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The chemistry of cobalt acetate. VIII. New members of the family of oxo-centred trimers, $[Co_3(\mu_3\text{-}O)(\mu\text{-}O_2CCH_3)_{5-p}(\mu\text{-}OR)_pL_5]^{2+}$ ($R = H$, alkyl, $L =$ ligand, $p = 0$–4). The preparation and characterisation of the trimeric tetrakis(μ-acetato)-(μ-hydroxo)-μ3-oxo-pentakis(pyridine)-tri-cobalt(III) hexafluorophosphate, $[Co_3(\mu_3\text{-}O)(\mu\text{-}O_2CCH_3)_4(\mu\text{-}OH)(C_5H_5N)_5][PF_6]_2$, and the preparation and crystal structure of the trimeric tris(μ-acetato)-(μ-hydroxo)-(μ-methoxo)-μ3-oxo-pentakis(pyridine)-tri-cobalt(III) hexafluorophosphate·methanol·water solvate $[Co_3(\mu_3\text{-}O)(\mu\text{-}O_2CCH_3)_3(\mu\text{-}OH)(\mu\text{-}OCH_3)(C_5H_5N)_5][PF_6]_2\cdot CH_3OH\cdot 0.25H_2O$

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Abstract

The isolation, characterisation and some reaction chemistry of salts of the new oxo-centred cobalt(III) acetate trimeric dications, $[Co_3(\mu_3\text{-}O)(\mu\text{-}O_2CCH_3)_4(\mu\text{-}OH)(C_5H_5N)_5]^{2+}$ (**15**), $[Co_3(\mu_3\text{-}O)(\mu\text{-}O_2CCH_3)_3(\mu\text{-}OH)(\mu\text{-}OCH_3)(C_5H_5N)_5]^{2+}$ (**16**) and $[Co_3(\mu_3\text{-}O)(\mu\text{-}O_2CCH_3)_3(\mu\text{-}OCH_3)_2(C_5H_5N)_5]^{2+}$ (**17**), and the X-ray crystal structure of (**16**)$[PF_6]_2\cdot CH_3OH\cdot 0.25H_2O$ (refined to $R(F) = 0.0639$, $R_w(F)$ 2 0.0569) are reported. The compound (**16**)$[PF_6]_2\cdot CH_3OH\cdot 0.25H_2O$ crystallises in space group $P2_1/n$ (No. 14). The oxo-centred trimer has a Co_3ON_5 core, with the μ3-O atom 0.707 Å out of the plane of the approximately isosceles triangle formed by the three near-octahedrally co-ordinated cobalt atoms. The Co···Co distances are 2.778(1), 2.796(1) and 3.326(1) Å, and the Co–(μ3-O) distances are 1.8865(4), 1.880(4) and 1.883(4) Å. The existence of an extensive series of compounds in 'cobalt(III) acetate' is discussed, and the trinuclear species shown to have stoichiometries described by $[Co_3(\mu_3\text{-}O)(OAc)_{6-x-n}(OR)_n(L)_{3+y+2x}]^{(x+1)+}$ $(0 \le y \le 3,\ 0 \le x \le (3-y),\ 0 \le n \le (5-x)$ $L =$ ancillary ligand, e.g. py, MeCN, H_2O, solvent).

Keywords: Cobalt acetate; Oxo-centred trimers; Ancillary ligands; X-ray crystal structures

1. Introduction

'Cobalt acetate' is the 'simplest' representative of perhaps one of the most complex homogeneous catalysts in use [1,2]. Cobalt carboxylates find extensive use in the oxidations of hydrocarbons. They find particular application in the oxidation of *p*-xylene to terephthalic acid or dimethyl terephthalate (the largest industrial use of homogeneous catalysts), the oxidations of other methylbenzenes to their respective acids, of cyclohexane to cyclohexanol and cyclohexanone in the generation of adipic acid for nylon synthesis, the oxidations of butane, acetaldehyde or ethanol to acetic acid and in the production of dodecanoic acid and lauryl lactam from cyclododecane. Ozone oxidation of $[Co(OAc)_2]$ to a

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species presumed to be '$[Co_3O(OAc)_6(AcOH)_3]$' improves the batch oxidation of butane.

Cobalt(II) acetate has long been known and its solid-state structure has been established [3,4]. However, the nature of 'cobalt(III) acetate' is less well understood. First reported as a solid in 1924 [5], cobalt(III) acetate has never been structurally characterised as an unique material. Although suggested to be a mixture of materials, the exact composition (if there is one) of that mixture has not been established. A significant advance in the understanding of this material was provided by the isolation of the pyridine-ligated trimer, $[Co_3O(OAc)_6(py)_3]$ (py = pyridine) [6]—structurally characterised only relatively recently as the symmetric trimer, $[Co_3O(OAc)_6(py)_3]^+$ (**1**) [7]. Other cobalt(III) trimers have been prepared and the compounds structurally characterised [8–12]. In addition, dimeric species have been isolated from 'cobalt(III) acetate' and structurally characterised [12,13].

These pyridine-ligated species have also been demonstrated to be catalytically active in hydrocarbon oxidations and so are of relevance to the industrial use of cobalt carboxylates. Thus, the Co(III) clusters, $[Co_3O(OAc)_{6-n}(OH)_n(py)_3][PF_6]$ ($n = 0$ (**1**), $n = 1$ (**2**)), have been shown to be catalyst precursors for the autoxidations of aromatic hydrocarbons [10]. The complexes are thought to be effective because they increase the rate of decomposition of hydroperoxides formed during hydrocarbon oxidations [14]. In addition, 'cobalt acetate' derivatives have been studied as potential structural models of biological systems [9,15].

We and others have reported the structures of a range of cationic and neutral cobalt(III) dimers, $[Co_2(\mu\text{-}OH)_2((\mu\text{-}OAc)(OAc)_2(py)_4]^+$ (**3**) [12], $[Co_2(\mu\text{-}OH)_2(\mu\text{-}OAc)_3(bpy)_2]^+$ (**4**) [9,13], trimers, $[Co_3(\mu_3\text{-}O)(OAc)_6(py)_3]^+$ (**1**) [7], $[Co_3(\mu_3\text{-}O)(\mu\text{-}OH)(OAc)_5(py)_3]^+$ (**2**) [10], $[Co_3(\mu_3\text{-}O)(\mu\text{-}OH)_2(OAc)_3(py)_5]^+$ (**5**) [12], $[Co_3(\mu_3\text{-}O)(\mu\text{-}OCH_2CH_2CH_2Ph)(OAc)_5(py)_3]^+$ (**6**) [11], $[Co_3(\mu_3\text{-}O)(\mu\text{-}OH)_3(OAc)_2(py)_6]^{2+}$ (**7**) [8], $[Co_3(\mu_3\text{-}O)(\mu\text{-}OH)_3((\mu\text{-}OAc)(\mu\text{-}OAc)(bpy)_3]^{2+}$ (**8**) [9,13], tetramers, $[Co_4(\mu_3\text{-}O)_4(OAc)_4(py)_4]$ (**9**) [8], $[Co_4(\mu_3\text{-}O)_4(OAc)_2(bipy)_4]^{2+}$ (**10**), and octamers, $[Co_8(\mu\text{-}OMe)_{16}(OAc)_8]$ (**11**) [16], as well as the mixed-valence octameric species, $[Co_8(\mu_3\text{-}O)_4(OMe)_4(\mu\text{-}OAc)_6(OH_n)]^{2+}$ ($n = 1, 2$) (**12**) [17], $[Co_8O_4(OAc)_6(OH)_4L_2]^{2+}$ (**13**) [18], $[Co_8O_4(O_2CPh)_{12}(solv)_4]$ (solv = DMF, MeCN, H_2O) (**14**) [19].

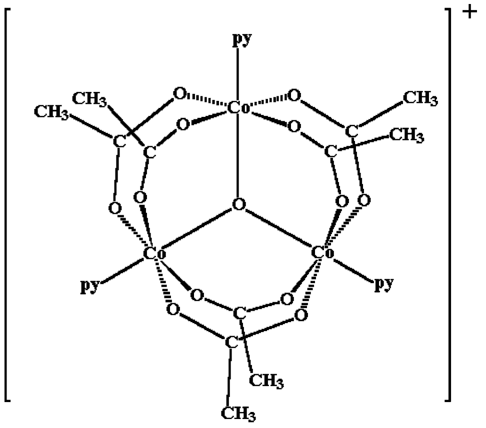
We report here the synthesis and characterisation of the dications, $[Co_3(\mu_3\text{-}O)(\mu\text{-}OH)(OAc)_4(py)_5]^{2+}$ (**15**), $[Co_3(\mu_3\text{-}O)(\mu\text{-}OH)(\mu\text{-}OMe)(OAc)_3(py)_5]^{2+}$ (**16**), and $[Co_3(\mu_3\text{-}O)(\mu\text{-}OMe)_2(OAc)_3(py)_5]^{2+}$ (**17**), which exemplify another structural type in the chemistry of cobalt acetate trimers.

2. Experimental

2.1. Chemicals

Warning: Perchlorate salts of metal complexes with organic ligands are potentially explosive and must be treated with care.

Cobalt(II) acetate tetrahydrate (Aldrich), acetic acid, sodium carbonate, sodium chloride (all Biolab), light



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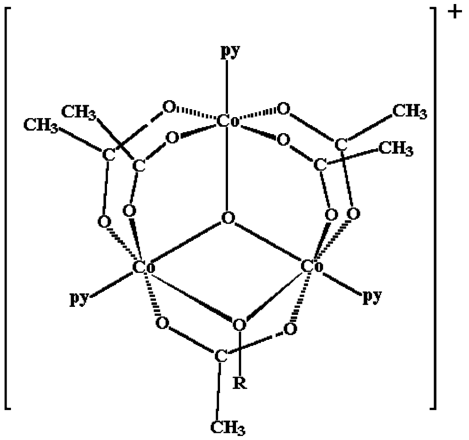
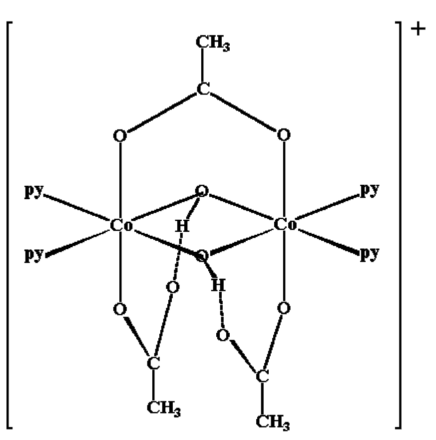


(R = H, 2)



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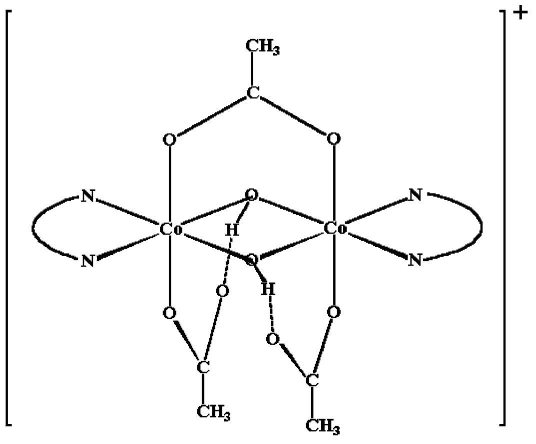

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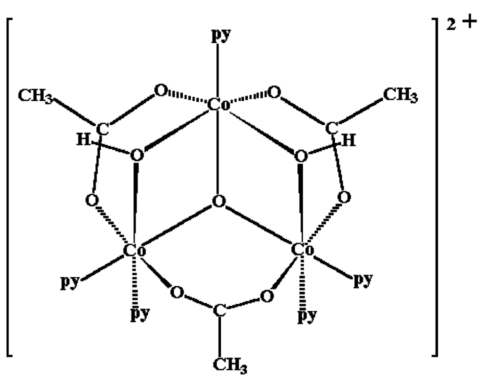

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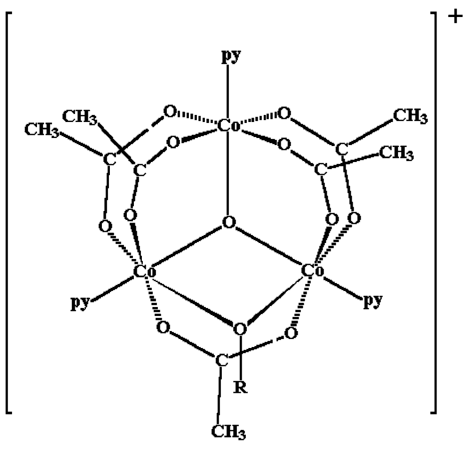
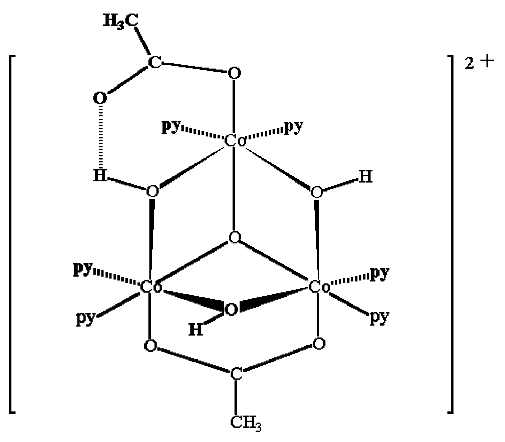
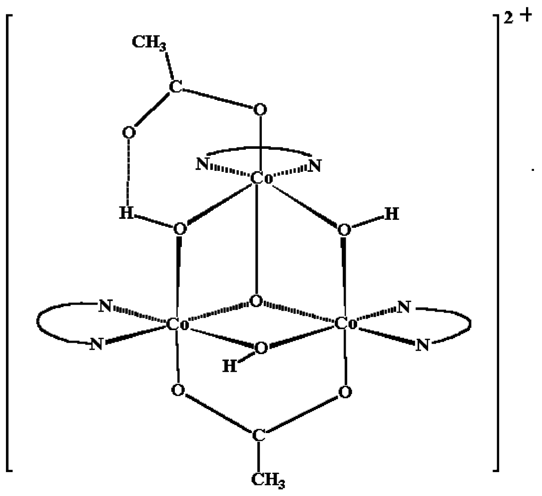


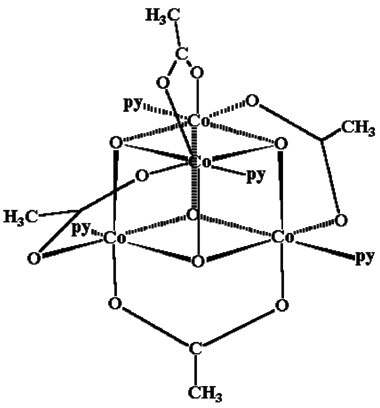
(**6** R = $CH_2CH_2CH_2Ph$)



(**7**)



(**8**)



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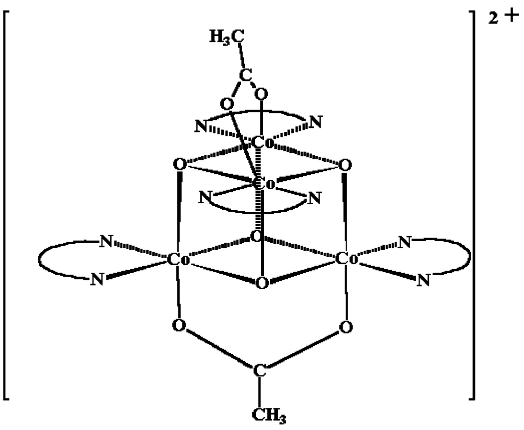

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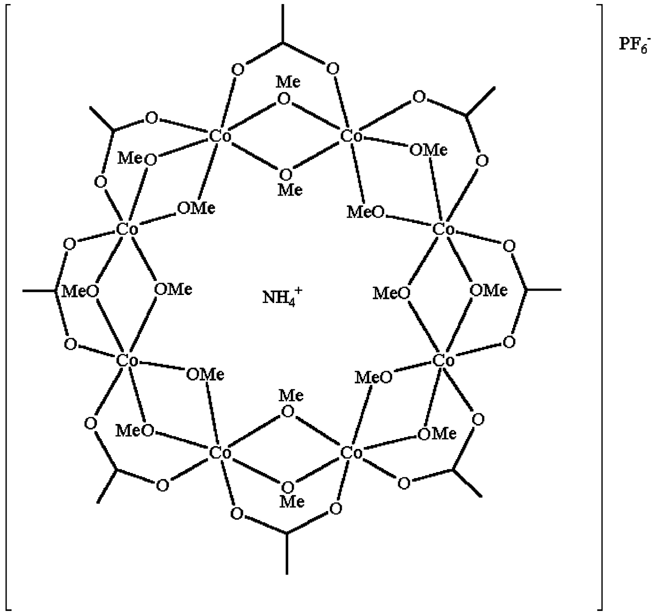

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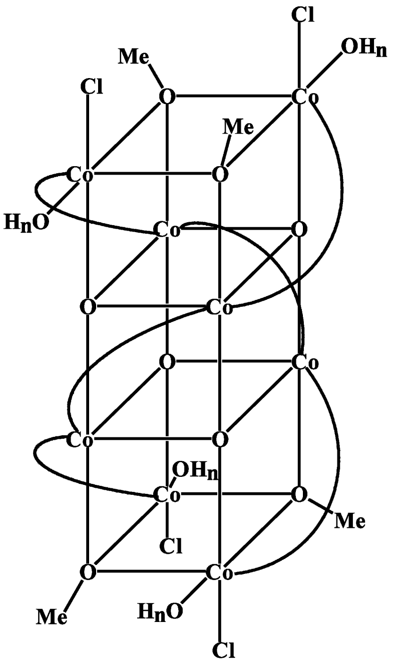
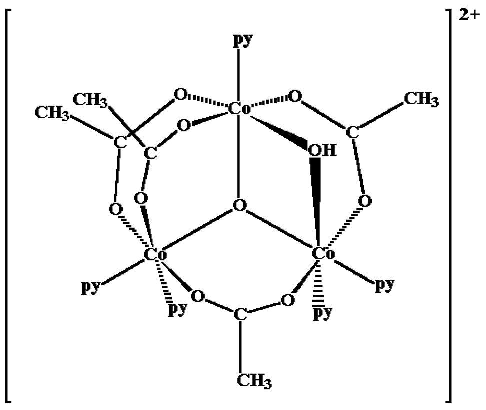


(12)

petroleum (BDH), acetic anhydride, ammonium hexafluorophosphate, dichloromethane, dimethylformamide, dimethylsulfoxide, ethanol, methanol, sodium perchlorate hydrate (all Merck), acetonitrile, chloroform, diethyl ether, pyridine (all Ajax) and hydrogen peroxide (27.5%, Pacific) were of analytical reagent grade and were used as received. Dimethylsulfoxide was dried over molecular sieves (4A) for several days before use. Deuterated chloroform, deuterated acetonitrile, perdeuteroacetic acid, perdeuteromethanol, deuterated dimethylsulfoxide, deuterated dichloromethane, deuterium oxide and tetramethylsilane (all Aldrich) were used as received. Cobalt(III) acetate was prepared as reported previously [8]. Ozone was produced by a Wallace and Tiernan laboratory ozonator (model BA-023012).



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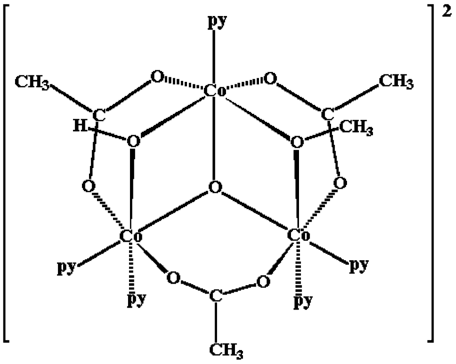

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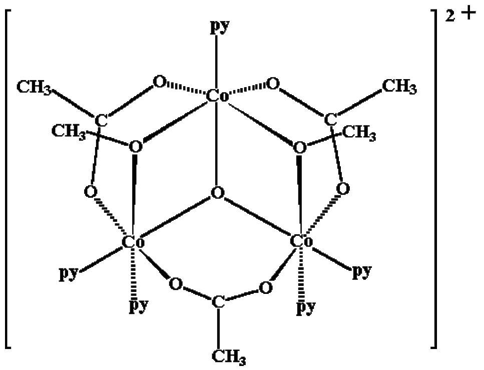

(17)

2.2. *Tetrakis(μ-acetato)(μ-hydroxo)-μ_3-oxo-pentakis(pyridine)tricobalt(III) hexafluorophosphate* $[Co_3(\mu_3\text{-}O)(\mu\text{-}OH)(\mu\text{-}OAc)_4(py)_5][PF_6]_2$ *(**15**$[PF_6]_2$)*

Cobalt(II) acetate tetrahydrate (3.13 g, 12.5 mmol), acetic acid (25 ml), and pyridine (2 g, 25.3 mmol) were combined and the mixture stirred overnight precipitating anhydrous cobalt(II) acetate. The mixture was ozonated (2 h, '250 V', ~50 l h^{-1}) with stirring. During ozonation the mixture changed colour from red/purple to dark brown/red. Ammonium hexafluorophosphate (1.36 g, 8.3 mmol), dissolved in water (5 ml), was then added with stirring. The resulting mixture was cooled to below 5 °C for 2 days. The resulting red/brown precipitate (0.80 g) was collected by filtration, washed with water ($<$ 20 ml), and dried over silica gel overnight. The solid was observed by solution ^{1}H NMR in CD_3CN to contain mainly the symmetric trimer, $[Co_3(\mu_3\text{-}O)(\mu\text{-}OAc)_6(py)_3][PF_6]$ ([**1**]$[PF_6]$), $[Co_3(\mu_3\text{-}O)(\mu\text{-}OH)(\mu\text{-}OAc)_5(py)_3][PF_6]$ ([**2**]$[PF_6]$) and $[Co_3(\mu_3\text{-}O)(\mu\text{-}OH)(\mu\text{-}OAc)_4(py)_5][PF_6]_2$ ([**15**]$[PF_6]_2$). The filtrate was combined with the water washings and left for another week at below 5 °C. More brown solid (1.90 g) was precipitated and was found by ^{1}H NMR in CD_3CN to contain a mixture of species including $[Co_3(\mu_3\text{-}O)(\mu\text{-}OH)(\mu\text{-}OAc)_5(py)_3][PF_6]$ ([**2**]$[PF_6]$), $[Co_3(\mu_3\text{-}O)(\mu\text{-}OH)(\mu\text{-}OAc)_4(py)_5][PF_6]_2$ ([**15**]$[PF_6]_2$), and $[Co_2(\mu\text{-}OH)_2((\mu\text{-}OAc)(OAc)_2(py)_3(H_2O)][PF_6]$. The remaining filtrate was extracted with dichloromethane (150 ml total) and the extract washed successively with water, sodium carbonate solution and sodium chloride solution. The brown solution was dried over anhydrous magnesium sulfate, filtered, the solvent evaporated and the solid dried at reduced pressure. The resulting brown solid (0.9 g) was found by solution ^{1}H NMR in CD_3CN to contain a mixture of species including $[Co_3(\mu_3\text{-}O)(\mu\text{-}OH)_2(\mu\text{-}OAc)_3(py)_5][PF_6]_2$ (**5**$[PF_6]_2$), dimers and $[Co_3(\mu_3\text{-}O)(\mu\text{-}OH)(\mu\text{-}OAc)_4(py)_5][PF_6]_2$ (**15**$[PF_6]_2$). The first solid was examined by TLC on flash silica using dichloro-

Table 1
^{1}H NMR chemical shifts (ppm) of the acetate, hydroxy, methoxy and pyridine protons for selected polynuclear cobalt(III) carboxylate species (200 MHz)

Complex	Solvent (reference)	Acetate methyl protons	Hydroxyl proton(s)	Pyridine α, β, χ-protons	Other protons
$[Co_3O(OAc)_6py_3][PF_6]$ [**1**]$[PF_6]$	CD_2Cl_2 (TMS)	2.11 (s, 18H)		8.90 (d, H), 8.08 (t, H), 7.70 (t, 6H)	
	CD_3CN (TMS)	2.07 (s, 18H)		8.90 (d, 6H), 8.15 (t, 3H), 7.74 (t, 6H)	
	$CDCl_3$ (TMS)	2.12 (s, 18H)		8.90 (d, 6H), 8.06 (t, 3H), 7.71 (t, 6H)	
	CD_3CO_2D (TMS)	2.06 (s, 18H)		8.98 (d, 6H), 8.17 (t, 3H), 7.78 (t, 6H)	
	CD_3OD (TMS)	2.10 (s, 18H)		8.98 (d, 6H), 8.16 (t, 3H), 7.77 (t, 6H)	
$[Co_3O(OMe)(OAc)_5py_3][PF_6]$ [**6a**]$[PF_6]$	CD_3CN (TMS)	2.22 (s, 3H), 2.20 (s, 6H), 1.87 (s, 6H)		9.27 (d, 2H), 8.68 (d, 4H), 8.31 (t, 1H), 8.21 (t, 2H), 7.93 (t, 2H), 7.79 (t, 4H)	0.73 (s, 3H)
	CD_2Cl_2 (TMS)	2.23 (s, 3H), 2.17 (s, 6H), 1.94 (s, 6H)		9.20 (d, 2H), 8.62 (d, 4H), 8.25 (t, 1H), 8.11 (t, 2H), 7.89 (t, 2H), 7.73 (t, 4H)	0.77 (s, 3H)
$[Co_3O(OMe)(OAc)_5py_3][ClO_4]$ [**6a**]$[ClO_4]$	CD_2Cl_2 (TMS)	2.23 (s, 3H), 2.18 (s, 6H), 1.95 (s, 6H)		9.20 (d, 2H), 8.63 (d, 4H), 8.25 (t, 1H), 8.12 (t, 2H), 7.89 (t, 2H), 7.75 (t, 4H)	0.77 (s, 3H)
	CD_3CN (TMS)	2.15 (s, 3H), 2.15 (s, 6H), 1.87 (s, 6H)		9.27 (d, 2H), 8.69 (d, 4H), 8.31 (t, 1H), 8.18 (t, 2H), 7.93 (t, 2H), 7.79 (t, 4H)	0.73 (s, 3H)
$[Co_3O(OMe)(OAc)_5py_3][PF_6]$ [**6a**]$[PF_6]$	CD_3OD (TMS)	2.20 (s, 3H), 2.20 (s, 6H), 1.92 (s, 6H)		9.27 (d, 2H), 8.69 (d, 4H), 8.31 (t, 1H), 8.18 (t, 2H), 7.93 (t, 2H), 7.79 (t, 4H)	0.80 (s, 3H)
$[Co_3O(OH)(OAc)_5py_3][PF_6]$ [**2**]$[PF_6]$	CD_2Cl_2 (TMS)	2.17 (s, 3H), 2.10 (s, 6H), 2.01 (s, 6H)	−4.27 (br, 1H)	9.19 (d, 2H), 8.74 (d, 4H), 8.25 (t, 1H), 8.11 (t, 2H), 7.89 (t, 2H), 7.73 (t, 4H)	
	CD_3CN (TMS)	2.08 (s, 3H), 2.05 (s, 6H), 1.95 (s, 6H)	−3.09 (s, 1H)	9.26 (d, 2H), 8.83 (d, 4H), 8.31 (t, 1H), 8.18 (t, 2H), 7.92 (t, 2H), 7.76 (t, 4H)	
	$CDCl_3$ (TMS)	2.18 (s, 3H), 2.15 (s, 6H), 2.02 (s, 6H)	−3.81 (br, 1H)	9.26 (d, 2H), 8.88 (d, 4H), 8.21 (t, 1H), 8.02 (t, 2H), 7.88 (t, 2H), 7.71 (t, 4H)	
	CD_3OD (TMS)	2.09 (s, 3H), 2.08 (s, 6H), 2.00 (s, 6H)	*	9.26 (d, 2H), 8.99 (d, 4H), 8.30 (t, 1H), 8.12 (t, 2H), 7.93 (t, 2H), 7.77 (t, 4H)	
$[Co_3O(OH)_2(OAc)_3py_5][PF6]_2$ [**5**]$[PF_6]_2$	CD_3CN (TMS)	2.56 (s, 3H), 2.23 (s, 6H)	−1.71 (s, 2H)	8.86 (d, 2H), 8.41 (d, 4H), 8.01 (m, 3H), 7.93 (d, 4H), 7.64 (m, 4H), 7.53 (t, 4H), 7.12 (t, 4H)	
	CD_2Cl_2 (TMS)	2.68 (s, 3H), 2.35 (s, 6H)	−2.3(br, 2H)	8.62 (d, 2H), 8.37 (d, 4H), 7.99 (m, 3H), 7.92 (d, 4H), 7.64 (t, 2H), 7.55 (t, 2H), 7.52 (t, 4H), 7.18 (t, 4H)	
	CD_3OD (TMS)	2.61 (s, 3H), 2.29 (s, 6H)	*	9.06 (d, 2H), 8.49 (d, 4H), 8.09 (m, 3H), 8.01 (d, 4H), 7.68 (m, 4H), 7.56 (t, 4H), 7.21 (t, 4H)	
$[Co_3O(OH)(OMe)(OAc)_3py_5][PF_6]_2$ [**16**]$[PF_6]_2$	CD_3CN (TMS)	2.68 (s, 3H), 2.49 (s, 3H), 2.16 (s, 3H)	−1.45 (s, 1H)	8.86 (d, 2H), 8.64 (d, 2H), 8.44 (d, 2H), 8.03 (m, 3H), 7.89 (d, 4H), 7.73 (t, 4H), 7.59 (t, 4H), 7.06 (m, 4H)	1.14 (s, 3H)
	CD_3OD (TMS)	2.76 (s, 3H), 2.56 (s, 3H), 2.22 (s, 3H)	*	9.12 (d, 2H), 8.74 (d, 2H), 8.48 (d, 2H), 8.05 (m, 3H), 7.84 (d, 4H), 7.74 (t, 4H), 7.62 (t, 4H), 7.18 (m, 4H)	1.12 (s, 3H)
$[Co_3O(OMe)_2(OAc)_3py_5][PF_6]_2$ [**17**]$[PF_6]_2$	CD_3CN (TMS)	2.82 (s, 3H), 2.41 (s, 6H)		?	1.31 (s, 6H)
	CD_3OD (TMS)	2.92 (s, 3H), 2.49 (s, 6H)		?	1.23 (s, 6H)
$[Co_3O(OH)(OAc)_4py_5][PF_6]_2$ [**15**]$[PF_6]_2$	CD_3CN (TMS)	2.57 (s, 3H), 2.41 (s, 3H), 2.22 (s, 3H), 2.13 (s, 3H)	−1.69 (s, 1H)	8.81 (d, 2H), 8.49 (d, 2H), 8.39 (d, 2H), 8.12 (t, 1H), 8.08 (t, 1H), 7.96 (t, 1H). 7.70 (t, 2H), 7.60 (t, 2H), 7.50 (t, 2H), 7.19 (br, d, 2H), 6.70 (br, t, 2H)	
	CD_2Cl_2 (TMS)	2.67 (s, 3H), 2.49 (s, 3H), 2.33 (s, 3H), 2.17 (s, 3H)	−2.76 (s, 1H)	8.84 (d, 2H), 8.44 (d, 2H), 8.37 (d, 2H), 8.03, 7.66, 7.51, (multiplets and broad peaks) 7.2 (br), 6.8 (br)	
$[Co_3O(OH)_3(OAc)_2py_6]^{2+}$ [**7**]$[PF_6]_2$	CD_3CN (TMS)	0.88 (s, 3H), 2.15 (s, 3H)	−2.75 (s, 1H), −0.36 (s, 1H), 5.17 (s, 1H)	9.5–6.8 (multiplets and broad peaks)	
	CD_2Cl_2 (TMS)	0.92 (s, 3H), 2.24 (s, 3H)	−3.33 (s, 1H), −1.61 (s, 1H), 5.62 (s, 1H)	9.6–6.8 (multiplets and broad peaks)	

methane–acetonitrile (4:1) and the three fractions (red; $R_f = 0.84$, brown; $R_f = 0.77$, and brown; $R_f = 0.45$) were confirmed by ^{1}H NMR spectroscopy to be the symmetric trimer, $[Co_3(\mu_3\text{-}O)(OAc)_6(py)_3][PF_6]$ (**1**$[PF_6]$), $[Co_3(\mu_3\text{-}O)(\mu\text{-}OH)(OAc)_5(py)_3][PF_6]$ (**2**$[PF_6]$), and $[Co_3(\mu_3\text{-}O)(\mu\text{-}OH)(\mu\text{-}OAc)_4(py)_5][PF_6]_2$ (**15**$[PF_6]_2$), respectively. Pure $Co_3(\mu_3\text{-}O)(OAc)_6(py)_3][PF_6]$ (**1**$[PF_6]$), $[Co_3(\mu_3\text{-}O)(\mu\text{-}OH)(OAc)_5(py)_3][PF_6]$ (**2**$[PF_6]$), and $[Co_3(\mu_3\text{-}O)(\mu\text{-}OH)(\mu\text{-}OAc)_4(py)_5][PF_6]_2$ (**15**$[PF_6]_2$) were subsequently isolated using column chromatography on flash silica. Large brown air sensitive crystals of $[Co_3(\mu_3\text{-}O)(\mu\text{-}OH)(\mu\text{-}OAc)_4(py)_5][PF_6]_2$ (**15**$[PF_6]_2$) were obtained upon slow diffusion of diethyl ether into dichloromethane solutions at low temperature (< 5 °C). The crystals lose solvent rapidly outside the mother liquor and several attempts to obtain a single crystal X-ray diffraction data set failed.

Anal. $[Co_3(\mu_3\text{-}O)(\mu\text{-}OH)(\mu\text{-}OAc)_4(py)_5][PF_6]_2$, Found: C, 34.82; H, 3.32; N, 6.07. $Co_3C_{33}H_{38}F_{12}N_5P_2O_{10}$ requires C, 35.01; H, 3.96; N, 6.19%.

Selected IR data (KBr): ν_{max} (cm^{-1}) 3517(vw), 3124(vw), 3091(vw), 3085(vw), 3057(vw), 3037(vw), 3010(vw), 2986(vw), 2942(vw), 2872(vw), 2484(vw), 1653(vw), 1608(w,sh), 1596(s), 1576(w), 1570(w), 1559(m), 1554(m), 1550(m), 1545(m), 1542(m), 1522(vw), 1507(vw), 1490(w), 1473(vw), 1451(vs), 1436(m,sh), 1429(m), 1420(m,sh), 1356(vw), 1241(vw), 1220(m), 1121(vw), 1070(w), 1046(vw), 1020(w), 986(vw), 966(vw), 959(vw), 876(m), 968(m), 853(sh), 842(vs), 789(vw), 767(m), 760(m), 740(vw), 725(vw), 705(m,sh), 700(s), 694(s), 668(vw), 651(vw), 647(w), 627(w), 558(s), 633(vw), 490(w), 473(vw), 462(vw), 419(vw), 415(vw), 410(vw), 403(vw).

Selected ^{1}H and ^{13}C NMR data (200 MHz; CD_3CN TMS), see Tables 1 and 2. Selected ESI MS data (*m*/*e*): 986.2 $[M-PF_6]^+$ (calc. 986.0), 420.8 $[M-2PF_6]^{2+}$ (calc. 420.5).

2.3. *Tris(μ-acetato)(μ-hydroxo)(μ-methoxo)-μ₃-oxo-pentakis(pyridine)tricobalt(III) hexafluorophosphate* $[Co_3(\mu_3\text{-}O)(\mu\text{-}OH)(\mu\text{-}OMe)(\mu\text{-}OAc)_3(py)_5][PF_6]_2$ *(**16**$[PF_6]_2$)*

2.3.1. *Air oxidation of cobalt(II) acetate tetrahydrate in methanol with pyridine*

A methanol (5 cm^3) solution of pyridine (0.5 g, 6 mmol) was added with stirring to a purple methanol (10 cm^3) solution of cobalt(II) acetate tetrahydrate (0.5 g, 2 mmol). Sodium hexafluorophosphate (~ 2.3 g, 1.3 mmol) in methanol (5 cm^3) was then added to the red/purple cobalt(II) solution. The solution was partially covered and allowed to slowly evaporate at room temperature (r.t.) over several weeks to months. The solution slowly turned dark brown and large crystals formed. The mixture was filtered and a solid (~ 0.1 g) containing a mixture of brown and red crystals was obtained. ^{1}H NMR in CD_3CN and CD_3OD showed the solid to contain a mixture of species including $[Co_3(\mu_3\text{-}O)(\mu\text{-}OH)(\mu\text{-}OMe)(\mu\text{-}OAc)_3(py)_5][PF_6]_2$ ([**16**]$[PF_6]_2$), and $[Co_2(\mu\text{-}OH)_2((\mu\text{-}OAc)(OAc)_2(py)_4][PF_6]$. Large dark brown, block-like crystals were physically separated from the other crystalline material. ^{1}H NMR in CD_3CN and ESI MS were used to identify the product as pure $[Co_3(\mu_3\text{-}O)(\mu\text{-}OH)(\mu\text{-}OMe)(\mu\text{-}OAc)_3(py)_5][PF_6]_2$ ([**16**]$[PF_6]_2$). A suitable crystal was used in a single crystal X-ray diffraction study. The filtrate was evaporated to dryness in air to form a dark brown solid ($\sim$ 0.36 g) which was found by ^{1}H NMR to be paramagnetic. The solid was washed through a short column of alumina with acetonitrile and the dark brown fraction obtained evaporated and dried in vacuo. ^{1}H NMR in CD_3CN showed the resulting brown solid to contain a mixture of species including $[Co_3(\mu_3\text{-}O)(\mu\text{-}OH)(\mu\text{-}OMe)(\mu\text{-}OAc)_3(py)_5]^{2+}$ (**16**), $[Co_3(\mu_3\text{-}O)(\mu\text{-}OMe)_2(\mu\text{-}OAc)_3(py)_5]^{2+}$ (**17**), $[Co_3(\mu_3\text{-}O)(\mu\text{-}OH)_2(\mu\text{-}OAc)_3(py)_5]^{2+}$ (**5**), $[Co_2(\mu\text{-}OH)_2((\mu\text{-}OAc)(OAc)_2(py)_4]^+$, and others not readily identified.

Spectroscopic data for $[Co_3(\mu_3\text{-}O)(\mu\text{-}OH)(\mu\text{-}OMe)(\mu\text{-}OAc)_3(py)_5][PF_6]_2$ ([**16**]$[PF_6]_2$). Selected IR data (KBr): ν_{max} (cm^{-1}) 3618 (vw), 3594(vw), 3566(vw), 3143(vw), 3117(vw), 3089(vw), 3054(vw), 3034(vw,sh), 3007(vw), 2995(vw), 2947(vw), 2929(vw), 2904(vw), 2813(vw), 2485(vw), 2403(vw), 2371(vw), 2317(vw), 2064(vw), 2022(vw), 2002(vw), 1967(vw), 1950(vw), 1942(vw), 1889(vw), 1868(vw), 1609(vw), 1582(s), 1570(m,sh), 1561(m,sh), 1534(vw), 1525(vw), 1521(w), 1507(vw), 1489(w), 1471(vw,sh), 1451(s), 1437(m), 1431(m), 1424(m), 1419(m), 1381(vw), 1374(vw), 1356(w), 1300(vw), 1244(vw), 1218(m), 1157(w), 1070(m), 1049(w), 1030(w), 1019(w), 993(vw), 975(vw), 963(vw), 877(m), 842(vs), 767(m), 740(vw), 700(s), 667(v,sh), 634(w,sh), 654(w), 650(w), 647(w), 627(w), 594(w), 558(s), 527(vw), 507(vw), 477(vw), 463(vw), 458(vw), 447(vw), 419(vw), 404(vw).

Selected ^{1}H and ^{13}C NMR data (200 MHz; CD_3CN, TMS), see Tables 1 and 2. Selected ESI MS data (*m*/*e*): 958.3 $[M^{2+}+PF_6^-]^+$, 879.3 $[M^{2+}+PF_6^- -py]^+$, 753.1 $[M^{2+}-OAc^-]^+$, 674.5 $[M^{2+}-OAc^- -py]^+$, 595.4 $[M^{2+}-OAc^- -2py]^+$ and 405.8 $[M^{2+}]^{2+}$.

2.3.2. *Diethyl ether promoted oxidation of cobalt(II) acetate tetrahydrate in methanol with pyridine*

A methanol (5 cm^3) solution of pyridine (0.5 g, 6 mmol) was added with stirring to a purple methanol (10 cm^3) solution of cobalt(II) acetate tetrahydrate (0.5 g, 2 mmol). Sodium hexafluorophosphate (~ 2.3 g, 1.3 mmol) in methanol (5 cm^3) was then added to the red/purple cobalt(II) solution. The solution was carefully layered with distilled diethyl ether (~ 20 ml) and left for 2–4 weeks during which time it slowly turned brown. Upon slow partial evaporation, large dark brown crystals formed. The crystals were filtered (0.05 g) and

Table 2
^{13}C NMR chemical shifts (ppm) of the acetate, hydroxy, methoxy and pyridine protons for selected polynuclear cobalt(III) carboxylate complexes (200 MHz)

Complex	Solvent (reference)	Acetate methyl carbons	Quaternary carbons	Pyridine carbons α	Pyridine carbons β	Pyridine carbons χ	Methoxide carbons
$[Co_3O(OAc)_6py_3][PF_6]$ [**1**][PF_6]	CD_2Cl_2 (TMS)	25.93	191.54	152.80	124.78	139.41	
$[Co_3O(OH)(OAc)_5py_3][PF_6]$ [**2**][PF_6]	CD_2Cl_2 (TMS)	27.02, (2), 25.59, (1), 24.90. (2)	191.42, (2), 190.94, (2), 189.55. (1)	152.86, 152.09	125.20, 125.08	139.19, 139.01	
	$CDCl_3$ (TMS)	27.08, (2), 25.65, (1), 25.12. (2)	191.69, (2), 191.55, (2), 190.25. (1)	153.18, 152.14	125.63, 125.57	139.78	
	CD_3CN (TMS)	26.90, (2), 25.41, (1), 25.05. (2)	191.92, (1), 191.72, (2), 190.44. (2)	153.11, 154.08	126.24, 126.29	140.76, 140.90	
$[Co_3O(OH)_2(OAc)_3py_5][PF_6]$ [**5**][PF_6]	CD_3CN (TMS)	26.46, (1), 24.84. (2)	189.65, (2), 187.66. (1)	153.61, 153.12, 152.85	126.15, 126.07, 125.94	140.67, 140.39	
$[Co_3O(OH)(OAc)_4py_5][PF_6]_2$ [**15**][PF_6]$_2$	CD_3CN (TMS)	24.68, 25.66, 26.72, 28.99	200.14, 191.33, 191.15, 189.50	151.65, 152.55, 152.89, 152.99, 154.52(br)	125.95, 126.06, 126.37, 126.41, 127.16(br)	139.98, 140.66, 140.93, 140.97, 141.61	
$[Co_3O(OH)(OMe)(OAc)_3py_5][PF_6]_2$ [**16**][PF_6]$_2$	CD_3CN (TMS)	24.75, 25.25, 26.58	190.20, 189.90, 188.12	152.75, 153.04, 153.23, 153.60	126.16, 126.43, 126.60	140.52, 140.82, 140.98, 141.06	54.39
$[Co_3O(OH)_3(OAc)_2py_6][PF_6]_2$ [**7**][PF_6]$_2$	CD_3CN (TMS)	24.73, 25.61	185.02, 189.85	151.93, 152.79, 153.84, 155.31, 156.47(br)	125.43, 126.16, 126.25, 126.45, 126.74	140.43, 140.66, 140.92, 141.06	
	CD_2Cl_2 (TMS)			151.*xx*, 151.25, 152.01	125.84	139.95	

identified by ^{1}H NMR in CD_3CN as $[Co_3(\mu_3\text{-}O)(\mu\text{-}OH)(\mu\text{-}OMe)(\mu\text{-}OAc)_3(py)_5][PF_6]_2$ ([**16**]$[PF_6]_2$). The remaining filtrate was left for another 2–4 weeks and evaporated to dryness. The residual solid was run through a short column of alumina with acetonitrile and the dark brown fraction evaporated and dried in vacuo. ^{1}H NMR in CD_3CN showed the brown solid to contain a mixture of species including $[Co_3(\mu_3\text{-}O)(\mu\text{-}OH)(\mu\text{-}OMe)(\mu\text{-}OAc)_3(py)_5]^{2+}$ (**16**), $[Co_3(\mu_3\text{-}O)(\mu\text{-}OMe)_2(\mu\text{-}OAc)_3(py)_5]^{2+}$ (**17**), $[Co_3(\mu_3\text{-}O)(\mu\text{-}OH)_2(\mu\text{-}OAc)_3(py)_5]^{2+}$ (**5**), $[Co_2(\mu\text{-}OH)_2((\mu\text{-}OAc)(OAc)_2(py)_4]^{+}$, , and others not readily identified.

2.4. *Tris(μ-acetato)bis(μ-methoxo)-μ$_3$-oxo-pentakis(pyridine)tricobalt(III) dication* $[Co_3(\mu_3\text{-}O)(\mu\text{-}OMe)_2(\mu\text{-}OAc)_3(py)_5]^{2+}$ *(17)*

Cobalt(II) acetate tetrahydrate (0.024 g, 0.10 mmol), sodium hexafluorophosphate (0.013 g, 0.07 mmol) and pyridine (0.042 g, 0.53 mmol) were added to deuterated methanol (0.912 g, ∼1 cm^3) in an NMR tube and the solution was stirred. The resulting bright pink solution and a white solid (undissolved sodium hexafluorophosphate) was ozonated for 15 min. After a few seconds of ozonation the solution turned dark brown and after 2 min had changed to an olive green colour. During the ozonation some solvent evaporated with the resulting volume approximately 0.75 cm^3. The paramagnetic solution was filtered through alumina and the brown solution analysed by ^{1}H NMR (see Table 1). The dication, $[Co_3(\mu_3\text{-}O)(\mu\text{-}OMe)_2(\mu\text{-}OAc)_3(py)_5]^{2+}$ (**17**), was observed to be present with a multitude of other species not easily or readily identifiable.

Selected ^{1}H NMR (200 MHz; CD_3CN, TMS): 2.92, 2.90, 2.88, 2,76, 2.72, 2.64, 2.61, 2.57, 2.50, 2.48, 2.46, 2.37, 2.33, 2.25, 2.22, 2.20, 2.18, 2.15, 2.08, 2.06, 2.00, 1.97, 1.94, 1.42, 1.39, 1.37. These data correspond to a mixture and include only the acetate resonances

2.5. *Reactions of 'cobalt(III) acetate'*

2.5.1. *In the presence of sodium perchlorate*

This reaction is similar to that previously reported [8]. 'Cobalt(III) acetate' (1.0 g, 4.2 mmol as '$Co(OAc)_3$') was quickly stirred in methanol (8 ml) and dissolved to form a dark green solution. Pyridine (0.4 g, 5.0 mmol) and sodium perchlorate hydrate (0.2 g, ∼1 mmol) dissolved in methanol (2 ml) were added with stirring and the mixture turned dark brown. After 1 h a brown solid (0.05 g) was isolated by filtration, washed with diethyl ether and dried in vacuo. The solid was identified by ESI MS and ^{1}H NMR in CD_3CN as a mixture of mainly $[Co_3(\mu_3\text{-}O)(\mu\text{-}OMe)(\mu\text{-}OAc)_5(py)_3]^{+}$ (**6a**), a smaller amount of $[Co_3(\mu_3\text{-}O)(\mu\text{-}OH)(\mu\text{-}OAc)_5(py)_3]^{+}$ (**2**), and other species not readily identified. The filtrate was left for another 10 h, precipitating more brown solid (0.58 g), which was collected by filtration and dried in vacuo. ^{1}H NMR in CD_3CN again showed the material to also consist of $[Co_3(\mu_3\text{-}O)(\mu\text{-}OMe)(\mu\text{-}OAc)_5(py)_3]^{+}$ (**6a**), and $[Co_3(\mu_3\text{-}O)(\mu\text{-}OH)(\mu\text{-}OAc)_5(py)_3]^{+}$ (**2**), with a smaller amount of other species not readily identified. The remaining green filtrate was evaporated and dried in vacuo to a dark green paramagnetic solid (0.61 g). The solid was washed down a short column of alumina with acetonitrile. The resulting yellow/brown fraction was evaporated, dried in vacuo and found using ^{1}H NMR in CD_3CN to consist of a mixture of species including $[Co_3(\mu_3\text{-}O)(\mu\text{-}OH)(\mu\text{-}OAc)_5(py)_3]^{+}$ (**2**), $[Co_3(\mu_3\text{-}O)(\mu\text{-}OMe)(\mu\text{-}OAc)_5(py)_3]^{+}$ (**6a**), $[Co_3(\mu_3\text{-}O)(\mu\text{-}OH)(\mu\text{-}OMe)(\mu\text{-}OAc)_3(py)_5]^{2+}$ (**16**), $[Co_3(\mu_3\text{-}O)(\mu\text{-}OMe)_2(\mu\text{-}OAc)_3(py)_5]^{2+}$ (**17**), $[Co_3(\mu_3\text{-}O)(\mu\text{-}OH)_2(\mu\text{-}OAc)_3(py)_5]^{2+}$ (**5**), $[Co_4(\mu_3\text{-}O)_4(\mu\text{-}OAc)_4(py)_4]$ (**9**), dimers and others not easily identified. A green band, which remained on the column, was eluted using methanol and was dried in vacuo. The ^{1}H NMR in CD_3OD of the resulting green solid showed a number of species present, currently unidentified, in low concentration. A purple (possibly paramagnetic) solid remained undissolved on top of the column.

2.5.2. *In the presence of ammonium hexafluorophosphate*

A similar procedure to that reported above was performed using ammonium hexafluorophosphate in place of sodium perchlorate hydrate. 'Cobalt(III) acetate' (1.0 g, 4.2 mmol as '$Co(OAc)_3$') was quickly stirred in methanol (8 ml) and dissolved to form a dark green solution. Pyridine (0.4 g, 5.0 mmol) and ammonium hexafluorophosphate (0.2 g, 1.2 mmol) dissolved in methanol (2 ml) were added with stirring and the mixture turned dark brown. After 24 h a brown solid (0.28 g) was isolated by filtration, washed with diethyl ether and dried in vacuo. The solid was identified by ESI MS and ^{1}H NMR in CD_3CN as a mixture of mainly $[Co_3(\mu_3\text{-}O)(\mu\text{-}OMe)(\mu\text{-}OAc)_5(py)_3]^{+}$ (**6a**) and $[Co_3(\mu_3\text{-}O)(\mu\text{-}OH)(\mu\text{-}OAc)_5(py)_3]^{+}$ (**2**) and lesser amounts of other species not readily identified. The filtrate was left for 24 h resulting in the precipitation of more solid (0.32 g). The ESI MS and ^{1}H NMR in CD_3CN showed the material to consist of $[Co_3(\mu_3\text{-}O)(\mu\text{-}OMe)(\mu\text{-}OAc)_5(py)_3]^{+}$ (**6a**), $[Co_3(\mu_3\text{-}O)(\mu\text{-}OH)(\mu\text{-}OAc)_5(py)_3]^{+}$ (**2**), $[Co_3(\mu_3\text{-}O)(\mu\text{-}OH)(\mu\text{-}OMe)(\mu\text{-}OAc)_3(py)_5]^{2+}$ (**16**), and $[Co_3(\mu_3\text{-}O)(\mu\text{-}OMe)_2(\mu\text{-}OAc)_3(py)_5]^{2+}$ (**17**) with smaller amounts of other species not readily identified. The remaining green filtrate was evaporated in air over several months and finally dried in vacuo. The resulting dark green paramagnetic solid (0.60 g) was washed down a short column of alumina with acetonitrile and the green/brown fraction evaporated and dried in vacuo. ^{1}H NMR in CD_3CN showed the solid to consist of a mixture of species including $[Co_4(\mu_3\text{-}O)_4(\mu\text{-}OAc)_4(py)_4]$ (**9**), dimers and other unidentified species.

2.6. Reactions of [$Co_3(\mu_3\text{-}O)(\mu\text{-}OH)(\mu\text{-}OAc)_5(py)_3$][$PF_6$] (**2**[$PF_6$])

2.6.1. With methanol at room temperature

A brown solution of [$Co_3(\mu_3\text{-}O)(\mu\text{-}OH)(\mu\text{-}OAc)_5(py)_3$][$PF_6$] (**2**[$PF_6$]), (0.027 g, 0.03 mmol) in methanol (5 ml) was slowly evaporated to dryness in air at r.t. over 3–4 weeks. The resulting brown solid was washed through a short column of alumina with acetonitrile. A pink (possibly paramagnetic) solid did not dissolve and remained at the top of the alumina bed while a bright green fraction adhered to the alumina. A brown fraction was eluted and dried in vacuo. The ^1H NMR in CD_3CN showed the presence of paramagnetic species. The solid (0.019 g) was purified through a second alumina column and the eluted brown solution evaporated and dried in vacuo. The ^1H NMR in CD_3CN showed the solid to contain a mixture of species including [$Co_3(\mu_3\text{-}O)(\mu\text{-}OH)(\mu\text{-}OAc)_5(py)_3$]$^+$ (**2**), [$Co_3(\mu_3\text{-}O)(\mu\text{-}OMe)(\mu\text{-}OAc)_5(py)_3$]$^+$ (**6a**), [$Co_3(\mu_3\text{-}O)(\mu\text{-}OH)(\mu\text{-}OMe)(\mu\text{-}OAc)_3(py)_5$]$^{2+}$ (**16**), [$Co_3(\mu_3\text{-}O)(\mu\text{-}OMe)_2(\mu\text{-}OAc)_3(py)_5$]$^{2+}$ (**17**), smaller amounts of [$Co_2(\mu\text{-}OH)_2((\mu\text{-}OAc)(OAc)_2(py)_4$]$^+$ and [$Co_3(\mu_3\text{-}O)(\mu\text{-}OH)_2(\mu\text{-}OAc)_3(py)_5$]$^+$ (**5**) and other species not easily identified. The reaction (on ca. 1/10 scale in CD_3OD) was also monitored by ^1H NMR.

2.6.2. With refluxing methanol

A brown mixture of [$Co_3(\mu_3\text{-}O)(\mu\text{-}OH)(\mu\text{-}OAc)_5(py)_3$][$PF_6$] (**2**[$PF_6$]), (0.057 g, 0.06 mmol) in methanol (10 ml) was refluxed for 80 min. The resulting olive/green solution was evaporated and dried by rotary evaporation. The ^1H NMR spectrum in CD_3CN showed the brown–olive solid (0.047 g) to contain a mixture of [$Co_3(\mu_3\text{-}O)(\mu\text{-}OMe)(\mu\text{-}OAc)_5(py)_3$]$^+$ (**6a**) > [$Co_3(\mu_3\text{-}O)(\mu\text{-}OH)(\mu\text{-}OAc)_5(py)_3$]$^+$ (**2**) > [$Co_3(\mu_3\text{-}O)(\mu\text{-}OH)(\mu\text{-}OMe)(\mu\text{-}OAc)_3(py)_5$]$^{2+}$ (**16**) > [$Co_3(\mu_3\text{-}O)(\mu\text{-}OMe)_2(\mu\text{-}OAc)_3(py)_5$]$^{2+}$ (**17**) and smaller amounts of other species not easily identified. The reaction (on ca. 1/10 scale in CD_3OD) was also monitored by ^1H NMR.

2.6.3. With refluxing methanol and acetonitrile

A brown solution of [$Co_3(\mu_3\text{-}O)(\mu\text{-}OH)(\mu\text{-}OAc)_5(py)_3$][$PF_6$] (**2**[$PF_6$]), (0.05g, 0.06 mmol) in methanol (2.5 ml) and CH_3CN (10 ml) was refluxed for 3 h. The solution was evaporated and dried in vacuo and the brown–olive solid (0.04 g) identified by ^1H NMR spectroscopy in CD_3CN to contain a mixture of [$Co_3(\mu_3\text{-}O)(\mu\text{-}OMe)(\mu\text{-}OAc)_5(py)_3$]$^+$ (**6a**) > [$Co_3(\mu_3\text{-}O)(\mu\text{-}OH)(\mu\text{-}OAc)_5(py)_3$]$^+$ (**2**) > [$Co_3(\mu_3\text{-}O)(\mu\text{-}OH)(\mu\text{-}OMe)(\mu\text{-}OAc)_3(py)_5$]$^{2+}$ (**16**) > [$Co_3(\mu_3\text{-}O)(\mu\text{-}OMe)_2(\mu\text{-}OAc)_3(py)_5$]$^{2+}$ (**17**) and a smaller amount of other species not easily identified. The solid was purified from a small amount of paramagnetic material by washing through a short alumina column with acetonitrile then methanol. A brown solid was obtained from the acetonitrile fraction by removal of the solvent in vacuo. Using ^1H NMR spectroscopy in CD_3CN the solid was found to have the same composition as that of the crude material. A small amount of a pale green solid was obtained from the green methanol fraction after the removal of the solvent in vacuo. A dilute CD_3OD solution of the solid was examined by ^1H NMR spectroscopy in CD_3CN.

2.7. Structure determination

A crystal of [$Co_3(\mu_3\text{-}O)(\mu\text{-}OH)(\mu\text{-}OMe)(\mu\text{-}OAc)_3(py)_5$][$PF_6$]$_2$ (**16**[PF_6]$_2$) was attached to a thin glass fibre and mounted on an Enraf–Nonius CAD4 diffractometer employing graphite monochromated Mo Kα radiation generated from a sealed tube. Cell constants were obtained from a least-squares refinement against 25 reflections located between 18.98° and 23.94° 2θ. Data were collected at 294.2 K. The intensities of three standard reflections measured every 60 min changed by 5.33% during the data collection and a correction was accordingly applied to the data, together with Lorentz and polarisation corrections and an analytical absorption correction.

Processing and calculations were undertaken with TEXSAN [20]. The structure was solved by direct methods with SHELXS-86 [21] and extended with difference maps generated by DIRDIF [22]. The asymmetric unit contains a trinuclear complex, two PF_6^- counterions, a methanol solvate molecule and a site modelled as a partially occupied water oxygen site. In general the non-hydrogen atoms were modelled with anisotropic displacement parameters and the hydrogen atoms were placed at calculated positions with group thermal parameters. The water oxygen and a fluorine atom were modelled with isotropic displacement parameters. The hydrogen of the bridging hydroxyl was placed on the basis of residual density in a final difference map. No hydrogen atoms were included in the model for the methanol and water molecules.

2.8. Crystal data

$C_{33}H_{41}Co_3F_{12}N_5O_{10.25}P_2$, M, 1138.44; monoclinic; space group, $P2_1/n$ (#14); a, 14.180(5); b, 20.010(6); c, 15.896(4) Å; β, 97.52(3°); V, 4471(2) Å^3; D_{calc}, 1.691 g cm^{-3}; Z, 4; crystal size, 0.50 × 0.22 × 0.08 mm; colour red; habit plate; λ(Mo Kα), 0.7107 Å; μ(Mo Kα), 1.280 mm^{-1}; T(analytical)$_{min,max}$, 0.752, 0.909; $2\theta_{max}$, 49.98°; hkl range, −16 16, 0 23, 0 18; N, 8259; N_{ind}, 8061 (R_{merge} 0.04065); N_{obs}, 5467 ($I > 2.00\sigma(I)$); N_{var}, 585; residuals[1], $R(F)$, 0.0639; $R_w(F)$, 0.0569; GoF(obs), 2.311; $\Delta\rho_{min,max}$, −0.60, 0.76 e Å^{-3}.

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[1] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = (\Sigma\ w(F_o - F_c)^2/\Sigma(wF_c)^2)^{1/2}$, $w = 1/[\sigma^2(F_o)]$.

3. Results and discussion

3.1. The Isolation of $[Co_3(\mu_3\text{-}O)(\mu\text{-}OH)(\mu\text{-}OAc)_4(py)_5][PF_6]_2$ ($\mathbf{15}[PF_6]_2$)

$[Co_3(\mu_3\text{-}O)(\mu\text{-}OH)(\mu\text{-}OAc)_4(py)_5][PF_6]_2$ ($\mathbf{15}[PF_6]_2$) was prepared by ozonation of a stirred mixture of cobalt(II) acetate tetrahydrate (3.125 g, 12.5 mmol), acetic acid (25 ml), and pyridine (2 g, 25.3 mmol; Co:py molar ratio 1:2), for 2 h, followed by the addition of aqueous ammonium hexafluorophosphate (1.36 g, 8.3 mol) and storage at below 5 °C for 2 days. A mixture of products was obtained, from which $[Co_3(\mu_3\text{-}O)(\mu\text{-}OH)(\mu\text{-}OAc)_4(py)_5][PF_6]_2$ ($\mathbf{15}[PF_6]_2$) was separated as large brown crystals, following fractional crystallisation and chromatography. $[Co_3(\mu_3\text{-}O)(\mu\text{-}OAc)_6(py)_3]^+$ (**1**) eluted ahead of $[Co_3(\mu_3\text{-}O)(\mu\text{-}OH)_2(\mu\text{-}OAc)_5(py)_3]^+$ (**2**). The more highly charged $[Co_3(\mu_3\text{-}O)(\mu\text{-}OH)(\mu\text{-}OAc)_4(py)_5]^{2+}$ (**15**), eluted as the last fraction. $[Co_3(\mu_3\text{-}O)(\mu\text{-}OH)(\mu\text{-}OAc)_4(py)_5]^{2+}$ (**15**), (Co:py = 3:5 and μ-OH:μ-OAc = 1:4) is intermediate in stoichiometry between $[Co_3(\mu_3\text{-}O)(\mu\text{-}OH)_2(\mu\text{-}OAc)_5(py)_3]^+$ (**2**), (Co:py = 1:1 and μ-OH:μ-OAc = 1:5) and $[Co_3(\mu_3\text{-}O)(\mu\text{-}OH)_2(\mu\text{-}OAc)_3(py)_5]^{2+}$ (**5**) (Co:py = 3:5 and μ-OH:μ-OAc = 2:3). More solid was obtained by leaving the filtrate with additional water for 1 week below 5 °C. The solid was observed to contain a mixture of species including $[Co_3(\mu_3\text{-}O)(\mu\text{-}OH)_2(\mu\text{-}OAc)_5(py)_3][PF_6]$ ($[\mathbf{2}][PF_6]$), and $[Co_3(\mu_3\text{-}O)(\mu\text{-}OH)(\mu\text{-}OAc)_4(py)_5][PF_6]_2$ ($[\mathbf{15}][PF_6]_2$) and the di-hydroxo-dinuclear species $[Co_2(\mu\text{-}OH)_2(\mu\text{-}OAc)(\mu\text{-}OAc)_2(py)_4]^+$. Extraction of the remaining filtrate in dichloromethane and neutralisation, washing and drying of the extract produced a solid in which a mixture of many species included the di-hydroxo-dinuclear cations, $[Co_2(\mu\text{-}OH)_2(\mu\text{-}OAc)(\mu\text{-}OAc)_2(py)_4]^+$, the oxo-trinuclear species, $[Co_3(\mu_3\text{-}O)(\mu\text{-}OH)(\mu\text{-}OAc)_4(py)_5][PF_6]_2$ ($[\mathbf{15}][PF_6]_2$), $[Co_3(\mu_3\text{-}O)(\mu\text{-}OH)_2(\mu\text{-}OAc)_3(py)_5][PF_6]_2$ ($[\mathbf{5}][PF_6]_2$), and others currently unidentified were observed.

The brown crystals were formulated as $[Co_3(\mu_3\text{-}O)(\mu\text{-}OH)(\mu\text{-}OAc)_4(py)_5][PF_6]_2$ ($\mathbf{15}[PF_6]_2$) on the basis of elemental analyses and the observation of ions corresponding to $\{[Co_3(\mu_3\text{-}O)(\mu\text{-}OH)(\mu\text{-}OAc)_4(py)_5][PF_6]\}^+$ and $[Co_3(\mu_3\text{-}O)(\mu\text{-}OH)(\mu\text{-}OAc)_4(py)_5]^{2+}$ in the EIS MS. Although diffraction quality crystals of salts of **15** could not be obtained, the structure of the dication was assigned as that of **15**, rather than the more symmetric isomer, **18**, on the basis of the ^1H and ^{13}C NMR spectra (Tables 1 and 2).

In particular, the ^1H and ^{13}C NMR spectra each contain four distinct acetate methyl resonances. The ^1H NMR spectrum also includes a resonance assignable to the proton of a bridging hydroxyl ligand, and a complicated set of resonances attributed to five pyridine ligands, four of which rotate only slowly about the Co–N axis on the ^1H NMR time scale at room temperature. The four acetate methyl resonances (δ 2.57, 2.41, 2.22 and 2.13) are observed in the region typical of bridging bidentate acetates (e.g. **5**; δ 2.56 and 2.23, **2**; δ 2.08, 2.05, and 1.95 and **1**; δ 2.07 all in CD_3CN, Table 1). The hydroxyl proton absorption is observed at δ −2.76 (CD_2Cl_2, 293 K). This upfield shift is typical of resonances of non-hydrogen bound bridging hydroxyl protons in oxo-centred cobalt(III) cationic trimers (e.g. **2**; δ −4.27 in CD_2Cl_2 and **5**; δ −1.71 in CD_3CN, Table 1). The pyridine proton absorptions appear as a complicated set of peaks due to five different pyridine environments. Interestingly the spectrum of **15** exhibits two broad pyridine proton absorptions at a comparatively high field with respect to the pyridine absorptions of the other oxo-centred cobalt(III) species (Table 1). Variable temperature experiments conducted on **15** indicate that at low temperatures (230 K) rotation of the pyridines slows considerably and the broad peaks are separated into individual proton absorptions. Unlike the dimeric species with *cis*-pyridine ligands which exhibit pyridine proton absorptions indicating free rotation of the ligand around the Co–N bond, **15**, which also contains *cis*-pyridine ligands on two of the three cobalt atoms, displays broad absorptions indicating restricted rotation. Restricted rotation of the pyridine ligands in solution at room temperature is not observed in similar experiments for the related species **5** or **16**.

3.2. Isolation of salts of $[Co_3(\mu_3\text{-}O)(\mu\text{-}OH)(\mu\text{-}OMe)(OAc)_3(py)_5]^{2+}$ (16)

Pink/red methanol solutions of sodium hexafluorophosphate, cobalt(II) acetate tetrahydrate and pyridine (molar ratio ~2:3:9) were left over several weeks to months in air. The solutions slowly turned dark brown indicating the oxidation of cobalt(II) to cobalt(III) and upon slow, partial evaporation, a mixture of brown and red crystalline materials was isolated. The crystalline materials were identified by solution ^1H NMR in CD_3CN and CD_3OD as containing a mixture of species including the dicationic, methoxo, oxo and hydroxo bridged, trinuclear species $[Co_3(\mu_3\text{-}O)(\mu\text{-}OH)(\mu\text{-}OMe)(\mu\text{-}OAc)_3(py)_5][PF_6]_2$ ($[\mathbf{16}][PF_6]_2$), and the monocationic, dihydroxy bridged, dinuclear species $[Co_2(\mu\text{-}OH)_2(\mu\text{-}OAc)(OAc)_2(py)_4][PF_6]$. Very large dark brown block-like crystals of $[\mathbf{16}][PF_6]_2$ were physically separated from the other crystalline materials. The related trinuclear dications **17** and **5**, the dinuclear cations $[Co_2(\mu\text{-}OH)_2(\mu\text{-}OAc)(OAc)_2(py)_4]^+$, and large clusters of radially arranged crystals of $[\mathbf{16}][PF_6]_2$, amongst other species not readily identified, were also often present, after evaporation of the remaining filtrate.

$[Co_3(\mu_3\text{-}O)(\mu\text{-}OH)(\mu\text{-}OMe)(\mu\text{-}OAc)_3(py)_5][PF_6]_2$ $[\mathbf{16}][PF_6]_2$, was characterised by vibrational, ^1H NMR, ^{13}C NMR, and electrospray ionisation mass spectro-

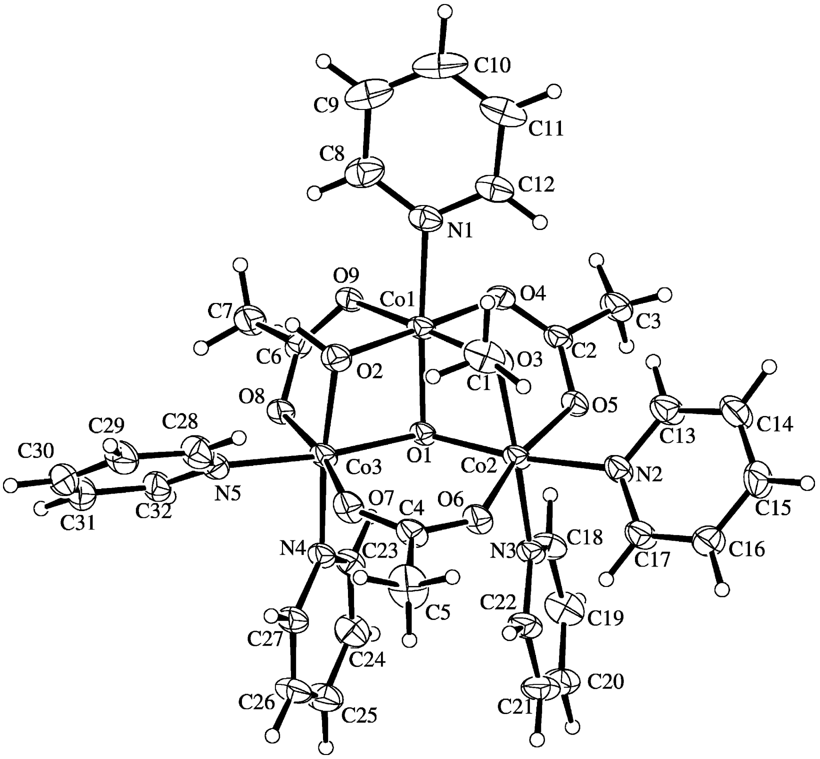


Fig. 1. ORTEP (25% probability) [29] illustration of the molecular structure of $[Co_3(\mu_3\text{-}O)(CH_3CO_2)_3(\mu\text{-}OH)(\mu\text{-}OCH_3)(C_5H_5N)_5][PF_6]_2$ (**16**), showing the atom numbering scheme.

scopies. The number of ^{1}H NMR acetate and pyridine resonances suggested a species of low symmetry, whilst the mass spectrum indicated an oxo-containing trinuclear species. This structure was confirmed by single crystal X-ray diffraction and is illustrated in Fig. 1.

The cobalt(II) solution was oxidised slowly and the rate of formation of the oxidation products was found to be variable due to the low oxidation potential of air and the varying exposure of the reaction mixture to the atmosphere (i.e. the relatively low and variable concentration of the oxidant). The time taken for the products to crystallise was also variable and found to be dependent on the rate of solvent evaporation. Nevertheless, the products observed and obtained were found to remain quite consistent regardless of the varying conditions.

3.3. Diethyl ether promoted oxidation of cobalt(II) acetate tetrahydrate in methanol with pyridine

In the presence of oxidants formed from the slow decomposition of diethylether [23], methanol solutions of cobalt(II) acetate tetrahydrate and pyridine were observed to undergo slow oxidation similar to those reactions performed in the presence of air.

Distilled diethyl ether (i.e. no stabiliser present) slowly breaks down in air to form peroxides, which facilitate the oxidation of cobalt(II) species. Due to the low concentration of oxidant (similar to the preparations using air (oxygen) as oxidant), oxidation and consequent formation of cobalt(III) species occurs very slowly (over weeks to months). Slow crystallisation of pyridine ligated cobalt(III) salts resulted as their concentration increased and as the solvent volume was reduced by evaporation.

Leaving the solutions to slowly oxidise and evaporate over weeks to months resulted in the formation of large dark brown crystals of [**16**]$[PF_6]_2$. Extending reaction times to more than several months and allowing the solvent to evaporate more slowly resulted in the formation of both large dark brown crystals of [**16**]$[PF_6]_2$ and red crystals of dinuclear $[Co_2(\mu\text{-}OH)_2(\mu\text{-}OAc)(OAc)_2(py)_4][PF_6]$. Separation of these materials was performed manually due to the large crystal size.

Oxidation of cobalt(II) in reactions involving non-distilled ether (with stabiliser present) were observed to proceed extremely slowly(over 6 months to 1 year) or not at all. A pink solid, which also often accompanied initial cobalt(III) products in distilled diethylether preparations when the layering was not done carefully was filtered and dried and identified as $[Co(II)_3(\mu\text{-}OAc)_4(py)_8][PF_6]_2$ [24].

^{1}H NMR solution spectra of the $[Co_3(\mu_3\text{-}O)(\mu\text{-}OMe)(\mu\text{-}OH)(\mu\text{-}OAc)_3(py)_5]^{2+}$ cation **16** exhibit individual and distinct proton absorptions due to bridging acetate, methoxo and hydroxyl ligands in addition to a complicated series of doublets and triplets due to the aromatic protons of five chemically non-equivalent pyridine ligands. The proton resonances are summarised in Table 1. The high-field proton absorption of the bridging hydroxyl proton ($\delta = -1.45$ ppm in CD_3CN) is typical of non-hydrogen bound bridging hydroxyl protons in trinuclear cobalt(III) clusters (Table 1). The chemical shift of the bridged-hydroxyl proton is shifted slightly downfield of those in the related species $[Co_3(\mu_3\text{-}O)(\mu\text{-}OH)_2(\mu\text{-}OAc)_3(py)_5]^{2+}$ which occur at $\delta = -1.71$ ppm in CD_3CN. Thus the presence of the more electron rich methyl group of the bridging methoxide and its steric effects alter the electronic nature of the $[Co(III)_3O]^{7+}$ core. The hydroxyl proton of $[Co_3(\mu_3\text{-}O)(\mu\text{-}OMe)(\mu\text{-}OH)(\mu\text{-}OAc)_3(py)_5]^{2+}$ undergoes ready exchange with deuterium at room temperature in CD_3CN solution in the presence of deuterium oxide.

The bridging methoxo ligand methyl protons also absorb at a relatively high-field ($\delta = 1.14$ ppm in CD_3CN) typical of protons on alkoxide-bridged trinuclear cobalt(III) clusters (Table 1). However, the high-field shift is not as pronounced as that of the methoxide protons in related $[Co_3(\mu_3\text{-}O)(\mu\text{-}OCH_3)(\mu\text{-}OAc)_5(py)_3]^+$ ($\delta = 0.77$ ppm in CD_3CN). Sumner and Steinmetz [11] report this unusual high-field chemical shift (typically 3 ppm upfield from the chemical shift observed for the uncomplexed alcohol) for all the hydrogen atoms $\propto$ to the bridging oxygen atom in the series of alkoxide-bridged complexes $[Co_3(\mu_3\text{-}O)(\mu\text{-}OR)(\mu\text{-}OAc)_5(py)_5]^+$ where R = methyl, ethyl, propyl, allyl, benzyl and 3-phenylpropyl. The relationship between the μ-alkoxide hydrogens and the cobalt-oxygen bonds is the reason suggested for the observed high-field chemical shift.

Slight differences in chemical shift are observed for the proton absorptions of the $[Co_3(\mu_3\text{-}O)(\mu\text{-}OMe)(\mu\text{-}OH)(\mu\text{-}OAc)_3(py)_5]^{2+}$ cation, **16**, in CD_3CN and CD_3OD solutions (Table 1).

CD_3OD and CD_3CN solutions of [**16**][PF_6] were observed to be stable for several months at room temperature. A similar stability was observed in CD_3OD solutions with several drops of added D_2O.

Solutions prepared from samples of solid [**16**][PF_6]$_2$, analysed by ^1H NMR, were observed to contain other cobalt(III) acetate containing species in small amounts (less than 10%). The trinuclear dications **5** and **17** usually accounted for most of the other species present. Currently unidentified species were occasionally present in small amounts.

Heating a CD_3OD solution of a salt of **16** with D_2O in an oil bath at 100 °C for 45 min resulted in the partial decomposition of **16** with little or no observable increase in concentration of **5** or other known cobalt(III) species.

The new oxo-centred trimeric species **15** is unstable in solution at room temperature and was observed by ^1H NMR in CD_3CN to revert to mainly the oxo-centred trimeric species **2** and lesser amounts of other species, presently unidentified. At room temperature full reversion takes less than 2 weeks. For this interconversion to occur one acetate ligand must be gained by **15** while two pyridine ligands are lost. Sumner has reported that **2** reverts in the presence of water in acetonitrile to **5** [12]. In wet dichloromethane **15** was observed to revert to the oxo-centred trimeric species **5**, possibly, but not necessarily, via **2**.

3.4. ESI MS

The ESI MS spectra of $[Co_3(\mu_3\text{-}O)(\mu\text{-}OMe)(\mu\text{-}OH)(\mu\text{-}OAc)_3(py)_5][PF_6]_2$ [**16**][PF_6]$_2$, in acetontrile at various cone voltages exhibits peaks due to $[M^{2+}+PF_6^-]^+$ (*m/e* 958.3), $[M^{2+}+PF_6^- - py]^+$ (*m/e* 879.3), $[M^{2+} - OAc^-]^+$ (*m/e* 753.1), $[M^{2+} - OAc^- - py]^+$ (*m/e* 674.5), $[M^{2+} - OAc^- - 2py]^+$ (*m/e* 595.4) and $[M^{2+}]^{2+}$ (*m/e* 405.8). Peaks due to small amounts of **5** as $[M^{2+}+PF_6^-]^+$ (*m/e* 944.3) and **17** as $[M^{2+}+PF_6^-]^+$ (*m/e* 972.4) were also observed. The mass spectrum of both methanol and acetontrile solutions of a single crystal of $[Co_3(\mu_3\text{-}O)(\mu\text{-}OMe)(\mu\text{-}OH)(\mu\text{-}OAc)_3(py)_5][PF_6]_2$ also produced small peaks corresponding to the species **5** and **17** in addition to **16**, indicative of a small amount of disproportionation of **16** in solution (the single crystal X-ray diffraction data of $[Co_3(\mu_3\text{-}O)(\mu\text{-}OMe)(\mu\text{-}OH)(\mu\text{-}OAc)_3(py)_5][PF_6]_2$ show no sign of any disorder or residual electron density and the thermal parameters are all reasonable thus suggesting that the single crystals are composed of **16** dications only).

3.5. X-ray crystallography

Large dark brown, block-like crystals of $[Co_3(\mu_3\text{-}O)(\mu\text{-}OH)(\mu\text{-}OMe)(OAc)_3(py)_5][PF_6]_2\cdot MeOH\cdot 0.25H_2O$ (**16**$[PF_6]_2\cdot MeOH\cdot 0.25H_2O$) were isolated in good yield following aerial oxidation of a methanolic solution of cobalt(II) acetate in the presence of pyridine and $NaPF_6$. Fig. 1 illustrates the structure of the cation and the atom numbering scheme. The atomic position parameters are deposited, important bond distances and angles are collected in Table 3.

The dication, $[Co_3(\mu_3\text{-}O)(\mu\text{-}OH)(\mu\text{-}OMe)(OAc)_3\text{-}(py)_5]^{2+}$ is an oxo-centred trinuclear cobalt cluster in which each cobalt atom is in a slightly distorted octahedral environment. Two cobalt atoms are each co-ordinated to two *cis*-pyridine ligands, whereas the third cobalt atom has a single co-ordinated pyridine ligand. One pyridine on each cobalt atom is *trans* to the common central μ_3-oxygen atom. A bidentate acetato ligand bridges each pair of cobalt atoms. The non-hydrogen atoms of each acetato ligand are coplanar, as are those of each pyridine ligand. The Co(py) centre is bridged to one $Co(py)_2$ centre by the μ-hydroxyo ligand and to the other $Co(py)_2$ centre by the μ-methoxo ligand. The bridging hydroxo and methoxo ligands are on the same side of the Co_3 triangle and on the opposite

Table 3
Selected interatomic distances of related dinuclear and trinuclear cations of cobalt(III)

Cation [a]	$Co-N_{aromatic}$ (Å)	$Co-(\mu_3-O)$ (Å)	$Co-O_{OAc}$ (Å)	$Co\cdots Co$ (Å)	μ_3-O to Co_3 plane (Å)	N to Co_3 plane (Å)	Reference
$[Co_3O(OH)(OMe)(OAc)_3(py)_5]^{2+}$	1.993(6) 1.984(6) 1.980(6) 1.975(6) 1.935(6)	1.882(4) 1.865(4)	1.906(4) 1.902(4) 1.912(4) 1.891(4) 1.898(4) 1.894(4)	3.326(1) 2.796(1) [h] 2.778(1) [d]	0.71	0.68, 0.81 0.84, −1.10 −1.32	this work
$[Co_3O(OAc)_6(py)_3]^+$	1.99(1)	1.845(8)	1.87(1)	3.194(1)	0.04	0.04	[7]
$[Co_3O(OAc)_5(OH)(py)_3]^+$	1.99	1.82	1.90	2.76 3.19, 3.18	0.38	−0.12, −0.32	[10]
$[Co_3O(OAc)_5(OR)(py)_3]^+$	1.98	1.782(4) 1.815(3)	1.91	2.781(1) 3.188(1) 3.194(1)	0.33		[11]
$[Co_3O(OAc)_3(OH)(py)_5]^{2+}$	1.963(5)	1.873(3)	1.897(3)	2.786(1) [d] 3.320(1) [e]	0.71	0.96, 0.71	[12]
$[Co_3O(OAc)_2(OH)_3(bpy)_3]^{2+}$	1.94(1)	1.896(11)	1.91(1) [b] 1.95(1) [c]	2.717(4) [f] 2.864(3) [g]	0.97		[9]
$[Co_3O(L)(OH)_3]^+$		1.896(2)	1.918(3)	2.83–2.84			[28]
$[Co_4O_4(O_2Ctol)_2(bpy)_4]^{2+}$	1.939(7)	1.880(6)	1.955(6)	2.790(2)	0.97		[9]
$[Co_2(OAc)_3(OH)_2(py)_4]^+$	1.957(3)	-	1.915(2) [b] 1.891(3) [c]	2.811(1)			[12]
$[Co_2(OAc)_3(OH)_2(bpy)_2]^+$	1.918(8)		1.916(6) [b]	2.793(2) 1.900(6) [c]			[9]

[a] L = ethylenediamine-*N*-acetate ($Co-O_{OAc}$=Co to carboxylate O distance), $O_2Ctol = O_2CC_6H_4$-*p*-Me, OR = $O(CH_2)_3C_6H_5$.

[b] To bridging bidentate acetate ligands.

[c] To monodentate acetate ligands.

[d] Bridged by one acetate and one hydroxyl ligand.

[e] Bridged only by one acetate ligand.

[f] Bridged by one acetate, one hydroxyl and one μ_3-oxo ligands.

[g] Bridged by one hydroxyl and one μ_3-oxo ligands.

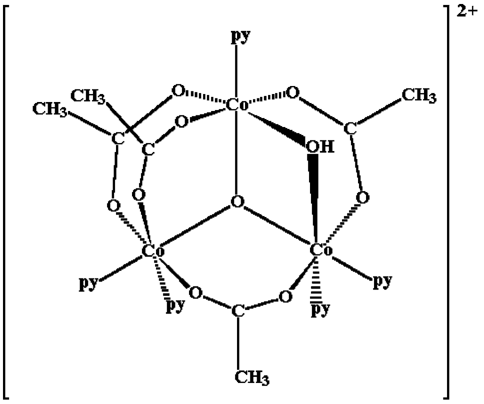
[h] Bridged by one acetate and one methoxide ligand.

side of the Co_3 triangle to the μ_3-oxo ligand. A similar disposition of μ_3-oxo and μ-hydroxo ligands is observed in $[Co_3O(OH)_2(OAc)_3(py)_5]^{2+}$ (**5**) [12]. There is no evidence of the other isomer in the crystal structure solution and there appears to be a single hydroxo ligand environment and a single methoxo ligand environment in the ^1H NMR spectrum in CD_3CN solution. Related $[Co_3(\mu_3-O)(OAc)_3]$ cores are observed in $[Co_3O(OH)_2(OAc)_3(py)_5]^{2+}$ (**5**) [12], $[LCo_3(\mu_3-O)(OAc)_3]^+$ (L = tetraphenoxo macrocyclic tetraanion) [25] and $[Co(II)_3(\mu_3-O)(OAc)_3(cat)]$ (cat = catecholate dianion) [26].

The cluster dication, $[Co_3(\mu_3-O)(\mu-OH)(\mu-OMe)(OAc)_3(py)_5]^{2+}$ (**16**), is composed of three cobalt atoms at the vertices of an approximately isosceles triangle (ave. Co···Co···Co angle 53° at each $Co(py)_2$ centre, 73° at the Co(OH)(OMe) centre), with Co···Co distances of 2.796(1) Å (OMe, OAc bridges), 2.778(1) Å (OH, OAc bridges) and 3.326(1) Å (single OAc bridge, opposite the 73° Co–Co–Co angle). These differ significantly from the Co···Co distance of 3.194(1) Å in the symmetric trimer, $[Co_3O(OAc)_6(py)_3]^+$ [7], and from the $[Co_2(\mu-OAc)_2]$ Co···Co distances (ave. 3.186 Å) in the cation, $[Co_3(\mu_3-O)(\mu-OH)(OAc)_5(py)_3]^+$ [10]. As expected, the distance between the two cobalt atoms bridged by a single bidentate acetate ligand exceeds those (2.900(5), 2.935(6) Å) of the cobalt atoms bridged by single hydroxides in the partial cubane dication, $[Co_3(\mu_3-O)(\mu-OH)_3(OAc)_2(py)_6]^{2+}$ [8], and the $[Co_2(\mu-OH)(\mu-OAc)]$ Co···Co separation (2.778 Å) is similar to that of 2.767(5) Å in the partial cubane dication, $[Co_3(\mu_3-O)(\mu-OH)_3(OAc)_2(py)_6]^{2+}$ [8]. The $[Co_2(\mu-OMe)(\mu-OAc)]$ Co···Co separation (2.796(1) Å) is slightly smaller than the corresponding distance (2.863 Å) in the octanuclear $[Co_8(\mu-OMe)_{16}(OAc)_8]$ [16].

The common μ_3-oxygen atom is slightly displaced from the centre of the Co_3 triangle, being 1.883(4), 1.865(4) and 1.880(4) Å from Co(1), Co(2) and Co(3), respectively. The Co(1)···O···Co angles are 95° (to Co(2)) and 97°(to Co(3)), whilst the Co(2)···O(1)···Co(3) angle is 125°.

The μ_3-oxygen atom lies 0.707 Å out of the plane defined by the three cobalt atoms, on the side opposite to the bridging hydroxo and methoxo ligands. The displacement of the μ_3-oxygen atom from the Co_3 plane is much greater in less symmetric tricobalt(III) cations. The effects of the substitution of uninegative, bidentate, bridging acetate ligands by uninegative, monodentate, bridging ligands (OH^-, OR^-) can be seen by comparing the present structure with those of $[Co_3O(OAc)_5(OH)(py)_3]^+$ (**2**), $[Co_3O(OAc)_5(OR)(py)_3]^+$ ($R = CH_2CH_2CH_2C_6H_5$, **6**), $[Co_3O(OAc)_3(OH)_2(py)_5]^{2+}$ (**5**), $[CoO(\eta^1\text{-}OAc)(\mu\text{-}OAc)(OH)_3(py)_6]^{2+}$ (**7**) and $[Co_3O(\eta^1\text{-}OAc)(\mu\text{-}OAc)(OH)_3(bpy)_3]^{2+}$ (**8**, bpy = bipyridine) and considering the latter two, partial cubane, structures, as derivatives of a planar, $[Co_3(\mu_3\text{-}O)]^{7+}$ trinuclear ion [9–12]. The pyridine nitrogen atoms, N(1), N(2) and N(5), *trans* to the central μ_3-oxygen atom are displaced 0.836, 0.809 and 0.680 Å, respectively, from the Co_3 plane, on the opposite side from the μ_3-oxygen atom.



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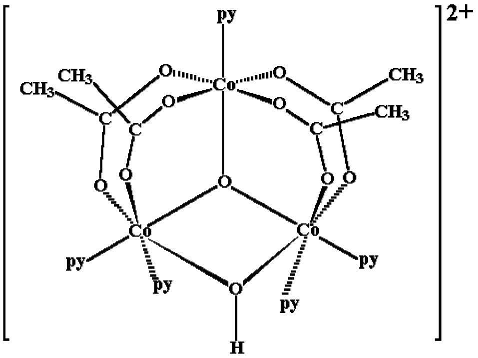


(18)

The pyridine ligands of the $[Co_3(\mu_3\text{-}O)(\mu\text{-}OH)(\mu\text{-}OMe)(OAc)_3(py)_5]^{2+}$ dication are oriented in a manner such that no van der Waals contacts occur with any other atom in the cluster. The *cis* pyridine ligands of Co(3) are tilted slightly, the angle between the respective planes being approximately 15°, while the *cis* pyridine ligands of Co(2) are in a 'butterfly' conformation, the angle between the respective planes being approximately 77°. Both these arrangements are observed in the three dinuclear $[Co_2(\mu\text{-}OH)(\mu\text{-}OAc)(OAc)_2(py)_4]^+$ isomers, as well as in other cobalt *cis* pyridine containing species. The pyridine ligands containing N(4) and N(5) on adjacent cobalt atoms bridged by an acetato and μ_3-oxo ligand are close to parallel (~ 16°), an orientation which minimises steric interactions and which is observed in other species. A significant difference between the present structure, $[Co_3(\mu_3\text{-}O)(\mu\text{-}OH)(\mu\text{-}OMe)(OAc)_3(py)_5]^{2+}$ (**16**), and that of the related, $[Co_3(\mu_3\text{-}O)(\mu\text{-}OH)_2(OAc)_3(py)_5]^{2+}$ (**5**) [12], is in the disposition of the pyridine ligands at the Co(py) centres. In $[Co_3(\mu_3\text{-}O)(\mu\text{-}OH)_2(OAc)_3(py)_5]^{2+}$ (**5**) [12], this pyridine ligand is roughly perpendicular to the Co_3 plane. Such an orientation in the present compound would apparently lead to unfavourable steric interactions between the Co(py) pyridine and the μ-OMe ligand, with the result that the Co(py) of $[Co_3(\mu_3\text{-}O)(\mu\text{-}OH)(\mu\text{-}OMe)(OAc)_3(py)_5]^{2+}$ (**16**), is roughly parallel to the Co_3 plane.

3.6. The families of 'cobalt(III) acetate' oligomers

The dication, $[Co_3(\mu_3\text{-}O)(OAc)_4(\mu\text{-}OH)(py)_5]^{2+}$ (**15**), represents a previously unreported structural motif in cobalt acetate chemistry. However, it is formally isomeric with structure **18** and is formally related to the structurally characterised dication, $[Co_3(\mu_3\text{-}O)(OAc)_3(\mu\text{-}OH)(\mu\text{-}OMe)(py)_5]^{2+}$ (**16**), by the replacement of a bridging acetato ligand of **15** by a bridging alkoxo ligand. These three dications, and the dication, $[Co_3(\mu_3\text{-}O)(OAc)_3(\mu\text{-}OH)_2(py)_5]^{2+}$ (**5**), the first of the structurally characterised cobalt acetate oxo-centred trimers, are members of a putative family of trimeric oxo-centred dications, $[Co_3(\mu_3\text{-}O)(OAc)_{5-n}(\mu\text{-}OR)_nL_5]^{2+}$ ($n = 0$–4, R = hydrocarbon). Two members of this family, $[Co_3(\mu_3\text{-}O)(OAc)_4(\mu\text{-}OH)(py)_5]^{2+}$ ($n = 1$) and $[Co_3(\mu_3\text{-}O)(OAc)_3(\mu\text{-}OH)_2(py)_5]^{2+}$ ($n = 2$), have been reported, leaving the species, $[Co_3(\mu_3\text{-}O)(OAc)_{5-n}(\mu\text{-}OR)_n(L)_5]^{2+}$ ($n = 0$, 3, 4) presently unknown. Similarly, the structurally characterised cations, $[Co_3(\mu_3\text{-}O)(OAc)_6(py)_3]^+$, $[Co_3(\mu_3\text{-}O)(OAc)_5(\mu\text{-}OH)(py)_3]^+$ and $[Co_3(\mu_3\text{-}O)(OAc)_5(\mu\text{-}OR)(py)_3]^+$ are the first two ($n = 0$, 1) members of the family of oxo-centred trimeric cations, $[Co_3(\mu_3\text{-}O)(OAc)_{6-n}(\mu\text{-}OR)_nL_3]^+$.

Two families of oxo-centred trimers can then be identified-$[Co_3(\mu_3\text{-}O)(OAc)_{6-n}(\mu\text{-}OR)_nL_3]^+$ ($n = 0$–5) and $[Co_3(\mu_3\text{-}O)(OAc)_{5-n}(\mu\text{-}OR)_nL_5]^{2+}$ ($n = 0$–4). Representative members of both of these families have been structurally characterised. How many oxo-centred cobalt trimers are then possible? Consideration of the known structures and the necessity of maintaining at least one bridging ligand per Co–Co vector leads to the following formula

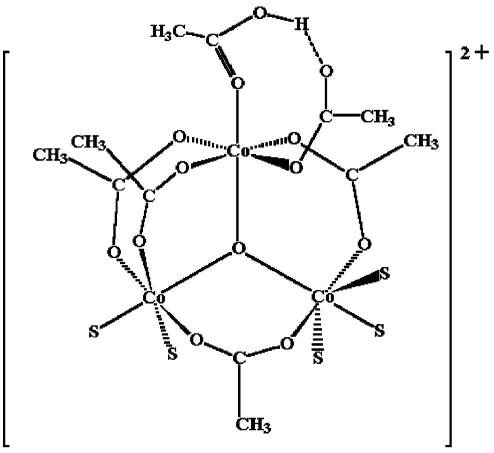
$$[Co_3(\mu_3O)(OAc)_{6-x-n}(OR)_n(py)_{3+2x}]^{(x+1)+} \quad (0 \le x \le 3,\ 0 \le n \le (5-x)) \tag{1}$$

for the stoichiometries (exclusive of considerations of geometric isomers) of the cobalt oxo-centred cationic trimers. Some of the species generated by this formula, for example, the family of trimeric cations, $[Co_3(\mu_3\text{-}O)(OAc)_{3-n}(\mu\text{-}OH)_nL_9]^{4+}$, may be improbable, but are stoichiometrically possible, and so are retained within the ranges specified.

However, we [8] and others [9,13] have reported partial cubane trimers, $[Co_3(\mu_3\text{-}O)(OAc)_2(\mu\text{-}OH)_3(py)_6]^{2+}$ and $[Co_3(\mu_3\text{-}O)(OAc)_2(\mu\text{-}OH)_3(bipy)_3]^{2+}$ which violate this stoichiometry. In particular, whereas the formula above assumes all acetato and alkoxo ligands to be bridging, the partial cubanes contain monodentate acetato ligands, hydrogen bonded to bridging hydroxyl ligands. The partial cubanes are 'pyridine-rich' by comparison with the formula (1), the presence of the extra pyridine requiring that an acetate become monodentate and hydrogen bonded to a hydroxo ligand. A general formula for the stoichiometries of oxo-centred cobalt trimers, which incorporates monodentate acetate ligands (as in partial cubane structures), is the following:

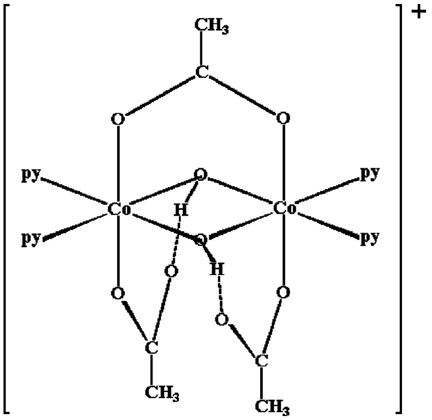
$$[Co_3(\mu_3O)(OAc)_{6-x-n}(OR)_nL_{(3+y+2x)}]^{(x+1)+} \quad (0 \le y \le 3,\ 0 \le x \le (3-x),\ 0 \le n \le (5-x)) \tag{2}$$

If only for steric reasons, not all members will be accessible for all ligands, L. Pyridine has been the ligand, L, commonly used, but other ligands can be substituted for pyridine, with appropriate adjustments to the stoichiometry. Bidentate ligands, such as bipy, will favour stoichiometries with $y = 1$ or 3. Pyridine can of course also be substituted by acetic acid to generate stoichiometries commonly assumed to be present in pyridine-free preparations and applications. However, ligands such as acetic acid, which provide sites for intramolecular hydrogen bonding of monodentate acetato ligands, allow an additional series of intramolecular hydrogen-bonded species for which $x = 0$ (e.g. a partial cubane, $[Co_3(\mu_3\text{-}O)(OAc)_5(AcOH)_6]^{2+}$ (**19**).



(19)

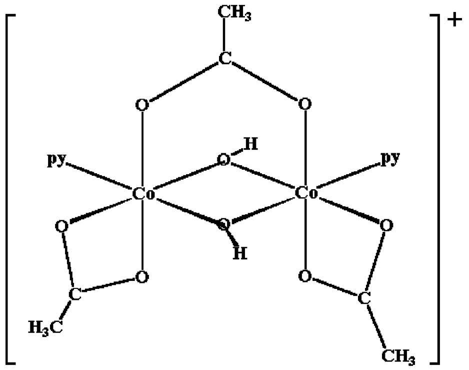
The foregoing has been limited to oxo-centred trimers. The existence of 'pyridine-rich' trimers, in which monodentate acetato ligands participate in intramolecular hydrogen-bonding not observed in other trimer families suggests comparison with the dimers, $[Co_2(\mu\text{-}OAc)(OAc)_2(\mu\text{-}OH)_2(py)_4]^+$ (e.g. **3**), first structurally characterised by Sumner [12].



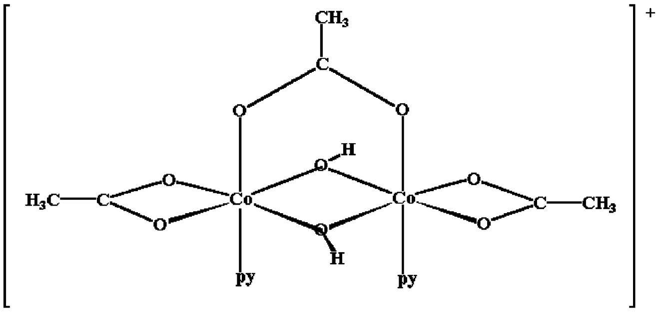
The dimers might also be classified as 'pyridine-rich'. In light of the foregoing, it is pertinent to ask whether an additional family of dimers, $[Co_2(OAc)_3(\mu\text{-}OH)_2(py)_2]^+$, without intramolecular hydrogen-bonding, (e.g. **20** or **21**) or **22** exists.
The chemistry of cobalt acetate dimers will be reported separately [24].

4. Conclusions

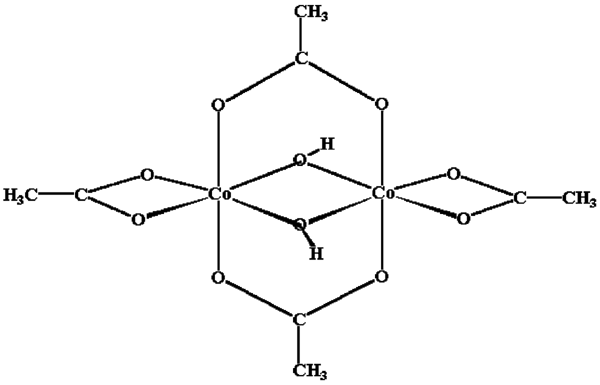
Formation of an array of pyridine-containing 'cobalt(III) acetate' species has been observed upon the ozone or peroxyacetic [27] oxidation of solutions containing cobalt(II) acetate tetrahydrate, acetic acid, water and pyridine. These species include the charged oxo-centred trimeric species **1**, **2**, **15**, **5**, **7**, dimers, the neutral cubane, **9**, and other species as yet unidentified.



(20)



(21)



(22)

The presence and concentration of resulting species after oxidation were found to be critically dependent on the method of preparation. Several species were observed to undergo rearrangement in solution after formation.

Heating reaction mixtures after oxidation was observed to cause decomposition and interconversion of reactive and thermally unstable species to other species. These resulting species have compositions, which typically reflect reaction stoichiometries.

Consequently heating reaction mixtures can be used in aiding selective isolation or synthesis of one or several species. Varying the stoichiometries of the reactants also aids in obtaining selectively one or several species, although in all cases trace amounts of other species were observed to be present. At high acetic acid:water ratios (> 2:1) the oxo-centred trimeric species **2** and **1** dominate reaction products and as the water content is decreased the symmetric oxo-centred trimer **1** is formed almost exclusively. Acetic anhydride can be used to synthesise this species selectively.

Conversely, as the amount of acetic acid decreases, species with lower acetate:cobalt ratios are formed, in which bridging acetate ligands are replaced by bridging hydroxyl ligands, such as in the dimeric species **3**, or **4**, and the trimeric oxo-centred species **5**. Increasing the pyridine concentration in turn increases the pyridine content within resulting cobalt(III) species. At high pyridine concentration the dimers are preferably formed (py:Co = 2:1). Interestingly, the highest pyridine to cobalt ratio for all the identified complexes of this type is 2. Descriptions of the isolation of the dimeric species will be reported separately [27].

The oxo-centred species **15**, **2** and **1** can be isolated from solutions of cobalt(II) acetate tetrahydrate and pyridine (molar ratio 1:2) in acetic acid (with no added water) which have been oxidised by ozone. Chromatography is employed in isolation of the species. **15**, (cobalt:pyridine = 3:5 and bridging hydroxyl:acetate = 1:4) which is intermediate in stoichiometry between **2** and **5** (cobalt:pyridine = 1:1 and 3:5 and bridging hydroxyl:acetate = 1:5 and 2:3, respectively).

A variety of dimers, trimers and tetramers has now been isolated as the products of oxidation of cobalt(II) acetate in the presence of pyridine. The trimers are $[Co_3(\mu_3\text{-}O)(OAc)_6(py)_3]^+$, $[Co_3(\mu_3\text{-}O)(OAc)_5(OR)(py)_3]^+$ (R = OH, alkyl), $[Co_3(\mu_3\text{-}O)(OAc)_3(OH)_2$-

$(py)_5]^{2+}$ and $[Co_3(\mu_3\text{-}O)(OAc)_2(OH)_3(py)_6]^{2+}$ [8,10–12]. The first three of these clusters can be considered as members of the groups $[Co_3(\mu_3\text{-}O)(OAc)_{6-n}(OR)_n(L)_3]^{+}$ ($n=0$–5) and $[Co_3(\mu_3\text{-}O)(OAc)_{5-n}(OR)_n(L)_5]^{2+}$ ($n=0$–4). The partial cubane can be classed as a member of the group $[Co_3(\mu_3\text{-}O)(OAc)_{5-n}(OH)_n(L)_6]^{2+}$ and requires at least one hydroxyl, rather than alkoxo, ligand to participate in hydrogen bonding with an acetato ligand. These clusters share a common structural motif of a triangle of cobalt atoms surrounding a central, triply bridging oxygen atom, with cobalt–cobalt vectors bridged by acetato, hydroxo or alkoxo ligands. On the basis of the limited structural data available, we have noted [8] that, as the number of acetato ligands decreases (i.e. as n increases) the μ_3-oxygen atom is located further out of the Co_3 plane by as much as 0.97 Å (in the partial cubane, $[Co_3(\mu_3\text{-}O)(OAc)_2(OH)_3(py)_6]^{2+}$). This displacement of a bridging oxygen atom from a Co_3 plane is slightly greater (1.01 Å) in the cubane, $[Co_4(\mu_3\text{-}O)_4(OAc)_4(py)_4]$[2]. As the bridging oxygen is displaced from the Co_3 plane its hybridisation must change. Presumably, the change in hybridisation will be accompanied by a change in reactivity. Different reactivities might then be expected between and within different cluster families, although reactivity studies on these clusters are extremely limited.

The dication, $[Co_3(\mu_3\text{-}O)(\mu\text{-}OH)(\mu\text{-}OAc)_4(py)_5]^{2+}$ (**15**), represents a previously unreported structural type in cobalt acetate chemistry. Based on the foregoing, it might be expected that the μ_3-oxygen atom of **15** will lie between 0.35 and 0.71 Å out of the Co_3 plane. Dication **15** is formally related to the structurally characterised dication, $[Co_3(\mu_3\text{-}O)(\mu\text{-}OH)(\mu\text{-}OMe)(\mu\text{-}OAc)_3(py)_5]^{2+}$ (**16**), by the replacement of a bridging acetato ligand by a bridging alkoxo ligand. An assessment of the structural types identified to date in the chemistry of ‘cobalt(III) acetate’/basic ligand derivatives suggests the possible existence of an extensive range of species.

5. Supplementary material

Full list of structure refinement data, atomic coordinates, bond lengths and angles, anisotropic displacement parameters and hydrogen atom parameters have been deposited with the Cambridge Crystallographic Data Centre as CCDC 178200. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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[2] We have also noted [8] that the neutral cubane, $[Co_4(\mu_3\text{-}O)_4(OAc)_4(py)_4]$, has been isolated from the cobalt acetate–pyridine system, rather than $[Co_4(\mu_3\text{-}O)_4(OAc)_2(py)_8]^{2+}$, the analogue of the known $[Co_4(\mu_3\text{-}O)_4(OAc)_2(bipy)_4]^{2+}$ [9]. The cubanes can be thought of as representatives of a family of clusters, $[Co_4(\mu_3\text{-}O)_4(OAc)_{6-m}L_{2m}]^{(m-2)+}$ ($m=0$–5).

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