 98.31(8).

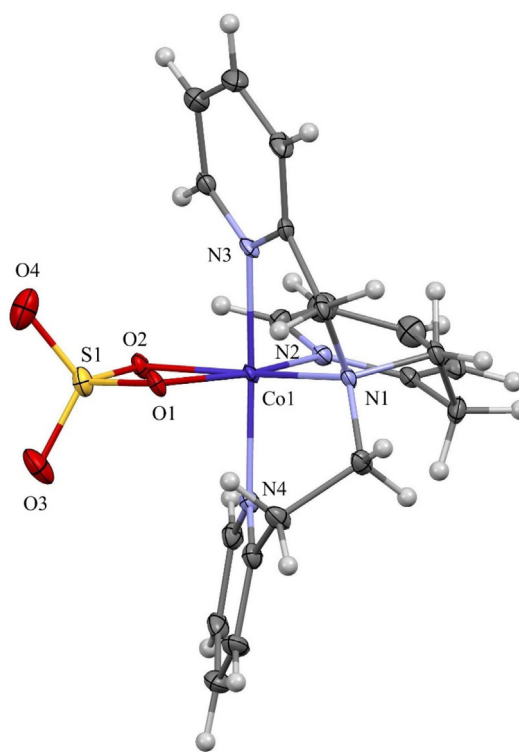**Fig. 3.** View of one of the two [Co(pmap)(O$_2$SO$_2$)]$^+$ cations present in the unit cell. Selected bond lengths (Å) and angles (°) Co(1)–N(14) 1.945(5); Co(1)–O(2) 1.932(4); Co(1)–N(13) 1.942(5); Co(1)–O(1) 1.934(4); Co(1)–N(11) 1.984(4); Co(1)–N(12) 1.964(5); S(1)–O(3) 1.436(5); S(1)–O(4) 1.437(5); S(1)–O(2) 1.537(4); S(1)–O(1) 1.528(4); O(2)–Co(1)–O(1) 73.18(15); O(2)–Co(1)–N(13) 85.71(18); O(1)–Co(1)–N(13) 92.04(18); O(2)–Co(1)–N(14) 89.15(19); O(1)–Co(1)–N(14) 89.75(18); N(13)–Co(1)–N(14) 173.82(19); O(2)–Co(1)–N(12) 165.79(17); O(1)–Co(1)–N(12) 92.86(18); N(13)–Co(1)–N(12) 92.35(19); N(14)–Co(1)–N(12) 93.5(2); O(2)–Co(1)–N(11) 95.49(17); O(1)–Co(1)–N(11) 168.33(18); N(13)–Co(1)–N(11) 84.18(19); N(14)–Co(1)–N(11) 92.91(19); N(12)–Co(1)–N(11) 98.32(19); O(3)–S(1)–O(4) 114.7(3); O(3)–S(1)–O(1) 110.9(2); O(4)–S(1)–O(1) 110.9(2); O(3)–S(1)–O(2) 110.7(2); O(4)–S(1)–O(2) 110.8(2); O(1)–S(1)–O(2) 97.5(2).

exhibit slightly shorter Co–O bonds (1.932 Å, 1.934 Å, 1.934 Å, 1.937 Å, 1.9260 Å, 1.9316 Å) and correspondingly larger O–Co–O bond angles (73.18°, 73.18°, 73.85°) than those previously reported (1.947 Å, 1.947 Å, 1.950 Å, 1.975 Å, 1.954 Å, 1.952 Å; 72.58°, 71.80°, 72.84°) [16–18].

Offset π-π interactions between ligand pyridyl rings of neighbouring cations are present in both complexes. [Co(pmea)(O$_2$SO$_2$)]ClO$_4$ displays a centroid-centroid distance of 3.820 Å while the analogous distance in [Co(pmap)(O$_2$SO$_2$)]ClO$_4$ is 3.866 Å.

3.3. Fluxional behaviour of [Co(pmea)(O$_2$SO$_2$)]$^+$

^{13}C NMR spectra have previously proven useful in distinguishing between geometric isomers of coordination complexes formed as a consequence of differing arm lengths of tripodal tetraamine ligands [7,25]. For example, the 5- and 6-isomers of [Co(pmap)(O$_2$CO)]$^+$ should display 3 and 5 peaks, respectively, in the aliphatic region of the ^{13}C NMR spectra; observation of 5 peaks showed that the crystallographically characterised 6-isomer was present in aqueous (D$_2$O) solution [7]. In this case, the ^{13}C NMR spectrum of [Co(pmap)(O$_2$SO$_2$)]$^+$ at 25.0 °C displays 5 peaks in the aliphatic region, showing that the 6-isomer observed in the crystal structure persists in solution. However, the ^{13}C NMR spectrum of [Co(pmea)(O$_2$SO$_2$)]$^+$ in this region at 25.0 °C displays 6 peaks, rather than the expected 3 for the 6-isomer of this ion, 4 for the 5-isomer, or 7 for a mixture of the two. VT-NMR confirmed this ion to be fluxional, as was also found for [Co(pmea)O$_2$CO]$^+$ [7]. At −30 °C in d_3-MeCN, 7

peaks are observed in the aliphatic region of the ^{13}C NMR spectrum of [Co(pmea)(O$_2$SO$_2$)]$^+$, consistent with the presence of both the 5- and 6-isomers, as was found in the solid state. However, integration of the ^{1}H spectrum at −30 °C (see below) gives a very different ratio of the isomers (~60:40) to that found in the X-ray structure (85:15), suggesting that isomerisation may occur in solution, as was seen in [Co(pmea)O$_2$CO]$^+$ (albeit only at high temperature). VT ^{1}H NMR was used to study the fluxional process in detail, and Fig. 4 shows spectra recorded over the temperature range −30 °C to 60 °C in d_3-MeCN.

The signals situated between δ = 4.00 and δ = 5.50 ppm arise from geminal coupling of the eight –CH$_2$– protons in the two rigid 5-membered chelate rings of the 5- and the 6-isomers of [Co(pmea)(O$_2$SO$_2$)]$^+$. At −30 °C, 6 sets of signals are observed, the lowest field of which comprises a pair of overlapping doublets. Integration of the doublet centred at 4.63 ppm strongly suggests that this arises from a pair of coincident doublets, one from each isomer. Hence all eight –CH$_2$– protons can be accounted for, and these are labelled **a**–**h** in Fig. 4. The NOESY spectrum at −30 °C shows that the **b** and **c** doublets centred at 5.22 ppm and 5.01 ppm are the only ones that display no correlation with the –CH$_2$–CH$_2$– protons of the 6-membered chelate ring, and these can therefore be assigned to the H$_a$ and H$_a$* protons of the 5-membered chelate rings (Fig. 5). Integration of the coupled **c** and **d** doublets, and the coupled **g** and **h** doublets, gives a ratio of ~1.6:1, reflecting the isomeric ratio of the 6- to the 5-isomer. As the temperature
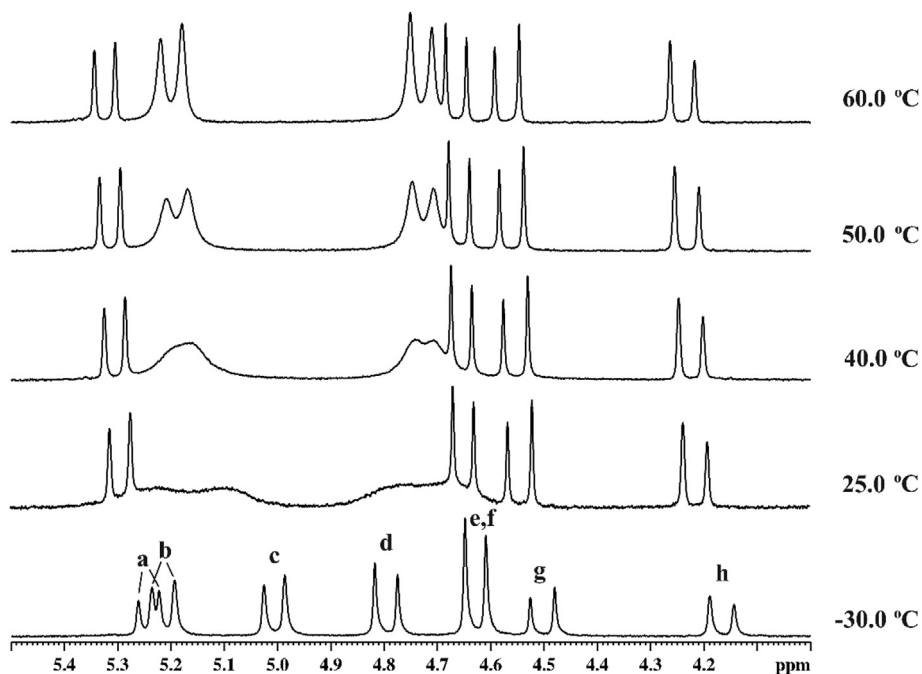
Fig. 4. Variable temperature ^{1}H NMR spectra of $[Co(pmea)(O_2SO_2)]^+$ over the chemical shift range δ = 4.00–5.50 ppm, recorded in d_3-MeCN.
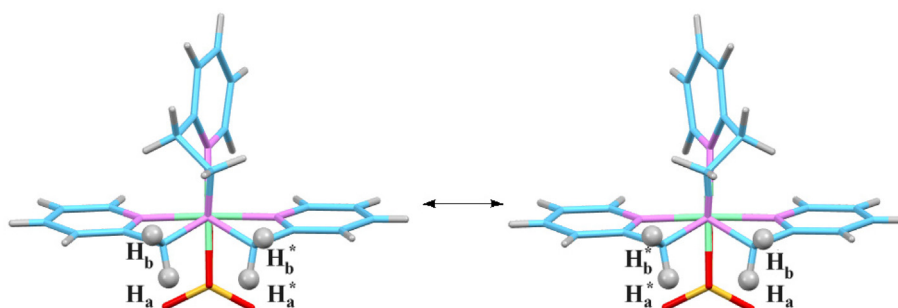

Fig. 5. The fluxional process involving 'flapping' of the six-membered chelate ring that renders H_a and H_a^*, and H_b and H_b^*, apparently equivalent at high temperature in the 6-isomer of the $[Co(pmea)(O_2SO_2)]^+$ cation.

is increased to 60 °C, the **b** and **c** doublets, and the **d** and one of the (**e, f**) doublets, gradually coalesce to give two doublets. This observation is consistent with a fluxional process occurring that results in the H_a, H_a^*, H_b and H_b^* protons of the 6-isomer, which are all inequivalent at low temperature, appearing as two sets of apparently equivalent protons at high temperature. This process involves 'flapping' of the unique six-membered chelate ring; at low temperatures, the chelate ring is 'frozen' in one of two possible conformations, rendering the –CH$_2$– protons in the five-membered chelate rings all inequivalent (Fig. 5). Increasing the temperature causes the six-membered chelate ring to 'flap' increasingly rapidly between its two possible conformations, and this leads to the H_a and H_a^* protons, and the H_b and H_b^* protons in the five-membered chelate rings becoming apparently equivalent through formation of a virtual mirror plane. The 5-isomer remains essentially unaffected by temperature, as the symmetry of this isomer means that there is no way that the protons in the five-membered chelate rings can be rendered apparently equivalent.

3.4. Attempted synthesis of $[Co(pmap)(O_2SO(OH))]^{2+}$

We have previously shown that tripyridyl tripodal tetradentate amine ligands confer significant stability to complexes containing chelated hydrogencarbonato and hydrogenphosphato ligands. With this in mind, we attempted to prepare and isolate a chelated hydrogensulfato complex starting from $[Co(pmap)(O_2SO_2)]ClO_4$, given that there is only one structurally characterised example of such a chelate in the literature, namely the Zr(IV) complex $[(L_{OEt})_2$-$Zr_2(SO_4)_2(HSO_4)_2]$, where L_{OEt} is the Kläui ligand $[Co(\eta^5$-$C_5H_5)\{P(O)(OEt)_2\}_3]^-$ [26] The pmap, rather than the pmea, complex was chosen, as the analogous chelated carbonate complex $[Co(pmap)(O_2CO)]^+$ showed the greatest stability in strongly acidic solution of all the carbonate complexes prepared. Cautious dissolution of $[Co(pmap)(O_2SO_2)]ClO_4$ (63 mg) in concentrated H_2SO_4 (1.00 mL) gave an intensely deep purple solution. Following standing for 4 days at room temperature, during which time no solid precipitated, water (1.00 mL) was carefully added. Over 3 weeks, red crystals slowly formed, but X-ray crystallography showed these to be unchanged starting material. The same protocol with both 70% HNO_3 and 70% $HClO_4$ failed to give a tractable hydrogensulfate complex. No crystals were obtained from the magenta nitric acid solution, while the magenta perchloric acid solution, curiously, given the oxidising nature of $HClO_4$, turned pale pink over the 3 weeks, indicative of formation of Co(II). In hindsight, the failure to obtain a chelated hydrogensulfate complex is not surprising, given that the sulfate ion is significantly less basic than both the

carbonate and phosphate ions (pKa (HSO$_4^-$) ~ 1.9; pKa (HCO$_3^-$) ~ 10.3, pKa (HPO$_4^{2-}$) ~ 12.3). However, the stability of the starting material in the strongly acidic H_2SO_4 and HNO_3 solutions is impressive, attesting to the truly substitution-inert nature of Co(III) complexes. [27]

4. Conclusions

We have synthesised and characterised two rare examples of Co(III) complexes containing chelated sulfato ligands, and have shown the utility of using both $(NH_4)_2[Ce(O_2NO)_6]$ and Oxone as oxidants in these syntheses. The fluxionality of the [Co(pmea)(O$_2$SO$_2$)]$^+$ ion, similar to that found in the [Co(pmea)(O$_2$CO)]$^+$ ion, shows that the pmea ligand is ideal for preparing complexes exhibiting fluxional processes that can be easily observed using VT-NMR, and it is likely that similar unrecognised fluxional processes are operational in other 6-coordinate complexes containing the pmea ligand [28–32]. We are currently investigating the synthesis of other Co(III) oxoanion complexes containing the pmea ligand in order to determine whether or not such fluxional behaviour is a general phenomenon.

CRediT authorship contribution statement

Poornasha K. Mohabeer: Investigation. **Bronte Carr:** Investigation. **Muhammad Hanif:** Investigation. **Christian Hartinger:** Formal analysis. **Tatiana Groutso:** Investigation. **Rebecca E. Jelley:** Writing - original draft, Visualization. **Tilo Söhnel:** Formal analysis. **Allan G. Blackman:** Conceptualization, Project administration, Resources, Writing - original draft, Writing - review & editing, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

CCDC 1969850 contains the supplementary crystallographic data for [Co(pmea)(O$_2$SO$_2$)]ClO$_4$, while CCDC 1969851 contains the supplementary crystallographic data for [Co(pmap)(O$_2$SO$_2$)]ClO$_4$. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Sup-

plementary data to this article can be found online at https://doi.org/10.1016/j.poly.2019.114303.

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