

Unique chains of alternating octahedral and tetrahedral cobalt(II) sites: crystal structures of the novel chloro-bridged complexes

$[\text{Co}_4(\mu\text{-Cl})_6\text{Cl}_2(\text{thf})_4(\text{MeOH})_2]_n$ and $\{[\text{Co}_4(\mu\text{-Cl})_6\text{Cl}_2(\text{thf})_4(\text{H}_2\text{O})_2]\cdot 2\text{THF}\}_n^\dagger$

Jean-Cyrille Hierso,^a Dianne D. Ellis,^b Anthony L. Spek,^b Elisabeth Bouwman*^a and Jan Reedijk^a

^a Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University, PO Box 9502, 2300 RA Leiden, The Netherlands. E-mail: bouwman@chem.leidenuniv.nl

^b Bijvoet Centre for Biomolecular Research, Crystal and Structural Chemistry, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands

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$[\text{Co}_4(\mu\text{-Cl})_6\text{Cl}_2(\text{thf})_4(\text{MeOH})_2]_n$, a *catena*-polycobalt(II) complex with an unusual linear chain of octahedral/tetrahedral/octahedral cobalt sites, is obtained quantitatively from the reaction between cobalt chloride hydrate and trimethylorthoformate in THF.

Literature reports on infinite polymeric chains based on copper, manganese or cobalt, indicate the most common routes to obtaining *catena*-complexes are to use polydentate ligands as bridges between metallic units,^{1–5} or to take advantage of potential intermolecular hydrogen bonding.⁶ Numerous copper complexes,^{2,6} and a few cobalt compounds were obtained in these ways.^{1,3–5} Halide-bridged polymeric structures have also been characterised for these metals.⁷ Interestingly, X-ray structure determinations describing chain-type cobalt complexes still remain scarce, apparently because these polymeric structures are difficult to grow as single crystals.⁸ Of the reported structures the majority feature repeating linear chloro-bridged chains of monomeric cobalt octahedra,^{7b} or elegant halide-bridged ‘zigzag’ chains (non-linear) as the polymeric network.^{8–10} We report the isolation and structural characterisation of a new family of inorganic polymers of cobalt, showing an unprecedented chain of three different cobalt sites.

$[\text{Co}_4(\mu\text{-Cl})_6\text{Cl}_2(\text{thf})_4(\text{MeOH})_2]_n$ **1** was obtained in quantitative yield from a mixture of $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$ and trimethylorthoformate in tetrahydrofuran solution.[†] Crystals used for X-ray diffraction were kept under dry diethyl ether to prevent any decomposition before measurements.[§] The structure of **1** consists of an infinite regular chain of three distinct successive cobalt sites (Fig. 1) connected in different ways. Co(1) and Co(3) are located on crystallographic inversion centres linked, respectively, by two and one bridging chloride ions to Co(2) centres. This creates a repeating pattern of tetranuclear units $[-\text{Co}(\text{thf})_2(\mu\text{-Cl})_2\text{CoCl}(\mu\text{-Cl})\text{Co}(\text{MeOH})_2(\text{thf})_2(\mu\text{-Cl})\text{CoCl}(\mu\text{-Cl})_2-]$, or more simply $[\text{Co}_4(\mu\text{-Cl})_6\text{Cl}_2(\text{thf})_4(\text{MeOH})_2]$. The strict asymmetric unit, from which the entire chain can be built, is formulated $[\text{Co}_2\text{Cl}_4(\text{thf})_2(\text{MeOH})]$. The geometry around Co(1) is octahedral having four μ -chloro bridges in equatorial sites, linked to two symmetry related Co(2) centres, and two thf molecules in axial positions, Co(1) thus being part of a CoCl_4O_2 chromophore. Each Co(2) centre is in a distorted tetrahedral environment made up of a terminal chloride and three μ -chloro bridges; two connected to Co(1) and the third bridged to Co(3). The bridging properties force the tetrahedral Cl(1)–Co(2)–Cl(2) angle to contract to $97.31(3)^\circ$, whilst the mono-bridged angle Cl(2)–Co(2)–Cl(4) has opened to $118.44(3)^\circ$. The coordination sphere around Co(3) consists of four oxygen donor atoms from two *trans*-thf and two *trans*-methanol molecules located at the

equatorial positions. The axial positions are occupied by the bridging atoms Cl(4) producing a CoCl_2O_4 chromophore. The longer Co(3)–Cl(4) distances relative to Co(3)–O, result in a tetragonal *elongation* along the pseudo-four-fold axis of the Co(3) octahedral environment. The Co(1)–Cl(2) bond length is very long, 2.5488(7) Å, so that in this case a pronounced compressed octahedral geometry, *i.e.* a tetragonal *contraction* along the pseudo-four-fold axis is suggested around the Co(1) atom.

The Co–Cl bond distances are in agreement with the values reported for tetrahedral and octahedral chloride geometries in related cobalt/chloride complexes.^{7,11,12} The terminal chloride on Co(2) is involved in a O–H...Cl hydrogen bond interaction to the *cis*-methanol molecule coordinated to Co(3). A closely related trinuclear cobalt chloride anion, $[\text{Co}_3\text{Cl}_8(\text{thf})_2]^{2-}$, has recently been described.¹³ The X-ray structure determination revealed three successive cobalt sites: tetrahedral/octahedral/tetrahedral each connected *via* di- μ -chloro bridges. The molecular structure of $\{[\text{Co}_4(\mu\text{-Cl})_6\text{Cl}_2(\text{thf})_4(\text{H}_2\text{O})_2]\cdot 2\text{THF}\}_n$ **2** (Fig. 2) is very similar to **1**, except that the methanol molecules coordinated to Co(3) are replaced by water molecules, and two additional thf molecules per tetranuclear unit have cocrystallised in the lattice. The most significant difference between the two complexes involves the hydrogen bonding network; both complexes form an intramolecular OH...Cl(terminal) interaction [O(1)...Cl(3) 3.041(2) Å, O(1)–H(1)...Cl(3) $170(4)^\circ$ in **1**; O(1)...Cl(3) 3.117(2) Å, O(1)–H(1B)...Cl(3) $168(3)^\circ$ in **2**]. In **2** the water molecule forms an additional strong intermolecular bond with the thf molecule in the lattice. This results

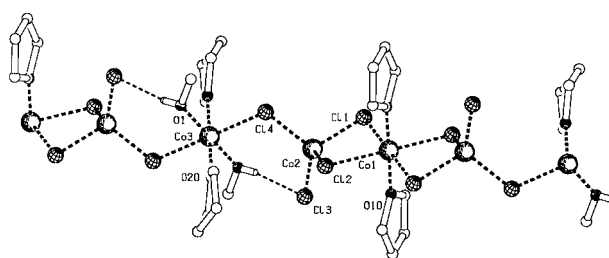


Fig. 1 Schematic representation of the crystal structure of **1**: H atoms omitted for clarity. Selected bond lengths (Å) and bond angles ($^\circ$): Co(1)–Cl(1) 2.4600(6), Co(1)–Cl(2) 2.5488(7), Co(1)–O(10) 2.0381(18), Co(2)–Cl(1) 2.2918(8), Co(2)–Cl(2) 2.2861(7), Co(2)–Cl(3) 2.2533(8), Co(2)–Cl(4) 2.2898(8), Co(3)–Cl(4) 2.5049(7), Co(3)–O(1) 2.067(2), Co(3)–O(20) 2.0696(19); Cl(1)–Co(1)–Cl(2) 86.64(2), Cl(1)–Co(1)–O(10) 88.43(5), Cl(2)–Co(1)–O(10) 89.97(6), Cl(1)–Co(2)–Cl(2) 97.31(3), Cl(1)–Co(2)–Cl(3) 115.20(3), Cl(1)–Co(2)–Cl(4) 108.37(3), Cl(2)–Co(2)–Cl(3) 110.39(3), Cl(2)–Co(2)–Cl(4) 118.44(3), Cl(3)–Co(2)–Cl(4) 107.24(3), Cl(4)–Co(3)–O(1) 89.72(6), Cl(4)–Co(3)–O(20) 89.52(6), O(1)–Co(3)–O(20) 91.22(8), Co(1)–Cl(1)–Co(2) 86.29(3), Co(1)–Cl(2)–Co(2) 84.34(2), Co(2)–Cl(4)–Co(3) 119.47(3), Co(3)–O(1)–H(1) 112(3). Hydrogen bonding geometries: distances (Å), O(1)–H(1)...Cl(3) 2.33(4), O(1)...Cl(3) 3.041(2); angle ($^\circ$), O(1)–H(1)–Cl(3) $170(4)$.

[†] Electronic supplementary information (ESI) available: elemental analysis, FTIR, VIS–NIR, temperature dependence of magnetic moment, data and apparatus for **1**. See <http://www.rsc.org/suppdata/cc/b0/b0032131/>

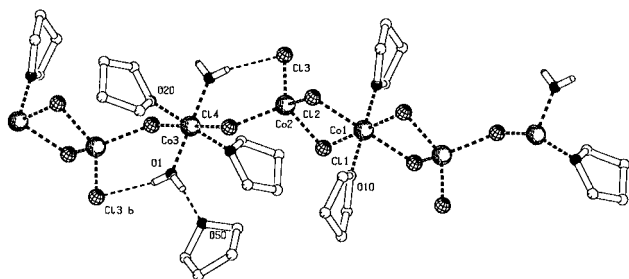
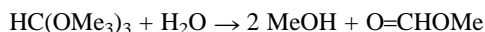


Fig. 2 Schematic representation of the crystal structure of **2**: hydrogen bonding geometries: distances (Å), O(1)–H(1B)···Cl(3) 2.36(3), O(1)···Cl(3) 3.117(2), O(1)–H(1A)···O(50) 1.81(3), O(1)···O(50) 2.625(3); angles (°), O(1)–H(1B)–Cl(3) 168(3), O(1)–H(1A)–O(50) 174(3). Bond lengths and angles generally differ from **1** by <0.05 Å and 2° respectively, except for Cl(2)–Co(2)–Cl(4) 109.57(3)° [118.44(3)° in **1**].

in a slight contraction of the tetranuclear unit in **2** compared to **1** [intra Co(1)···Co(3) distances in the two complexes: 7.3608(2) Å for **1** and 7.0407(3) Å for **2**].

VIS–NIR spectroscopy in diffuse reflectance of **1** shows the dominance in intensity of tetrahedral coordination typical bands (a broad band at 6600 cm⁻¹, and a more intense band at 15000 cm⁻¹). The bands corresponding to an octahedral environment around cobalt are present but partially obscured (shoulders at 12000 and 19000 cm⁻¹). Temperature dependent solid-state magnetic susceptibility (χ_{m}) measurements on crystals of **1** were performed. The effective magnetic moment ($\mu_{\text{eff}}/\text{Co}_2$) slowly decreases from 7.27 μ_{B} at 260 K to 6.91 μ_{B} at 80 K, and then more steeply to 4.72 μ_{B} at 12 K. It then increases rapidly to 6.66 μ_{B} at 5 K. The observed μ_{B} of 7.27 at 260 K is close to the spin-only value of 6.93 μ_{B} for a dinuclear high-spin Co^{II} ($S = 3$) system. Octahedral and tetrahedral Co^{II} ions can behave as spin-1/2 and spin-3/2 depending on temperature and spin–orbit coupling. The temperature dependence of μ_{eff} is thus consistent with linear repeating Co^{II} dimers with $S = 3/2$ at higher temperatures. The decrease of μ_{eff} between 100 and 12 K is likely due to depopulation of higher Kramers levels, and the increase at 12 K is ascribed to weak ferromagnetic interactions possibly occurring between di- μ -chloro linked Co^{II}.^{7a}

Previously, tetranuclear [M₄(μ_3 -Cl)₂(μ -Cl)₄Cl₂(thf)₆] species (M = Co, Fe) have been synthesised from anhydrous metal chlorides in THF, and only in the case of manganese was a polymeric compound isolated.⁹ It has now been shown that cobalt in presence of THF can also form polymeric species. Compound **2** has been isolated repeatedly from attempts of recrystallisation of a cobalt chloride oxime microcrystalline powder,^{14,15} in a mixture of THF–diethyl ether as solvent; experiments are ongoing to obtain the product by a more direct route. The mechanisms of formation of **2**, and especially the insertion of residual water molecules are not yet completely understood; nevertheless, we assume that the weak oxime ligands are readily replaced by water and THF molecules during the time of crystallisation. From the previous observations, it is clear that the thermodynamic driving force leading to this family of self-assembly compounds should be important. If we consider **1**, MeOH is generated *in situ* from the action of trimethylorthoformate on water following the global equation:



as a consequence the MeOH:THF molar ratio is *ca.* 1:20. Assuming the coordination abilities of THF and MeOH are similar, the explanation for the formation of the complex should be self-assembly likely continuously carried out in the coordination sphere of cobalt or at least in a close vicinity to the metal centres. This means that methanol molecules should be readily accessible to grow the structure, despite their poor ratio relative to THF. These two examples show that unusual self-assembly can occur even in the absence of polydentate ligands. Further studies are in progress to extend this class of compounds.

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Notes and references

‡ Although the synthesis can be carried out in air, experiments under inert atmosphere using Schlenk techniques and a vacuum line ensure the protection of the sensitive final product. To 0.2 g (0.85 mmol) of CoCl₂·6H₂O was added an excess of trimethylorthoformate (1.5 ml). The mixture was gently heated (50 °C) in 15 ml of THF until complete dissolution of the solid. After cooling to ambient temperature for 30 min, the deep blue solution was evaporated to dryness resulting in a shiny blue powder which is very moisture sensitive (0.17 g, 0.39 mmol, yield 92%). From a diethyl ether–tetrahydrofuran two layer recrystallisation, nice shiny blue prisms suitable for X-ray diffraction can be obtained after a few hours.

§ Data were collected on a Nonius Kappa CCD area detector, using Mo-K α radiation with a graphite monochromator ($\lambda = 0.71073$ Å), on a rotating anode at 150 K. Lorentz polarisation and absorption corrections were applied in both instances. Refinement was carried out using full-matrix least squares on F^2 (SHELXL-97).

Crystal data: for **1**: C₉H₂₀Cl₄O₃Co₂, $M_r = 435.91$, monoclinic, space group $P2_1/c$ (no. 14), $a = 10.9390(3)$, $b = 12.1510(4)$, $c = 12.6313(3)$ Å, $\beta = 103.068(2)^\circ$, $V = 1635.47(8)$ Å³, $F(000) = 880$, $Z = 4$, $\mu(\text{Mo-K}\alpha) = 2.677$ mm⁻¹. 15654 reflections measured, 3728 independent, $R_{\text{int}} = 0.0501$. Refinement converged at $wR2$ value of 0.0682, $R1 = 0.0330$ [for 2975 reflections with $F_o > 4\sigma(F_o)$].

For **2**: C₈H₁₈Cl₄O₃Co₂·C₄H₈O: $M_r = 493.99$, triclinic, space group $P\bar{1}$ (no. 2), $a = 8.6714(3)$, $b = 10.8418(3)$, $c = 11.8514(5)$ Å, $\alpha = 76.563(2)$, $\beta = 77.804(2)$, $\gamma = 68.245(2)^\circ$, $V = 996.81(6)$ Å³, $F(000) = 504$, $Z = 2$, $\mu(\text{Mo-K}\alpha) = 2.210$ mm⁻¹. 10959 reflections measured, 4520 independent, $R_{\text{int}} = 0.0381$. Refinement converged at $wR2$ value of 0.0651, $R1 = 0.0314$ [for 3674 reflections with $F_o > 4\sigma(F_o)$].

CCDC 182/1676. See <http://www.rsc.org/suppdata/cc/b0/b0032131/> for crystallographic files in .cif format.

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