Mixed antimonate-phosphonate ligands as polydentate bridging oxygen donors†

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A new class of oxygen donor ligands is described and preliminary results using these ligands are given which show they can be used to make polymetallic cages.

Devising new ligands to bind to metal centres underpins much of coordination chemistry. Recently, within our work on polymetallic cages, we have been following up original work by Kingsley and Chandrasekhar, who showed that phosphonates could be used as bridging ligands for 3d-metals.[1] We, and others, have used these ligands to make polymetallic cages of iron,[2] manganese,[3] vanadium,[4] cobalt,[5] nickel,[6] copper[7] and zinc.[8] We have also examined antimonates as possible ligands, and found polycondensation products result which suggest antimonates could be used as inorganic cryptands.[9] As no condensation is observed for phosphonates, and polycondensation is found for antimonates we reasoned that mixing phosphonic acids and stibonic acids might lead to partial condensation and polydentate oxygen donor ligands. Main group phosphonates have been studied for a number of years by Roesky[10] and others,[11] but not, to our knowledge, used as ligands for transition metals.

The known compound *p*-chlorophenylstibonic acid ($ArSbO_3H_2$) was made by a literature method.[12,13] When it is reacted with two equivalents of $PhPO_3H_2$ in toluene a condensation product, $[(SbAr)_4O_2(O_3PPh)_4(HO_3PPh)_4]$ **1** results in 60% yield.‡ Crystallographic studies§ show **1** contains four Sb centres arrangedin an elongated tetrahedron with approximate D_{2d} symmetry (Fig. 1, Sb and P centres shown as polyhedra); two μ_2-oxides are found on the elongation axis bridging pairs of Sb centres, and each Sb···Sb edge is bridged by two phosphonate/hydrogen phosphonate groups. Within every phosphonate group, two O-atoms bind to an Sb centre and one does not; H-bonds are present between pairs of these O-atoms (O···O distances vary from 2.37 to 2.51 Å), therefore half of these groups are phosphonate and half hydrogenphosphonate.

When **1** (0.135 mmol) is reacted with cobalt acetate tetrahydrate (0.27 mmol) in MeOH under solvothermal conditions, with a mixture of LiOMe/pyridine as base $[Co_2(SbAr)_4O_4(O_3PPh)_4(OMe)_4py_2]$ **2** is formed (Fig. 2).‡§ At the core of the structure is a cube with the four Sb centres, both Co centres and two of the four P atoms at the vertices; the Sb centres form a central plane with pairs of Co- and P-atoms at opposite ends of body diagonals of the cube. The additional phosphonates bridge between the Co sites and the two Sb atoms on the neighbouring edge of the cube. There is also a μ_3-oxide bridging these centres and the Co–Sb edges are each bridged by a μ-methoxide. The two Co-sites are six-coordinate, bound to an oxide, two methoxides, two O-donors from phosphonate and a terminal pyridine. Each Sb is also six-coordinate, bound to five O-donors and aryl group. Each phosphonate is bound to two Sb and one Co centre.

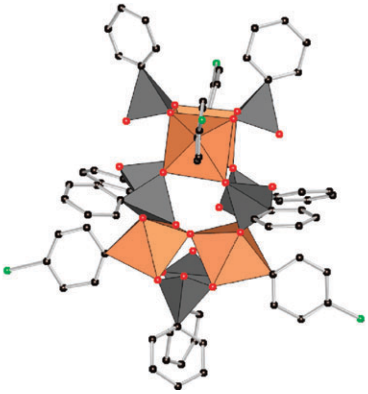

Fig. 1 The structure of **1** in the crystal. Sb, orange; P, silver; O, red; C, black; Cl, light green. H atoms omitted for clarity.

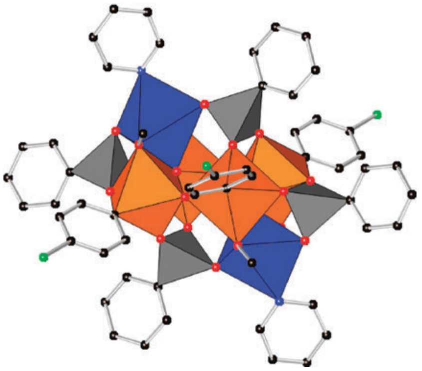

Fig. 2 The structure of **2** in the crystal. Colours as Fig. 1 plus Co blue polyhedra, N small blue spheres.

The reaction appears to be quite general, and isostructural compounds form with nickel or copper acetate.‡ Within the cobalt series, the pyridine can be replaced by 3- and 4-picoline, 4-phenylpyridine, 4-ethylpyridine, quinoline and pyrazole. With pyrazine (pyz), 4,4′-bipyridyl and 1,2-bis(4-pyridyl)ethene, polymers are formed; the structure of $[Co_2(SbAr)_4O_4(O_3PPh)_4(OMe)_4(pyz)_2]_n$ **3** is shown in Fig. 3.§ The repeat unit is essentially identical to that in **2**.

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If **1** and cobalt acetate are reacted together in MeCN in a ratio of 2.5 : 1, with Et_3N/py as the bases, $[Co_4(SbAr)_5O_9(O_3PPh)_6(py)_4]$ **4** is formed (Fig. 4).‡§ The structure contains an almost planar "bowtie" of five Sb centres, with the outer edges of the bowtie bridged by two oxides. A Co site is found above each of these outer edges, bound to the oxide which is therefore μ_3-bridging between two Sb and one Co. Two further Co sites are found above the central Sb, with a μ_3-oxide bridging between them and to the central Sb. Four further μ_3-oxides are found, which bridge between the central Sb, an exterior Sb and a Co above the central Sb. The six phosphonates fall into two groups. Two of the six bridge between two exterior Sb and the Co above them. Four of the six bridge between a single exterior Sb and two Co sites. A terminal pyridine ligand is found attached to each Co centre, with each Co being six-coordinate. The change between **2** and **4** is presumably due to the presence of methoxide in the reaction which gives **2**. The formula of **4** suggests it should be a dianion; the packing of **4** in the lattice leaves considerable voids and we suspect that these voids contain the disordered cations. Bond lengths involving cobalt are typical for Co^{II} and therefore we have no structural evidence for the presence of Co^{III}, which would also allow charge to be balanced.

Other mixed Sb-P cages can also be made by similar chemistry. If $ArSbO_3H_2$ is reacted with two equivalents of *t*-butylphosphonic acid in MeCN, $[(SbAr)_2(HO_3P^tBu)_6O]$ **5** results in 50% yield.‡ The structure of **5** shows a central pair of Sb centres, bridged by a μ_2-oxide, with the Sb···Sb contact also bridged by a pair of hydrogen-phosphonate ligands (Fig. 5).§ Two terminal hydrogen-phosphonates are also found attached to each antimony site.

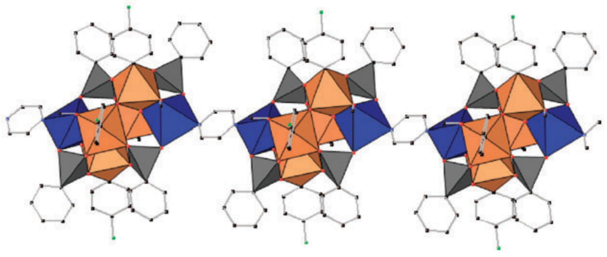

Fig. 3 The core and structure of **3** in the crystal. Colours as Fig. 2.

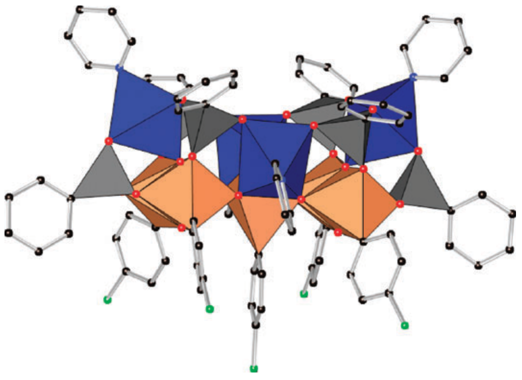

Fig. 4 The core and structure of **4** in the crystal. Colours as Fig. 2.

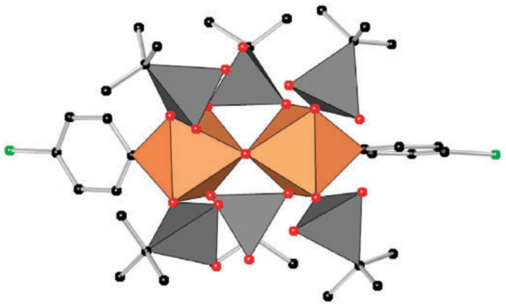

Fig. 5 The core and structure of **5** in the crystal. Colours as Fig. 1.

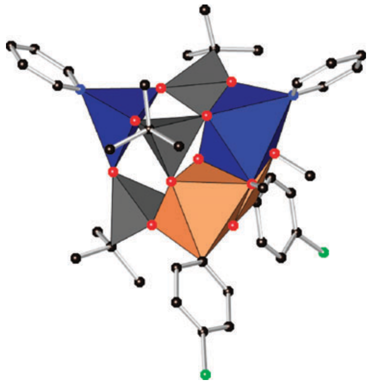

Fig. 6 The structure of **6** in the crystal. Colours as Fig. 2.

If **5** is reacted with cobalt acetate in MeOH with LiOMe/py, as a base, under solvothermal conditions $[Co_2(SbAr)_2(O_3P^tBu)_3O_2(OMe)_2(py)_2]$ **6** is formed (Fig. 6).‡§ The cage contains two Co and two Sb centres at the vertices of a distorted tetrahedron. Three of the faces of the tetrahedron are capped by *t*-butylphosphonates, while the fourth face contains two μ-methoxides, bridging Sb–Co edges, and a μ_2-oxide bridging the Sb–Sb edge. A second oxide is found inside the tetrahedron, with a μ_4-bonding mode with a much longer contact (2.56 Å) to the cobalt centre at the fourth vertex. This cobalt centre is five-coordinate, with a trigonal bipyramidal coordination geometry; the μ_4-oxide lies on the trigonal axis *trans* to a terminal pyridine with three O-atoms from phosphonates completing the coordination sphere. The cobalt centre in the unique face of the tetrahedron is six-coordinate, bound to the μ_4-oxide, two μ-methoxides, two O-atoms from phosphonates and a terminal pyridine.

Initial conclusions from this study are: firstly, pro-ligands are formed which are the product of partial condensation of the stibonic and phosphonic acids. The exact product is influenced by the steric, and possibly electronic, requirements of the group within the phosphonic acid precursor. These pro-ligands are protonated, and addition of base is necessary to cause them to coordinate to metal centres. It is necessary to form the pro-ligand prior to reaction with the metal salts, otherwise insoluble metal phosphonates form in preference to complexes **2–4** and **6**. Secondly, for both **1** and **5** the Sb : P ratio is higher in the pro-ligand than in the product; our hypothesis is that the change in this ratio is because a byproduct of the reactions is an insoluble metal phosphonate complex. Thirdly, it is clear these polydentate oxygen donor ligands can be used to produce polymetallic complexes; it remains to be seen whether these new complexes will have useful properties.

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Notes and references

‡ **1**: *p*-Chlorophenylstibonic acid ($ArSbO_3H_2$) (0.4 g, 1.4 mmol) and phenylphosphonic acid (0.44 g, 2.8 mmol) were mixed in toluene (30 cm^3) and the mixture was refluxed for 3 h. The solution was cooled, filtered and the toluene was removed under reduced pressure. The residue was dissolved in CH_2Cl_2 and filtered. Slow diffusion of hexane into the filtrate led to crystals of **1** after one week. Yield 60%. Found (Calc.) for $C_{72}H_{64}Cl_4O_{26}P_8Sb_4$: C 38.84 (38.92), H 2.55 (2.90), P 11.12 (11.15), Sb 21.78 (21.92).

2: Compound **1** (0.3 g, 0.135 mmol) and cobalt acetate tetrahydrate (0.067 g, 0.27 mmol) were taken in a bomb. 6 mL of methanol, 0.021 g (0.540 mmol) of LiOMe and 0.05 mL of pyridine were added. The bomb was sealed properly and mixture was heated at 100 °C for 12 h and then cooled slowly. Coloured crystals of **2** were obtained at the base of bomb. The crystals were washed with ether and dried. Yield 30%. Found (Calc.) for $C_{62}H_{58}O_{20}N_2Sb_4Co_2P_4Cl_4$: C 36.27 (36.77), H 2.57 (2.86), N 1.29 (1.43), P 6.27 (6.32), Sb 22.13 (24.85), Co 5.74 (6.01).

3: As for **2**, but replacing pyridine with pyrazine (0.05 mL). Yield 20%. Found (Calc.): C 33.97 (34.61), H 2.44(2.76), N 1.30 (1.44), P 6.74 (6.37), Sb 22.91 (25.06), Co 5.78 (6.06).

4: Compound **1** (0.30 g, 0.135 mmol) and cobalt acetate tetrahydrate (0.134 g, 0.54 mmol) were placed in a bomb. MeCN (6 mL), triethylamine (0.114 ml, 0.81 mmol) and pyridine (0.075 mL) were added. The bomb was sealed and mixture was heated at 100 °C for 12 h and then cooled slowly. The MeCN solution was filtered and kept for slow evaporation. Crystals of **4** were formed over two weeks. Yield: 25%. Found (Calc.) for $C_{86}H_{70}O_{27}N_4Sb_5Co_4P_6Cl_5$: C 37.31 (36.97), H 2.73 (2.52), N 2.42 (2.00), P 6.08 (6.65), Sb 20.86 (21.65), Co 8.27 (8.44).

5: 0.4 g (1.4 mmol) of *p*-chlorophenylstibonic acid ($ArSbO_3H_2$) and 0.43 g (2.8 mmol) of *tert*-butylphosphonic acid were taken in a 100 mL flask. 20 mL of acetonitrile was added and the mixture was stirred for 24 h. It was then filtered and filtrate was placed for crystallization by slow evaporation. Crystals of **5** formed after one week. Yield 60%. Found (Calc.) for $C_{36}H_{72}Cl_2O_{19}P_6Sb_2$: C 33.72 (33.03), H 4.89 (5.54), P 13.40 (14.19), Sb 18.06 (18.60).

6: Compound **5** (0.13 g, 0.10 mmol) and cobalt acetate tetrahydrate (0.10 g, 0.40 mmol) were placed in a bomb. Methanol (6 mL), LiOMe (0.023 g, 0.60 mmol) and pyridine (0.05 mL) were added. The bomb was sealed and mixture was heated at 100 °C for 12 h and then cooled slowly. The methanol solution was filtered and kept for slow evaporation. Crystals of **6** were formed over two weeks but contaminated with a coloured powder. Extraction with CH_2Cl_2 led to a pure material. Yield: 40%. Found (Calc.) for $C_{36}H_{51}O_{13}N_2Sb_2Co_2P_3Cl_2$: C 34.43 (34.72), H 4.10 (4.12), N 2.11 (2.25), P 7.55(7.46), Sb 18.62 (19.55), Co 9.10 (9.46).

§ *Crystal data*: **1**: $C_{77}H_{66}Cl_{14}O_{26}P_8Sb_4$, triclinic, $P\bar{1}$, a = 13.7395(10), b = 15.1579(11), c = 25.9751(13) Å, α = 75.215(5), β = 88.085(5), γ = 72.951(6), V = 4995.6(6) Å^3, M = 2638.36, crystal size 0.25 × 0.15 × 0.10 mm, T = 100(2), λ = 0.71073 Å, D_c = 1.754 g cm^{-3}, Z = 2, 28 051 reflections collected, 10 266 independent (R_{int} = 0.0787), $R(F)$ = 0.0797 and wR_2 = 0.2102 for $I > 2\sigma(I)$ [$R(F)$ = 0.1120, wR_2 = 0.2234 for all data]. **2**: $C_{62}H_{58}Cl_4Co_2N_2O_{20}P_4Sb_4$, monoclinic, $P2_1/n$, a = 12.3692(3), b = 12.0030(4), c = 24.8174(7) Å, β = 101.803(3)°, V = 3606.67(18) Å^3, M = 2021.64, crystal size 0.20 × 0.12 × 0.10 mm, T = 100(2), λ = 0.71073 Å, D_c = 1.862 g cm^{-3}, Z = 2, 23484 reflections collected, 7343 independent (R_{int} = 0.0305), $R(F)$ = 0.0268 and wR_2 = 0.0604 for $I > 2\sigma(I)$ [$R(F)$ = 0.0438, wR_2 = 0.0656 for all data]. **3**: $C_{28}H_{26}Cl_2CoNO_{10}P_2Sb_2$, triclinic, $P\bar{1}$, a = 11.221(5), b = 11.658(5), c = 14.044(5) Å, α = 74.222(5), β = 77.714(5), γ = 70.916(5)°, V = 1655.2(12) Å^3, M = 971.77, crystal size 0.20 × 0.20 × 0.10 mm, T = 100(2), λ = 0.71073 Å, D_c = 1.950 g cm^{-3}, Z = 2, 15 385 reflections collected, 6731 independent (R_{int} = 0.0267), $R(F)$ = 0.0301 and wR_2 = 0.0724 for $I > 2\sigma(I)$ [$R(F)$ = 0.0494, wR_2 = 0.0843 for all data]. **4**: $C_{94}H_{82}Cl_5Co_4N_8O_{27}P_6Sb_5$, tetragonal, $P43_12$, a = 16.8698(7), b = 16.8698(7), c = 40.0183(12) Å, V = 11388.8(8) Å^3, M = 2963.22, crystal size 0.40 × 0.30 × 0.2 mm, T = 100(2), λ = 0.71073 Å, D_c = 1.728 g cm^{-3}, Z = 4, 102 156 reflections collected, 11 687 independent (R_{int} = 0.1096), $R(F)$ = 0.1080 and wR_2 = 0.2119 for $I > 2\sigma(I)$ [$R(F)$ = 0.1087, wR_2 = 0.2123 for all data]. **5**: $C_{36}H_{62}Cl_2O_{19}P_6Sb_2$, triclinic, $P\bar{1}$, a = 10.4506(19), b = 11.6444(18), c = 22.684(3) Å, α = 94.982(13), β = 99.542(14), γ = 90.679(13)°, V = 2711.0(8) Å^3, M = 1299.08, crystal size 0.30 × 0.15 × 0.10 mm, T = 100(2), λ = 0.71073 Å, D_c = 1.591 g cm^{-3}, Z = 2, 29 942 reflections collected, 9551 independent (R_{int} = 0.0604), $R(F)$ = 0.0547 and wR_2 = 0.1259 for $I > 2\sigma(I)$ [$R(F)$ = 0.1040, wR_2 = 0.1413 for all data]. **6**: $C_{36}H_{51}Cl_2Co_2N_2O_{13}P_3Sb_2$, monoclinic, $P2_1/n$, a = 9.9052(2), b = 22.5257(5), c = 20.5666(4) Å, β = 91.694(2)°, V = 4586.85(16) Å^3, M = 1244.96, crystal size 0.40 × 0.15 × 0.15 mm, T = 100(2), λ = 0.71073 Å, D_c = 1.803 g cm^{-3}, Z = 4, 25 685 reflections collected, 9325 independent (R_{int} = 0.0306), $R(F)$ = 0.0309 and wR_2 = 0.0676 for $I > 2\sigma(I)$ [$R(F)$ = 0.0542, wR_2 = 0.0811 for all data]. Data collection, structure solution and refinement used SHELXL.[14]

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