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# The chemistry of cobalt acetate—IV.† The isolation and crystal structure of the symmetric cubane, tetrakis[( $\mu$ -acetato)( $\mu_3$ -oxo) (pyridine)cobalt(III)] · chloroform solvate, [Co<sub>4</sub>( $\mu_3$ -O)<sub>4</sub>( $\mu$ -CH<sub>3</sub>CO<sub>2</sub>)<sub>4</sub>(C<sub>5</sub>H<sub>5</sub>N)<sub>4</sub>] · 5CHCl<sub>3</sub> and of the dicationic partial cubane, trimeric, [( $\mu$ -acetato)(acetato)tris( $\mu$ -hydroxy)( $\mu_3$ -oxo) hexakispyridinetricobalt(III)]hexafluorophosphate · water solvate, [Co<sub>3</sub>( $\mu_3$ -O)( $\mu$ -OH)<sub>3</sub> ( $\mu$ -CH<sub>3</sub>CO<sub>2</sub>)(CH<sub>3</sub>CO<sub>2</sub>)(C<sub>5</sub>H<sub>5</sub>N)<sub>6</sub>][PF<sub>6</sub>]<sub>2</sub> · 2H<sub>2</sub>O

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Abstract—The isolation from "cobalt(III) acetate" and characterisation by single crystal X-ray diffraction (refined to R = 0.087,  $R_w = 0.084$ ) of the symmetric neutral cubane,  $[Co_4(\mu_3-O)_4(\mu-CH_3CO_2)_4(C_5H_5N)_4]$ , and of the hexafluorophosphate salt (refined to R = 0.078,  $R_w = 0.073$ ) of the trimeric dication, the partial cubane,  $[Co_3(\mu_3-O)(\mu-OH)_3(\mu-CH_3CO_2)(CH_3CO_2)(C_5H_5N)_6]^{2+}$ , are reported. The cubane crystallises as its chloroform solvate,  $[Co_4(\mu_3-O)_4(\mu-CH_3CO_2)_4(C_5H_5N)_4] \cdot 5CHCl_3$ , whilst the partial cubane crystallises as its water solvate,  $[Co_3(\mu_3-O)(\mu-OH)_3(\mu-CH_3CO_2)(CH_3CO_2)(C_5H_5N)_6][PF_6]_2 \cdot 2H_2O$ . The cubane and partial cubane dication have average  $Co \cdots Co$  distances of 2.818(8), 2.683(6) and 2.918(6), 2.767(5) Å, respectively, and average  $Co-\mu_3$ -O distances of 1.86 and 1.91 Å, respectively. (C) 1998 Elsevier Science Ltd. All rights reserved

Keywords: cobalt acetate; cubane; trimeric.

Metal carboxylates have attracted extensive study because of the range of structural types and magnetic, bonding, catalytic, etc. properties which they exhibit. Thus, for example, a trimeric iron species of the basic acetate, oxo-centred type has been isolated from solutions which oxidise alkanes, and copper acetate and chromium acetate were the first compounds for which  $\delta$ - and quadruple metal-metal bonding were postulated [1–4]. Cobalt carboxylates are of particular practical interest as they are the most widely used industrial homogeneous catalysts, predominantly for the oxidations of a variety of hydrocarbons [5–11]. Paradoxically, however, the structure and composition of "[Co(OAc)<sub>3</sub>]" (OAc = CH<sub>3</sub>COO<sup>-</sup>) are incompletely established [12–22]. Although "well defined green octahedrons" were reported in 1924 and a trimeric structure was proposed in 1929 [13,14], amorphous materials are generally produced from the variety of preparative methods developed by various workers [13–15,22–26]. Thus, "[Co(OAc)<sub>3</sub>]" has been postulated to consist of various combinations of monomers, dimers, trimers and mixed valence trimers.

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Analogous triangular, homo- and heteronuclear, single and mixed valence, oxo-centred basic acetate derivatives have long been known for many transition metals, whilst related dimeric, hydroxy-bridged cobalt(III) amine cations were prepared by Werner [27–29].

A significant breakthrough in the structural chemistry of "cobalt(III) acetate" was reported in 1973 by Uemura et al., who showed that crystalline derivatives could be isolated from "cobalt(III) acetate" by the addition of aromatic nitrogen bases as co-ligands [26]. Thus, for example, addition of pyridine and  $NaClO_4 \cdot H_2O$  to a methanolic solution of "cobalt(III) acetate", prepared by ozonolysis of cobalt(II) acetate tetrahydrate in acetic acid, produced [Co<sub>3</sub>O(OAc)<sub>6</sub>  $(py)_{3}$ [ClO<sub>4</sub>] (py = C<sub>5</sub>H<sub>5</sub>N), formulated, on the basis of solid state infra-red spectra and powder X-ray diffraction, to contain the cation (1). Solid  $[Co_3O(OAc)_6(py)_3][ClO_4]$  was obtained in less than quantitative yield. However, structural characterisation of "cobalt(III) acetate", its constituents or its derivatives was still lacking. Subsequently, Sumner reported the crystallographic characterisation of salts of the symmetric, dinuclear, hydroxy-bridged cation,  $[Co_2(\mu-OH)_2(\mu-OAc)(OAc)_2(py)_4]^+$ , (2), and the trinuclear, oxo-centred cations,  $[Co_3(\mu_3-O)(\mu-OH)_2(\mu$  $OAc_{3}(py)_{5}^{2+}$ , (3) and  $[Co_{3}(\mu_{3}-O)(\mu-OR)(\mu-OAc)_{5}]$  $(py)_{3}$ <sup>+</sup>, (4), using the strategy used by Uemura to obtain crystalline, pyridine-containing derivatives [30,31,34].

We have recently shown that dimeric cations such as (5) and (6) can also be isolated from "cobalt(III) acetate" solutions using pyridine as a co-ligand [32]. The cations (5) and (6) are formally derived from (2) by the successive interchange on each cobalt atom of a pyridine ligand with the non-hydrogen bonded acetate oxygen atom.

Recently, we reported the structure of the "parent", symmetric cation  $[Co_3(\mu_3-O)(\mu-OAc)_6(py)_3]^+$ , (7) [33], previously isolated by Sumner and Steinmetz

from metal-catalysed autoxidation reactions, and prepared by them from the reaction of  $[Co_3(\mu_3-O)(\mu-OH)(\mu-OAc)_5(py)_3]^+$ , (4a), with acetic acid/acetic anhydride [34].

$$[Co_{3}O(OH)(OAc)_{5}(py)_{3}]^{+} + HOAc \xrightarrow{Ac_{2}O.-H_{2}O} (4a)$$

$$[Co_{3}O(OAc)_{6}(py)_{3}]$$
(7)

Trinuclear  $[Co_3(\mu_3-O)(\mu-OH)(\mu-OAc)_5(py)_3]^+$ , (4a), was itself prepared in 81% yield as its  $PF_6^-$  salt by the addition of aqueous  $NH_4PF_6$  to a solution obtained from the peracetic acid oxidation of cobalt(II) acetate in warm aqueous acetic acid in the presence of pyridine.

In attempting to produce stable analogues of potential models of the photosynthetic water oxidation centre in plants and bacteria, Dimitrou et al. prepared in good (69%) yield,  $[Co_2(\mu-OH)_2(\mu-OAc)(OAc)_2]$  $(bpy)_2$ [[ClO<sub>4</sub>], (8, bpy = bipyridyl), the bipyridyl analogue of (2), by  $H_2O_2$  (3 equivalents) oxidation of  $[Co(OAc)_2(H_2O)_4]$  in methanol/water at 50°C in the presence of bipyridine, followed by the addition of LiClO<sub>4</sub> [35]. A similar reaction at room temperature in ethanol/water with a deficiency of bipyridine and excess (10 equivalents) of H<sub>2</sub>O<sub>2</sub> yielded (51% as the  $ClO_4^-$  salt) the partial cubane dication  $[Co_3(\mu_3-O)(\mu_3-O)]$ OH)<sub>3</sub>( $\mu$ -OAc)(OAc)(bpy)<sub>3</sub>]<sup>2+</sup> (9). Reaction of (8) with Li<sub>2</sub>O<sub>2</sub> in hot dimethylsulfoxide generated the  $ClO_4^-$  salt of the dicationic cubane,  $[Co_4(\mu_3-O)_4(\mu OAc_{2}(bpy)_{4}^{2+}$ , (10), in 64% yield. Although not isolated from, nor hitherto observed in, typical "cobalt-(III) acetate" solutions, structures of the types (9) and (10) are clearly of interest in the examination of the constitution of "cobalt(III) acetate".

Similarly, oxidation of  $[Co(PhCO_2)_2]$  with aqueous  $H_2O_2$  in dimethylformamide or acetonitrile leads to the mixed-valence octanuclear  $[Co_8(\mu_4-O)_4]$ 









(4a R = H, 4b R = 3-phenylpropyl)









 $(PhCO_2)_{12}(L)_3(H_2O)]$  (L = DMF, MeCN, H<sub>2</sub>O) [36, 37]. We have recently shown that the mixed valence octanuclear  $[CO_8(\mu_4-O)_4(\mu-OAc)_6(\mu-OMe)_4(Cl)_4(OH_n)_4]$  (n = 1 or 2) is produced in good yield during the recrystallisation of "cobalt(III) acetate"

from methanol over several months in the presence of a halide source such as  $CH_2Cl_2$  or AX (A = H<sup>+</sup>, Li<sup>+</sup>, NH<sub>4</sub><sup>+</sup>; X = Cl<sup>-</sup>) [38].

In continuation of our studies on the constitution of "cobalt(III) acetate" we report here the isolation



(10)

from "cobalt(III) acetate"/pyridine of the neutral cubane,  $[Co_4(\mu_3-O)_4(\mu-OAc)_4(py)_4]$ , (11), the synthesis of the partial cubane, the trinuclear dication,  $[Co_3(\mu_3-O)(\mu-OH)_3(\mu-OAc)(OAc)(py)_6]^{2+}$ , (12), as its hexafluorophosphate salt, and the structural characterisation of these compounds.

#### **EXPERIMENTAL**

**WARNING**: perchlorate salts are potentially explosive and must be treated with care.

## Chemicals

Cobalt(II) acetate tetrahydrate and lithium peroxide (both Aldrich), acetic acid (Biolab), light petroleum (BDH), acetic anhydride, ammonium hexafluorophosphate, dichloromethane, dimethylformamide, dimethylsulfoxide, ethanol, methanol and sodium perchlorate hydrate (all Merck), acetonitrile, chloroform, 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.

The compounds  $[Co_2(\mu-OH)_2(\mu-OAc)(OAc)_2(py)_4][PF_6], (2)[PF_6] and (5)[PF_6], <math>[Co_3(\mu_3-O)(\mu-OAc)_6(py)_3][PF_6], (7)[PF_6], and [Co_3(\mu_3-O)(\mu-OH)(\mu-OAc)_5(py)_3][PF_6], (4a)[PF_6], were prepared by published methods [32,34]. "Cobalt(III) acetate" was prepared using the following adaptation of a reported method [26]. Cobalt(II) acetate tetrahydrate (12.5 g, 0.05 mol) was stirred overnight in acetic acid (125 cm<sup>3</sup>) precipitating anhydrous pink cobalt(II) acetate with some pink cobalt(II) acetate remaining dissolved. The mixture was then ozonated (20 1 (O<sub>2</sub>)/h) with a$ 

Wallace and Tiernan laboratory ozonator (model BA-023012) ("250 V") for 19 h. The solution turned from pink to dark brown within several minutes. The resulting green solution was evaporated *in vacuo* at < 20°C to give dark green crude "cobalt(III) acetate" (11.0 g). Crude "cobalt(III) acetate" (10.0 g) was then crushed and dissolved in chloroform (~200 cm<sup>3</sup>) and the solution filtered. Light petroleum (60–80°C; ~500 cm<sup>3</sup>) was then added to the filtrate and the green "pure" "cobalt(III) acetate" isolated by filtration and dried *in vacuo* (8.1 g, 69% as "Co(OAc)<sub>3</sub>"). Selected IR data (KBr) :  $v_{max}/cm^{-1}$ . 1576 (vs), 1420 (vs), 1347 (w), 1044 (w), 1030 (w), 957 (w), 890 (w), 805 (w), 747 (vw), 720 (vw), 698 (s), 631 (m), 581 (vw), 496 (w), 414 (w).

# Tetrakis[ $(\mu$ -acetato- $\kappa O$ : $\kappa O'$ )- $\mu_3$ -oxo-(pyridine)cobalt (III)], [Co<sub>4</sub>( $\mu_3$ -O)<sub>4</sub>( $\mu$ -OAc)<sub>4</sub>(py)<sub>4</sub>] (11)

Method A—Formation from "cobalt(III) acetate". In a sealed vessel, pyridine (0.4 g, 5 mmol) and NaClO<sub>4</sub>· $nH_2O$  (0.2 g, ~1 mmol) were added to a dark green solution of "pure" "cobalt(III) acetate" (1.0 g, 4.2 mmol as "Co(OAc)<sub>3</sub>") in methanol (10 cm<sup>3</sup>) and the mixture stirred briefly. The mixture was left at room temperature for 1 h and filtered. Small brown crystals were collected by filtration, washed with diethyl ether and dried in air (0.01 g). The solid was identified by ESI/MS and solution 'H NMR in CD<sub>3</sub>CN and CD<sub>2</sub>Cl<sub>2</sub> as a mixture of mainly  $[Co_3(\mu_3 - \mu_3)]$  $O(\mu-OMe)(\mu-OAc)_5(py)_3][ClO_4]$ , a smaller amount of (4a)[ClO<sub>4</sub>] and another species not readily identified. The filtrate was left for another 10 h, precipitating more solid (0.3 g) which was collected by filtration and dried over silica gel. The 'H NMR in CD<sub>3</sub>CN and CD<sub>2</sub>Cl<sub>2</sub> showed the material also consisted of (4a)[ClO<sub>4</sub>] and [Co<sub>3</sub>( $\mu_3$ -O)( $\mu$ -OMe)( $\mu$ -OAc)<sub>5</sub>(py)<sub>3</sub>] [ClO<sub>4</sub>], as well as other products not easily identified by <sup>1</sup>H NMR. After removal of the solvent in vacuo, a dark brown paramagnetic solid was obtained (0.58 g). The solid was washed through alumina with acetonitrile, to give an olive/green solution. The solvent was removed and the solid dried in vacuo. <sup>1</sup>H NMR in CD<sub>3</sub>CN showed the solid to contain a mixture of species including the cubane, (11), (5), (2), (3)and other species not easily or previously identified by 200 MHz <sup>1</sup>H NMR. Selected IR data (KBr):  $v_{max}/cm^{-1}$  3110 (w), 3071 (w), 3046 (w), 3005 (w), 2926 (w), 1606 (w), 1550 (sh, s), 1540 (vs), 1485 (m), 1451 (m), 1414 (s), 1338 (m), 1214 (m), 1152 (w), 1073 (w), 1048 (w), 1019 (vw), 761 (m), 694 (s), 647 (sh), 632 (s), 585 (m), 572 (m). UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>): 604 (sh) nm ( $\varepsilon_{\rm M} = 509 \,{\rm M}^{-1} \,{\rm cm}^{-1}$ ), 484 (sh) nm ( $\varepsilon_{\rm M} = 893 \,{\rm M}^{-1}$ cm  $^{-1}$  ), 364 nm ( $\epsilon_{M}=9342~M^{-1}\,cm^{-1}$  ).  $^{1}H$  NMR (200 MHz; CD<sub>3</sub>Cl):  $\delta$  8.37 (d, 8H),  $\delta$  7.59 (t, 4H),  $\delta$  7.16  $(t, 8H), \delta 1.99 (s, 12H).$ <sup>13</sup>C NMR (200 MHz; CD<sub>3</sub>Cl):  $\delta$  186.86,  $\delta$  153.47,  $\delta$  124.46,  $\delta$  138.62,  $\delta$  26.63.  $ESI/MS: 853 ([M+H]^+), 774 ([M+H-py]^+), 695$  $([M + H - 2py]^+).$ 

Method B-Direct ozonation oxidation method. Cobalt(II) acetate tetrahydrate (3.125 g, 12.5 mmol) was dissolved in water (25 cm<sup>3</sup>). Acetic acid (10 cm<sup>3</sup>, 18 M) and pyridine (1.00 g, 12.6 mmol) were then added to the mixture and stirred (1 h). The reaction mixture was then ozonated (2 h) during which the solution changed colour from pink/red to dark olive/ brown. After ozonolysis the reaction mixture was immediately and quickly heated ( $\sim 65^{\circ}$ C) and ammonium hexafluorophosphate (1.36 g, 8.3 mmol) dissolved in water (5 cm<sup>3</sup>) was added. The resulting mixture was allowed to cool to room temperature and subsequently kept at low temperature (5d,  $<5^{\circ}$ C). The product mixture of small crystals (2.6 g) was collected by filtration, washed with water, and dried over silica gel overnight. <sup>1</sup>H NMR indicated that the solid contained a mixture of mainly  $(4a)[PF_6]$  with smaller amounts of (3)[PF<sub>6</sub>]<sub>2</sub> and a material formulated as  $[Co(\mu-OH)_2(\mu-OAc)(OAc)_2(py)_3(solvent)]$  $[PF_6]$  [32] and trace amounts of the dimeric species (2)  $[PF_6]$ . The filtrate was again kept at low temperature for several days after which a second crop of solid material was filtered, washed with a little water and dried (0.02 g). The remaining filtrate was extracted into methylene chloride  $(3 \times 50 \text{ cm}^3)$ , the combined methylene chloride extracts washed with water, hydrogen carbonate solution and finally sodium chloride solution and the solvent removed by rotary evaporation at room temperature. The resulting brown solid was finally dried in vacuo (0.55 g). The solid obtained from the methylene chloride extract was found to contain a mixture of mainly the oxo-centred trimers (7)  $[PF_6]$ , (4a)  $[PF_6]$ , (3)  $[PF_6]_2$  and the cubane (11) as observed by solution 'H NMR and TLC. The cubane, (11), can be isolated from the mixture using column chromatography.

Method C—Preparation from  $[Co_2(\mu-OH)_2(\mu-OH$  $OAc)(OAc)_2(py)_4][PF_6]$ . A procedure similar to that reported [35] for the preparation of  $[Co_4(\mu_3-O)_4(\mu_2 OAc_{2}(bpy)_{4}^{2+}$  was used to synthesise  $[Co_{4}(\mu_{3}-O)_{4}(\mu_{2}-O)_{4}(\mu_{3}-O)_{4}($ OAc)<sub>4</sub>(py)<sub>4</sub>]. Crystals suitable for X-ray crystallographic analysis were obtained by this method. Under nitrogen,  $[Co_2(\mu-OH)_2(\mu-OAc)(OAc)_2(py)_4]$  $[PF_6]$  ((2)[PF<sub>6</sub>]) (0.079 g, 0.1 mmol) and lithium peroxide (0.023 g, 0.5 mmol) were stirred and heated to 55°C (15 min) in dimethylsulphoxide (5 cm<sup>3</sup>). The original red solution changed colour to olive/brown during the reaction and after cooling the reaction mixture was filtered. Chloroform (25 cm<sup>3</sup>) was added to the filtrate and the mixture left stoppered  $(<5^{\circ}C)$ . Over one week large dark olive crystals formed and were subsequently filtered, dried in air and identified as pure (11) (0.01 g, 23%) by using solution <sup>1</sup>H NMR and IR. The salts  $(5)[PF_6]$ ,  $(7)[PF_6]$ ,  $(4a)[PF_6]$ , or  $(12)[PF_6]_2$  can be used in place of (2)[PF<sub>6</sub>], with yields of 21, 27, 48 and 8%, respectively, depending on the crystallisation time and temperature. Similarly, (4a) [PF<sub>6</sub>] can be reacted with Li<sub>2</sub>O<sub>2</sub> as above, but in DMF, rather than in DMSO to produce predominantly (11). Alternatively, (4a)[PF<sub>6</sub>] can be

reacted as above with DMSO in the presence or absence of KOH (in place of  $Li_2O_2$ ) to give (11) in yields of 23 and 58%, respectively.

Acetato( $\mu$ -acetato- $\kappa O$ :  $\kappa O'$ )-tris( $\mu_3$ -hydroxo)- $\mu_3$ -oxohexakis(pyridine)tricobalt(III) hexafluorophosphate, [Co<sub>3</sub>( $\mu_3$ -O)( $\mu$ -OH)<sub>3</sub>( $\mu$ -OAc)(OAc)(py)<sub>6</sub>][PF<sub>6</sub>]<sub>2</sub>, (12) [PF<sub>6</sub>]<sub>2</sub>

Method A-Direct ozonation oxidation method. Cobalt(II) acetate tetrahydrate (3.125 g, 12.5 mmol) dissolved in water (25 cm<sup>3</sup>) was stirred with pyridine (2.00 g, 25.3 mmol) and the pink/red solution ozonated (2 h). The resulting dark brown solution was quickly heated ( $\sim 70^{\circ}$ C) and added to an aqueous solution of ammonium hexafluorophosphate (1.36 g, 8.3 mmol in 5 cm<sup>3</sup>). After cooling to room temperature a brown solid was collected by filtration, washed with water, and dried over silica gel overnight (3.7 g). Solution <sup>1</sup>H NMR in CD<sub>3</sub>CN showed the solid to contain a mixture of species including (5), (3), (2), (12), (6)and trace amounts of other species. The filtrate was extracted into methylene chloride  $(3 \times 100 \text{ cm}^3)$ , the combined methylene chloride extracts evaporated to 5 cm<sup>3</sup> and layered with diethylether. After 24 h a brown solid was filtered (0.6 g) and was found to consist of a mixture of (2), (5), (12), (6), (3) and trace amounts of other species as identified by solution <sup>1</sup>H NMR in CD<sub>3</sub>CN.

Method B. The synthesis of  $[Co_3(\mu_3-O)(\mu-OH)_3(\mu OAc)(OAc)(py)_6][PF_6]_2$  was adapted from that reported for  $[Co_3(\mu_3-O)(\mu-OH)_3(\mu-OAc)(OAc)(bpy)_3]$  $[ClO_4]_2$  [35]. Cobalt(II) acetate tetrahydrate (1.24 g, 5.0 mmol) was dissolved in water  $(4 \text{ cm}^3)$  and subsequently stirred (15 min) with ethanol (24  $\text{cm}^3$ ) and pyridine (0.8 g, 10.1 mmol) to form a purple solution. The stirred cobalt(II) solution was treated dropwise with hydrogen peroxide (5.8 cm<sup>3</sup>) over  $\sim$  45 min. The solution changed colour to dark brown and increased in temperature to 37°C during the addition of hydrogen peroxide. Ammonium hexafluorophosphate (0.55 g, 3.4 mmol) dissolved in ethanol (2 cm<sup>3</sup>) and water  $(1 \text{ cm}^3)$  was then added and the solution was stirred briefly (5 min) and then left covered at room temperature. After one week a microcrystalline solid (typically  $\sim 0.22$  g) was separated by filtration, the filtrate was retained and the solid was dried over silica gel. The crude dried solid was extracted into acetonitrile and a small amount of purple paramagnetic material was removed by filtration. The acetonitrile was evaporated and the resulting brown solid was found to contain mainly  $(12)[PF_6]_2$  with trace amounts of  $(5)[PF_6]$  and  $(3)[PF_6]_2$  as identified by <sup>1</sup>H NMR in CD<sub>3</sub>CN. The remaining original reaction mixture filtrate was cooled ( $<5^{\circ}$ C) for one week and then filtered. A brown precipitate (0.15 g) was obtained from the supernatant and found (<sup>1</sup>H NMR) to contain a mixture of species including  $(5)[PF_6]$ ,  $(3)[PF_6]_2$ ,  $(12)[PF_6]_2$  with others as yet unidentified.

The remaining dark brown filtrate was evaporated to dryness in vacuo to give a dark brown solid (1.42 g). 'H NMR in CD<sub>3</sub>CN, after filtration through alumina, revealed the extract contained a mixture of pyridine containing species including (2)[PF<sub>6</sub>], (5)[PF<sub>6</sub>],  $(3)[PF_6]_2$ , and others as yet unidentified. Pure brown/orange (12)[PF<sub>6</sub>]<sub>2</sub> ( $Rf \simeq 0.24$ ) was obtained by chromatographing small amounts of the first microcrystalline material through a short column of flash silica using 4:1 methylene chloride: acetonitrile as eluent after examination by TLC ((5)[PF<sub>6</sub>],  $Rf \simeq 0.35$ and (3)[PF<sub>6</sub>]<sub>2</sub>,  $Rf \simeq 0.43$ ). Anal. [Co<sub>3</sub><sup>111</sup>( $\mu_3$ -O)( $\mu$ -OH)<sub>3</sub>( $\mu$ -OAc)<sub>2</sub>(py)<sub>6</sub>][PF<sub>6</sub>]<sub>2</sub> (12)[PF<sub>6</sub>]<sub>2</sub>. Selected IR data (KBr): v<sub>max</sub>/cm<sup>-1</sup> 1609 (w), 1490 (w), 1451 (m), 1385 (w), 1331 (w), 1218 (w), 1074 (w), 1049 (w), 1021 (w), 880 (m), 844 (vs), 765 (w), 700 (m), 693 (m), 600 (br), 558 (s). Selected <sup>1</sup>H NMR (200 MHz;  $CD_3CN, TMS$ ): -2.75 (s, 1H), -0.36 (s, 1H), 0.88 (s, 3H), 2.15 (s, 3H), 5.17 (s, 1H). <sup>13</sup>C NMR (200 MHz; CD<sub>3</sub>CN, TMS): 24.73, 25.61, 156.5, 151.93, 152.79, 153.84, 155.31, 155.48, 125.43, 126.16, 126.25, 126.45, 126.74, 140.43, 140.66, 140.92, 141.06, 185.02, 189.85. ESI/MS: 981.0 ( $[M-PF_6]^+$ ), 418 ( $[M-PF_6]^+$ )  $2PF_6]^{2+}$ ).

#### Structure determinations

Discrete single dark green-olive crystals of the cubane,  $[Co_4(\mu_3-O)_4(\mu-OAc)_4(py)_4] \cdot 5CHCl_3$ , ((11) · 5CHCl<sub>3</sub>), were obtained as the CHCl<sub>3</sub> solvate by leaving a DMSO solution in contact with CHCl<sub>3</sub> for several weeks below 5°C. Crystals of (11) · 5CHCl<sub>3</sub> lost solvent readily. Accordingly a green plate was quickly mounted and cooled to  $-50^{\circ}$ C. Small prismatic red crystals of the  $PF_6^-$  salt of the partial cubane,  $[Co_3(\mu_3-O)(\mu-OH)_3(\mu-OAc)(OAc)(py)_6][PF_6]_2 \cdot 2H_2O,$ ((12)  $[PF_6]_2 \cdot 2H_2O$ ), were obtained by slow crystallisation from the mother liquor over two weeks. X-ray diffraction measurements were made with a Rigaku AFC7R diffractometer employing graphite monochromated Cu- $K_{\alpha}$  radiation generated with a 12 kW direct drive rotating anode. Primitive cell constants were obtained from a least-squares refinement using the setting angles of 22(25) (for the cubane, ((11) · 5CHCl<sub>3</sub>), and (in parentheses) partial cubane,  $((12)[PF_6]_2 \cdot 2H_2O)$ , respectively) reflections in the range  $41.15(18.40) < 2\theta < 69.80(23.78)^{\circ}$ . The data were collected at  $-50(21) \pm 1^{\circ}$ C using  $\omega - 2\theta$  scans to a maximum  $2\theta$  value of 110.1(100.1)°. Omega scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.19(0.34). The data were collected with scans of  $(1.47(1.21) + 0.35 \tan \theta)^{\circ}$  at a speed of  $32.0(16.0)^{\circ}/\text{min}$ (in omega). The weak reflections  $(I < 15.0\sigma(I))$  were rescanned up to 10 scans, and the counts were accumulated. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2:1. Over the course of data collection, the intensities of three representative reflections, measured every 150 reflections, decreased by 3.2(3.8)%. Empirical absorption corrections based on azimuthal scans of three reflections were applied to each set of data, with transmission factors ranging from 0.33(0.73) to 1.00. The data were also corrected for Lorentz and polarisation effects.

All calculations were performed using the teXsan crystallographic software package [39]. The structures were solved by direct methods and expanded using Fourier techniques [40,41]. The solution of the cubane structure in Pnma (#62), revealed a  $[Co_4(\mu_3-O)_4(\mu_3-$ OAc)<sub>4</sub>(py)<sub>4</sub>] cluster bisected by a mirror plane and surrounded by five chloroform molecules distributed over six sites (a chloroform on a general site was assigned half occupancy). Two chloroform molecules straddle the same mirror that splits the complex, and one of these has a two-fold rotational disorder about the mirror plane. Not all of the non-hydrogen atoms could be refined anisotropically. Hydrogen atoms were included in the full matrix refinement at calculated positions with group temperature factors. Hydrogen atoms were not attached to four of the five chloroform molecules. In the case of the partial cubane salt.  $[Co_3(\mu_3-O)(\mu-OH)_3(\mu-OAc)(OAc)]$  $(py)_{6}$  [PF<sub>6</sub>]<sub>2</sub>, the limited data obtained from the small crystal, (1765 observed reflections,  $(I > 1.5\sigma(I))$  precluded the anisotropic refinement of all of the nonhydrogen atoms. Hydrogen atoms were included in the full matrix refinement at calculated positions with group temperature factors. The hydroxyl and water hydrogen atoms could not be located and were not included at calculated positions in the refinement model. One of the hexafluorophosphate counterions was found to be severely disordered.

The residual weighting scheme for each solution was based on counting statistics and included a statistical uncertainty factor (p = 0.003). Neutral atom scattering factors were taken from Cromer and Waber [42]. Anomalous dispersion effects were included in the structure factor calculation [43], and the values for  $\Delta f'$  and  $\Delta f''$  were those of Creagh and McAuley [44]. The values for the mass attenuation coefficients are those of Creagh and Hubbell [45].

Full tables of bond lengths and angles, listings of atomic coordinates, observed and calculated structure factors and anisotropic thermal parameters are available as supplementary material (Tables S1–S16). Selected interatomic bond lengths and bond angles are given in Tables 2–5.

### Crystal data

 $C_{33}H_{34}Cl_{15}Co_4N_4O_{12}, M = 1446.18$ , orthorhombic, space group, *Pnma*, (62), a = 10.181(4), b = 21.655(2), c = 27.407(6) Å, U = 6043(2) Å<sup>3</sup>,  $D_c$ (Z = 4) = 1.590 g cm<sup>-3</sup>, F(000) = 2876.00,  $\lambda(Cu-K_{\alpha}) = 1.54178$  cm<sup>-1</sup>,  $\mu(Cu-K_{\alpha}) = 150.00$  cm<sup>-1</sup>. Specimen : green blade,  $0.52 \times 0.17 \times 0.05$  mm. N = 3978,  $C_{34}H_{36}Co_3O_{10}P_2F_{12}N_6$ , M = 1155.42, monoclinic, space group,  $P2_{1/c}$ , (14), a = 20.340(4), b = 12.730(2), c = 20.585(4) Å,  $\beta = 114.80(1)$ , U = 4839(2) Å<sup>3</sup>,  $D_c$ (Z = 4) = 1.586 g cm<sup>-3</sup>, F(000) = 2324.00,  $\lambda$ (Cu- $K_{\alpha}$ ) = 1.54178 cm<sup>-1</sup>,  $\mu$ (Cu- $K_{\alpha}$ ) = 95.20 cm<sup>-1</sup>. Specimen : red prism,  $0.20 \times 0.10 \times 0.08$  mm. N = 5465,  $N_0$  $(I > 1.5\sigma(I)) = 1765$ , range of hkl 0–20, 0–12, –20– 20, R = 0.078,  $R_w = 0.073$ , residual extrema +0.66, -0.40 e Å<sup>-3</sup>.

### **RESULTS AND DISCUSSION**

Following the procedure of Uemura et al., the known trimers,  $[Co_3(\mu_3-O)(\mu-OR)(\mu-OAc)_5(py)_3]^+$ (R = H, Me), were isolated as their brown  $ClO_4^-$  or  $PF_6^-$  salts from methanol solutions of "cobalt(III) acetate" and pyridine. These materials were not known at the time of the work of Uemura et al. who correctly predicted that the structure of the solid first precipitated by this method differs from that of the  $[M_3(\mu_3-O)(OAc)_6(solvent)_3]^{n+}$  species known at that time. Small amounts of additional, as yet unidentified, species were also precipitated in the present work, the total amount of characterised and uncharacterised precipitated salts accounting for approximately half of the "cobalt(III) acetate". Removal of the solvent left a dark brown paramagnetic solid, found to consist of the neutral diamagnetic tetramer  $[Co_4(\mu_3-O)_4(\mu_3 OAc_4(py_4]$ , (11), in a mixture of other species, some previously identified, others currently unidentified. The tetramer was characterised by vibrational, electronic, <sup>1</sup>H and <sup>13</sup>C NMR and electrospray mass spectroscopies. The single 'H NMR resonance due to the acetate protons ( $\delta$  1.99 ppm in CD<sub>3</sub>CN) and the simple set of pyridine resonances suggested a species of high symmetry in solution, whilst the mass spectrum indicated a tetramer. This structure was confirmed as a cubane by single X-ray diffraction and is illustrated in Fig. 1.

The cubane,  $[Co_4(\mu_3-O)_4(\mu-OAc)_4(py)_4]$ , (11), can also be isolated by direct ozonolysis of [Co(OAc)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>] in water/acetic acid/pyridine (25/10/1 v/v), followed by precipitation of (4a), (3) and (2) with  $NH_4PF_6$ , extraction into dichloromethane and chromatographic separation from (7), (4a) and (3), or by reaction of  $Li_2O_2$  with the dimers (2) or (5) or with the trimers (7), (4a) or with the trinuclear partial cubane (12) in dimethylsulfoxide or with the trinuclear (4a) in dimethylformamide. Alternatively, trimeric (4a) can be heated in dimethylsulfoxide in the presence or absence of KOH. The reaction of (2) with  $Li_2O_2$  in DMSO is analogous to the preparation of  $[Co_4(\mu_3-O)_4(\mu-OAc)_2(bipy)_4]^{2+}$  by Dimitrou et al. [35]. Interestingly, the neutral cubane,  $[Co_4(\mu_3-O)_4(\mu-OAc)_4(py)_4]$ , is formed, rather than



Fig. 1. ORTEP [46] illustration of the cubane,  $[Co_4(\mu_3-O)_4(\mu_$ 

 $[Co_4(\mu_3-O)_4(\mu-OAc)_2(py)_8]^{2+}$ , the analogue of the known bipyridyl derivative.

Ozonation of  $[Co(OAc)_2(H_2O)_4]$  in water/pyridine (13/1 v/v), followed by brief heating results in a mixture of products. The partial cubane dication,  $[Co_3(\mu_3 -$ O) $(\mu$ -OH)<sub>3</sub> $(\mu$ -OAc) $(OAc)(py)_6$ <sup>2+</sup>, (12), can be isolated from this mixture as its  $PF_6^-$  salt. Alternatively, oxidation of [Co(OAc)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>] by H<sub>2</sub>O<sub>2</sub> in water/ ethanol/pyridine (4/24/1 v/v) followed by treatment with  $NH_4PF_6$  generates an unidentified paramagnetic purple solid from which  $(12)[PF_6]_2$  can be chromatographically separated from salts of the dimeric cations (2) and (5) and of the trimeric cation (3). The compound was characterised spectroscopically (vibrational, <sup>1</sup>H NMR, <sup>13</sup>C NMR and electrospray mass spectra). A trinuclear formulation is suggested by the mass spectrum, whilst the <sup>1</sup>H NMR indicates two different acetate and three different hydroxyl (one of which is involved in hydrogen bonding) environments in solution. Restricted rotation of some of the pyridine ligands about the Co-N axes is also suggested by the 'H NMR spectrum. The trinuclear structure of the cation was confirmed by single crystal X-ray crystallography and is illustrated in Fig. 2. Salient NMR data of these compounds are collected in Table 1.

The cubane has possibly previously escaped notice as a "constituent" or derivative of "cobalt(III) acetate" because of its high solubility in the solvents used, its colour and lack of charge. Indeed, the formation of the cubane from salts of any of (2), (5), (12), (4a) or (7) in d<sup>6</sup>-DMSO can be monitored by <sup>1</sup>H NMR. The predominant species is invariably the cubane (11) with some free pyridine and trace amounts of other, at present unidentified, species. The variable yields of



Fig. 2. ORTEP [46] illustration of the trimeric partial cubane dication,  $[Co_3(\mu_3-O)(\mu-OH)_3(\mu-OAc)(OAc)(py)_6]^{2+}$ , (12), showing the atom numbering scheme.

cubane from the different preparations are thus mainly due to the high solubility of this neutral species. Solution <sup>1</sup>H NMR spectra in  $CD_2Cl_2$ ,  $D_2O$ , CD<sub>3</sub>CN, CD<sub>3</sub>OD and (CD<sub>3</sub>)<sub>2</sub>SO at room temperature are consistent with the solid state structure and retention of  $T_d$  symmetry in these solvents. However, a different <sup>1</sup>H NMR spectrum is obtained in CD<sub>3</sub>CO<sub>2</sub>D at room temperature. Two pyridine environments are apparent, consistent with the formation of the diprotonated species,  $[Co_4(\mu_3-O)_2(\mu-OH)_2(\mu-OAc)_4(py)_4]^{2+}$ . After further rearrangements over several weeks at room temperature, the oxo-centred trimers, (2) and (7) were observed as the predominant species. However, in CD<sub>3</sub>OD at room temperature, <sup>1</sup>H NMR shows the cubane (11) to be stable for several months, unlike (4a), for example, which slowly converts to other species in this solvent.

### X-ray crystallographic analysis of (11)

Single crystals of (11) are composed of discrete  $[Co_4(\mu_3-O)_4(\mu-OAc)_4(py)_4]$  molecules with the five chloroform molecules of crystallisation per tetramer located in large channels in the crystal lattice between the tetramers. The tetranuclear species contains four cobalt atoms and four oxygen atoms located at alternate corners of a slightly distorted cube in a typical  $[M_4(\mu_3-O)_4]$  cubane type arrangement. Every cobalt atom is surrounded by a slightly distorted octahedron of two oxygen atoms from bridging acetate ligands, a nitrogen atom of a pyridine ligand and three neighbouring  $[Co_4(\mu_3-O)_4]$  core oxygen atoms.

Each  $[Co_4(\mu_3-O)_4(\mu-OAc)_4(py)_4]$  molecule is bisected by a crystallographic mirror plane. Consequently, two Co···Co distances are observed, that (average 2.818 Å) bridged by two oxo ligands only, and that (average 2.683 Å) bridged by two oxo ligands

Complex	Solvent (ref.)	Methyl protons	Hydroxyl and methoxy proton(s)	Pyridine protons
[Co <sub>3</sub> O(OAc) <sub>6</sub> (py) <sub>3</sub> ][PF <sub>6</sub> ]	CD <sub>3</sub> CN	2.07		8.90 (d, 6H),
	(TMS)	(s, 18H)		8.15 (t, 3H),
				7.74 (t, 6H)
$[Co_3O(OMe)(OAc)_5(py)][PF_6]$	CD <sub>3</sub> CN	2.15 (s, 3H),	0.73 (s, 3H)	9.27 (d, 2H),
	(TMS)	2.15 (s, 6H),		8.68 (d, 4H),
		1.87 (s, 6H)		8.31 (t, 1H),
				8.21 (t, 2H),
				7.93 (t, 2H),
				7.79 (t, 4H)
[Co <sub>3</sub> O(OH)(OAc) <sub>5</sub> (py)][PF <sub>6</sub> ]	CD <sub>3</sub> CN	2.08 (s, 3H),	-3.09 (s, 1H)	9.26 (d, 2H),
	(TMS)	2.05 (s, 6H),		8.83 (d, 4H),
		1.95 (s, 6H)		8.31 (t, 1H),
				8.18 (t, 2H),
				7.92 (t, 2H),
				7.76 (t, 4H)
$[\mathrm{Co}_4\mathrm{O}_4(\mathrm{OAc})_4(\mathrm{py})_4]$	CD <sub>3</sub> CN	1.99 (s, 12H)		8.37 (d, 8H),
	(TMS)			7.58 (t, 4H),
	· · · ·			7.09 (t, 8H)
$[Co_2O(OH)_2(OAc)_2(pv)_2][PE_2]_2$	CD <sub>3</sub> CN	0.88 (s, 3H), 2.15 (s, 3H)	-2.75 (s, 1H),	9.5 - 6.85
	(TMS)		-0.36 (s. 1H).	(multiplets &
	、 /		5.17 (s, 1H)	broad peaks)

 Table 1. Selected spectrophotometric data for selected polynuclear cobalt(III) carboxylate species. <sup>1</sup>H NMR chemical shifts (ppm) of the acetate, hydroxy and pyridine protons in some cobalt complexes (200 MHz)

Table 2. Selected intramolecular distances (Å) involving the nonhydrogen atoms for  $[Co_4O_4(OAc)_4(py)_4] \cdot 5CHCl_3$ , (11)  $\cdot 5CHCl_3$ 

			and and an example in the set of
Co(1) - Co(1)	2.817(7)	Co(2) - O(1)	1.86(1)
Co(1)Co(2)	2.685(6)	Co(2) - O(2)	1.83(2)
Co(1)—Co(3)	2.680(6)	Co(2)-O(5)	1.96(2)
Co(2)—Co(3)	2.818(8)	Co(2)—O(5)	1.96(2)
Co(1)—O(1)	1.86(1)	Co(2)—N(2)	1.97(3)
Co(1)—O(2)	1.91(1)	Co(3)—O(1)	1.83(1)
Co(1)O(3)	1.88(1)	Co(3)—O(1)	1.83(1)
Co(1)—O(4)	1.94(2)	Co(3)—O(3)	1.89(2)
Co(1)—O(6)	1.95(2)	Co(3)—O(7)	1.98(2)
Co(1)—N(1)	1.97(2)	Co(3)—O(7)	1.98(2)
Co(2)—O(1)	1.86(1)	Co(3)—N(3)	1.98(3)

Estimated standard deviations in the least significant figure are given in parentheses.

and a bidentate acetate ligand. These distances are marginally shorter (oxo bridged) and longer (carboxylate bridged) than the corresponding distances (average 2.852(2) and 2.665(2) Å) in  $[Co_4(\mu_3-O)_4(\mu-OAc)_2(bpy)_4]^{2+}$ , (10) [35]. The bis-oxo bridged  $Co\cdots Co$  distances have no exact parallel in the known structures of tri- and tetranuclear pyridineligated basic cobalt(III) acetate complexes; however, the oxo/carboxylate bridged  $Co\cdots Co$  distances are the shortest yet reported in these species. The pyridine planes containing N(2) and N(3) are inclined at 18.3(8)° and those containing N(1) and N(1\*) are inclined at  $16.4(8)^{\circ}$ . The N(1) to N(1\*) contact is 3.37(4) Å and that between N(2) and N(3) is 3.26(4) Å.

Each cobalt-centred octahedron is tilted slightly into the cubane core presumably because of steric interactions between the pyridine ligands which are oriented perpendicular to the cube faces bridged by two oxo ligands only and because of the bridging acetate arrangement around the  $[Co_4(\mu_3-O)_4]$  core. The core  $\mu_3$ -oxygen atoms are on average 1.01(1) Å out of their respective trimeric Co<sub>3</sub> planes.

Other structural parameters of (11) are similar to those of species containing the  $[Co_4(\mu_3-O)_4]^{4+}$  (or  $[Co_4(\mu_4-O)_4]^{4+}$ ) core;  $[Co_4(\mu_3-O)_4(\mu-O_2CC_6H_4-p-Me)_2$ (bpy)\_4]^{2+},  $[Co_4(\mu_3-O)_3(\mu_3-OH)(\mu-O_2CC_6H_4-p-Me)_2$ (bpy)\_4]^{3+},  $[Co_4(\mu_4-O)_4(\mu-O_2CPh)_{12}(MeCN)_3(H_2O)]$ and  $[Co_8(\mu_4-O)_4(\mu_3-OMe)_4(\mu-O_2CMe)_6(O)_4(Cl)_4]$  [35– 38].

## X-ray crystallographic analysis of (12) [PF<sub>6</sub>]<sub>2</sub>

The dication of  $[Co_3(\mu_3-O)(\mu-OH)_3(\mu-OAc)(OAc)$ (py)<sub>6</sub>][PF<sub>6</sub>]<sub>2</sub>·2H<sub>2</sub>O is an oxo-centred trinuclear cobalt-(III) cluster containing six pyridine, one bidentate bridging acetate, one monodentate acetate, and three bridging hydroxyl ligands. Each cobalt atom is situated in a slightly distorted octahedral environment. The  $[Co_3(\mu_3-O)(\mu-OH)_3]$  core can be considered as a partial cubane, lacking the fourth cobalt atom to

Table 3. Selected intramolecular bond angles (7) involving the nonhydrogen atoms f	for
$[Co_4O_4(OAc)_4(py)_4]$ · 5CHCl <sub>3</sub> , (11) · 5CHCl <sub>3</sub>	

O(1)Co(1)O(2)	86.3(7)	O(5)—Co(2)—O(5)	95(1)
O(1)-Co(1)-O(3)	87.3(7)	O(5)—Co(2)—N(2)	91.6(8)
O(1)Co(1)O(4)	87.5(6)	O(5)—Co(2)—N(2)	91.6(8)
O(1)—Co(1)—O(6)	88.6(7)	O(1)Co(3)O(1)	81.2(9)
O(1)-Co(1)-N(1)	178.6(7)	O(1)—Co(3)—O(3)	87.7(7)
O(2)—Co(1)—O(3)	83.7(6)	O(1)—Co(3)—O(7)	91.2(6)
O(2)—Co(1)—O(4)	90.5(7)	O(1)—Co(3)—O(7)	171.2(7)
O(2)—Co(1)—O(6)	172.2(7)	O(1) - Co(3) - N(3)	93.6(8)
O(2) - Co(1) - N(1)	94.7(8)	O(1)—Co(3)—O(3)	87.7(7)
O(3)—Co(1)—O(4)	172.5(8)	O(1)—Co(3)—O(7)	171.2(7)
O(3)—Co(1)—O(6)	90.1(7)	O(1)—Co(3)—O(7)	91.2(6)
O(3) - Co(1) - N(1)	93.8(9)	O(1) - Co(3) - N(3)	93.6(8)
O(4)—Co(1)—O(6)	95.2(7)	O(3)—Co(3)—O(7)	87.7(6)
O(4) - Co(1) - N(1)	91.5(8)	O(3)—Co(3)—O(7)	87.7(6)
O(6)—Co(1)—N(1)	90.4(7)	O(3)—Co(3)—N(3)	178(1)
O(1)—Co(2)—O(1)	79.6(9)	O(7)—Co(3)—O(7)	96.1(9)
O(1)—Co(2)—O(2)	88.5(7)	O(7)Co(3)N(3)	91.2(7)
O(1)—Co(2)—O(5)	92.6(7)	O(7)—Co(3)—N(3)	91.2(7)
O(1)Co(2)O(5)	171.1(8)	Co(1)O(1)Co(2)	92.4(7)
O(1)—Co(2)—N(2)	93.1(8)	Co(1)O(1)Co(3)	93.2(7)
O(1)—Co(2)—O(2)	88.5(7)	Co(2)—O(1)—Co(3)	99.5(6)
O(1)—Co(2)—O(5)	171.1(8)	Co(1) - O(2) - Co(1)	95.0(9)
O(1)—Co(2)—O(5)	92.6(7)	Co(1)—O(2)—Co(2)	91.7(8)
O(1)—Co(2)—N(2)	93.1(8)	Co(1)—O(2)—Co(2)	91.7(8)
O(2)Co(2)-O(5)	87.0(7)	Co(1) - O(3) - Co(1)	97.3(9)
O(2)Co(2)O(5)	87.0(7)	Co(1)—O(3)—Co(3)	90.7(7)
O(2)—Co(2)—N(2)	178(1)	Co(1)O(3)Co(3)	90.7(7)

Estimated standard deviations in the least significant figure are given in parentheses.

achieve a full cubane ( $[Co_4(\mu_3-O)_4]$ ) configuration. Alternatively the molecule can be viewed as consisting of three edge sharing octahedra sharing a central  $\mu_3$ oxygen atom at a common vertex.

Each pair of cobalt atoms is bridged by a hydroxyl ligand. The atoms Co(2) and Co(3) are also bridged by a bidentate acetate ligand. Atom Co(1) is coordinated to the oxygen of a monodentate acetate

Table 4. Selected intramolecular distances (Å) involving the nonhydrogen atoms for  $[Co_3O(OH)_3(OAc)_2(py)_6][PF_6]_2$ .  $2H_2O$ , (12)[PF<sub>6</sub>]<sub>2</sub>·2H<sub>2</sub>O

Co(1)—Co(2)	2.900(5)	Co(2)-O(3)	1.92(1)
Co(1)-Co(3)	2.935(6)	Co(2)—O(5)	1.95(2)
Co(2)— $Co(3)$	2.767(5)	Co(2) - N(3)	1.95(2)
Co(1)—O(1)	1.92(1)	Co(2)—N(4)	1.99(3)
Co(1)-O(2)	1.93(1)	Co(3)—O(1)	1.92(1)
Co(1)—O(4)	1.94(1)	Co(3)—O(3)	1.88(1)
Co(1)—O(7)	1.91(2)	Co(3)O(4)	1.93(1)
Co(1) - N(1)	1.99(2)	Co(3)—O(6)	1.92(2)
Co(1)—N(2)	1.88(2)	Co(3)—N(5)	1.95(2)
Co(2)—O(1)	1.90(1)	Co(3)—N(6)	1.97(2)
Co(2)—O(2)	1.93(1)		

Estimated standard deviations in the least significant figure are given in parentheses.

ligand. This monodentate acetate ligand is hydrogen bonded to the hydroxyl ligand bridging Co(1) and Co(2). Two pyridine ligands complete the coordination about each cobalt atom.

The  $\mu_3$ -O atom is approximately 0.96 Å out of the  $Co_3$  plane, a displacement similar to that (0.97 Å) in the bipyridine-containing partial cubane,  $[Co_3(\mu_3 -$ O) $(\mu$ -OH)<sub>3</sub> $(\mu$ -OAc) $(OAc)(bpy)_3$ <sup>2+</sup>, (9) [35].

The hydrogen bonding distance between the acceptor monodentate acetate carbonyl oxygen atom and the hydroxyl oxygen donor atom is approximately 2.63(2) Å, typical of distances involved in similar bridging hydroxyl/monodentate acetate hydrogen bonding interactions observed within the dimeric species (2), (5) and (6) [32].  $[Co_3(\mu_3-O)(\mu-OH)_3]$  $(\mu$ -OAc)(OAc)(py)<sub>6</sub>][PF<sub>6</sub>]<sub>2</sub>·2H<sub>2</sub>O crystallises in the centrosymmetric space group  $P2_1/c$  (#14); therefore both enantiomers of the molecule are present in the unit cell. The structural parameters of (11) and (12) may be compared with those of related polynuclear basic acetate cobalt(III) species collected recently [33].

## CONCLUSIONS

To our knowledge isolation of a cubane ([Co<sub>4</sub>( $\mu_3$ -O)<sub>4</sub>]) type moiety from "cobalt(III) acetate" chem-

O(1) - Co(1) - O(2)	81.5(6)	Co(1)—O(1)—Co(2)	98.9(6)
O(1) - Co(1) - O(4)	80.6(6)	Co(1) - O(1) - Co(3)	99.8(6)
O(1) - Co(1) - O(7)	95.8(6)	Co(2)—O(1)—Co(3)	92.9(6)
O(1) - Co(1) - N(1)	171.1(8)	Co(1) - O(2) - Co(2)	97.5(6)
O(1) - Co(1) - N(2)	94.4(8)	Co(2)O(3)Co(3)	93.3(6)
O(2) - Co(1) - O(4)	92.4(6)	Co(1)O(4)-Co(3)	98.8(6)
O(2)Co(1)O(7)	91.5(6)	O(3)—Co(2)—N(4)	178(1)
O(2) - Co(1) - N(1)	93.6(7)	O(5) - Co(2) - N(3)	92.6(8)
O(2) - Co(1) - N(2)	175.1(8)	O(5)—Co(2)—N(4)	89.0(9)
O(4)Co(1)O(7)	174.2(7)	N(3)—Co(2)—N(4)	92(1)
O(4) - Co(1) - N(1)	92.2(7)	O(1)—Co(3)—O(3)	85.6(6)
O(4) - Co(1) - N(2)	89.6(8)	O(1)—Co(3)—O(4)	80.9(6)
O(7) - Co(1) - N(1)	91.8(7)	O(1)Co(3)O(6)	93.1(6)
O(7)Co(1)N(2)	86.2(8)	O(1)-Co(3)-N(5)	94.7(8)
N(1)-Co(1)-N(2)	90.8(9)	O(1)—Co(3)—N(6)	177.4(9)
O(1)-Co(2)-O(2)	82.1(6)	O(3)—Co(3)—O(4)	85.3(6)
O(1)Co(2)O(3)	85.2(6)	O(3)—Co(3)—O(6)	90.9(7)
O(1)Co(2)O(5)	91.4(7)	O(3)—Co(3)—N(5)	179.1(8)
O(1) - Co(2) - N(3)	171.7(9)	O(3)—Co(3)—N(6)	91.8(9)
O(1)Co(2)N(4)	95.0(9)	O(4)—Co(3)—O(6)	173.1(7)
O(2)Co(2)O(3)	86.7(6)	O(4)Co(3)N(5)	94.0(7)
O(2)Co(2)O(5)	172.6(7)	O(4)—Co(3)—N(6)	98.8(9)
O(2)Co(2)N(3)	93.4(8)	O(6)—Co(3)—N(5)	89.8(8)
O(2)Co(2)N(4)	95.0(9)	O(6)Co(3)N(6)	87(1)
O(3)Co(2)O(5)	89.2(7)	N(5)—Co(3)—N(6)	88(1)
O(3)Co(2)N(3)	87.6(8)		

Table 5. Selected intramolecular bond angles (°) involving the nonhydrogen atoms for  $\label{eq:cost} [Co_3O(OH)_3(OAc)_2(py)_6] [PF_6]_2 \cdot 2H_2O, \ (12) [PF_6]_2 \cdot 2H_2O$ 

Estimated standard deviations in the least significant figure are given in parentheses.

istry is unprecedented with the exception of the octameric cobalt acetate species  $[Co_8(\mu_4-O)_4(\mu-OAc)_6(\mu_3-OMe)_4(Cl)_4(OH_n)_4]$  (*n* = 1 or 2) which contains the " $[Co_4(\mu_3-O)_4]$ " unit "capped" by two  $[Co_2(\mu_3-OMe)_2]$ dimers [38].

The presence of cubane and partial cubane type structures in "cobalt(III) acetate" formed from the ozonation oxidation of cobalt(II) acetate tetrahydrate in acetic acid has not been suggested previously, despite much investigation on this system. This unusual neutral pyridine-containing cobalt(III) acetate cubane  $[Co_4(\mu_3-O)_4(\mu-OAc)_4(py)_4]$  was isolated from solutions of cobalt(III) acetate in methanol after the addition of pyridine. The cubane has also been synthesised from the ozone oxidation of cobalt(II) acetate solutions containing pyridine and directly from various pyridine containing cobalt(III) acetates. The isolation of the cubane and of the mixed valence octameric cobalt acetate species from cobalt acetate solutions, suggests that cobalt cubanes and related structures may be significant in the chemistry of cobalt acetates. Similar species with acetic acid in place of pyridine may be constituents of "cobalt(III) acetate". Thus, for example, the possibility that pyridine ligands simply took the place of solvent acetic acid or water ligands without substantially altering the reaction chemistry was suggested by the report that the cobalt-(III) clusters,  $[Co_3(\mu_3-O)(\mu-OH)_n(OAc)_{6-n}(py)_3][PF_6]$ 

(n = 0, 1), are catalyst precursors for the autoxidation of aromatic hydrocarbons [30].

We have noted previously that the  $\mu_3$ -oxygen atom is located in the Co<sub>3</sub> plane of the symmetric trimer,  $[Co_3(\mu_3-O)(\mu-OAc)_6(py)_3]^+, (7)$ , and that as the bidentate bridging carboxylate ligands are successively replaced by monodentate bridging ligands, the  $\mu_3$ -oxygen atom is displaced from the Co<sub>3</sub> plane [33]. A change in the hybridization of the  $\mu_3$ -oxygen atom from  $sp^2$  to  $sp^3$  and a corresponding change in reactivity accompanies this displacement from the Co<sub>3</sub> plane. The present pair of complexes complete the series of pyridine ligated acetate derivatives with the  $\mu_3$ -oxygen atom displacement being 0.04, ~0.35, 0.71, 0.96 and 1.01 Å for  $[Co_3(\mu_3-O)(\mu-OAc)_6(py)_3]^+$ , (7),  $[Co_3(\mu_3-O)(\mu-OR)(\mu-OAc)_5(py)_3]^+$ , (4),  $[Co_3(\mu_3-O)(\mu-OR)(\mu-OAc)_5(py)_3]^+$ O) $(\mu$ -OH)<sub>2</sub> $(\mu$ -OAc)<sub>3</sub> $(py)_5]^{2+}$ , (3),  $[Co_3(\mu_3-O)(\mu-$ OH)<sub>3</sub>( $\mu$ -OAc)(OAc)(py)<sub>6</sub>]<sup>2+</sup>, (12) and [Co<sub>4</sub>( $\mu$ <sub>3</sub>-O)<sub>4</sub>( $\mu$ - $OAc_4(py_4]$ , (11), respectively. The Co···Co separations in these pyridine ligated "cobalt(III) acetate" derivatives vary over about 0.5 Å, from  $\sim$  3.2 Å when the cobalt atoms have a  $(\mu$ -O) $(\mu$ -OAc)<sub>2</sub> bridge, to ~2.7 Å for a  $(\mu$ -O)<sub>2</sub> $(\mu$ -OAc) bridge. In all these derivatives, the Co-N and Co-O (acetate) distances are relatively constant at 1.96-1.99 Å and 1.87-1.99 Å, respectively, and the Co-( $\mu_3$ -O) distances vary between 1.80 and 1.92 Å [33].

Protonation of the cubane core has been achieved

and may be possible to a greater extent than with the bipyridine containing cubane where charge build-up was suggested to inhibit further protonation. The demonstration of the  $[Co_4(\mu_3-O)_4]^{n+}$  core within the mixed valence octanuclear,  $[Co_8(\mu_4-O)_4(\mu-OAc)_6(\mu_3-OMe)_4(Cl)_4(OH_n)_4]$  (n = 1 or 2), and of the ready synthesis of  $[Co_4(\mu_3-O)_4(\mu-OAc)_4(py)_4]$ , (11) in solution suggests a hitherto unexpected importance of this  $[Co_4(\mu_3-O)_4]^{n+}$  unit in cobalt acetate chemistry.

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