Aggregation of carbamato ligands around the $[Co_4O]^{6+}$ core. Synthesis and structure of the cluster $[Co_4O(O_2CNC_9H_{18})_6]$ prepared by a novel oxo-transfer reaction of the nitroxyl free radical 2,2,6,6-tetramethylpiperidin-1-oxyl with $[Co_2(CO)_8]$

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The novel oxo-centred tetrahedral cobalt cluster $[Co_4O]^{6+}$ bridged by six carbamato ligands is prepared in high yield when reacting $[Co_2(CO)_8]$ with an excess of the nitroxyl radical 2,2,6,6-tetramethylpiperidin-1-oxyl; the molecular structure of the title compound is determined by a single-crystal X-ray analysis.

The nitroxyl radical 2,2,6,6-tetramethylpiperidin-1-oxyl (tmpo) is easily oxidized electrochemically (271 mV) in a reversible one-electron step in acetonitrile to the oxoammonium ion.[1] Organic oxoammonium salts characterized by Rey and coworkers[2] have found wide application in selective oxidations of alcohols to aldehydes and ketones as reported by Ma and Bobbit[3] and Semmelhack *et al.*[4] On the other hand, tmpo is a powerful paramagnetic ligand when studying magnetic interactions between metal centres and ligands[5] or in the design of new magnetic materials.[6] We have shown that tmpo is also a valuable spin scavenger of metal carbonyl radicals generating diamagnetic electron-deficient complexes like $[V(CO)_3(tmpo)]$, $[Mn(CO)_3(tmpo)]$ and $[Co(CO)_2(tmpo)]$ **2**, containing a η^2-bonded tmpo ligand.[7] A metal (^{51}V, ^{55}Mn, ^{59}Co) NMR investigation revealed that these strained three-membered metallacycles exhibit extremely low metal shieldings.[8] Our preceding work on photolysis of $[Co_2(CO)_8]$ with tmpo in equimolar amounts proved that only the deep red 16-electron metallaoxaziridine $[Co(CO)_2(tmpo)]$ **2** is obtained.[7] But a fourfold excess of tmpo reacts at room temperature with $[Co_2(CO)_8]$ in pentane or benzene in minutes generating the blue carbamato complex $[Co_4O(O_2CNC_9H_{18})_6]$ **1** in high yield ($>80\%$).

None of numerous attempts to characterize **1** by spectroscopy were conclusive. Standard crystallization procedures failed as well, but suitable single crystals (deep blue plates) were obtained by means of a crystallization box equipped with a heating block described by Hulliger.[10] A single-crystal structure analysis of **1** establishes the structure† shown in Fig. 1.

The molecular structure consists of an oxo-centred tetrahedron of Co^{II} atoms each edge of which is bridged by carbamato ligands. Only one structural determination of a $Co_4(\mu_4\text{-}O)$ complex has been reported so far, $[\{Ir(aet)_3\}_4Co_4]Br_6$ (aet = 2-aminoethanethiolate),[11b] with cobalt–oxygen bond lengths in the range 193–195 pm as found in **1**.

The mechanism of formation of **1** is not yet understood but an excess of tmpo is required for oxo transfer and simultaneously CO insertion into the radical tmpo creating carbamato ligands has to take place. When adding more tmpo to the planar coordinated compound $[Co(CO)_2(tmpo)]$ **2** an immediate colour change to blue **1** is also observed, indicating a stepwise formation of **1** and **2** as an intermediate. Surprisingly, even when performing the reaction of $[Co_2(CO)_8]$ with tmpo without solvent, **1** is formed in high yield. Attempts to identify **1** by mass spectrometry were not informative since no molecular ions or high mass fragments were observed. Only ions such as formamide and other unidentified species were detected. No EPR signal could be observed down to −196 °C. The ^{17}O NMR‡ spectrum exhibits two broadened signals at δ 279 and 79. Only very few comparable systems have been studied by ^{17}O NMR, making the assignment difficult. We attribute the signal at δ 279 to the oxygens of the carbamato ligand since carboxylates lie in this range.[9] The central μ_4-oxygen at δ 79 is comparable to the shift of the dimeric oxo-bridged $[Re_2(O)_2(\mu\text{-}O)_2(\eta^5\text{-}C_5Me_5)_2]$ [Re–O–Re (δ 104), Re=O (δ 747)] reported by Herrmann and coworkers[9] or to the shift of polyoxometalates containing the $Mo_4(\mu_4\text{-}O)$ group (δ 123) studied by Klemperer.[9]

The $M_4(\mu_4\text{-}O)$ group is present in many binary metal oxides and is also known in some coordination complexes, such as in the basic metal acetates $[M_4(\mu_4\text{-}O)(\mu\text{-}O_2CMe)_6]$ (M = Be, Zn).[11] Compounds containing such oxo bridging groups are of interest in chemistry,[11] biochemistry,[12] magnetochemistry[13] and catalysis.[14] The $Mn_4(\mu_4\text{-}O)$ functional group appeared to be unknown for most heavier transition-metal elements but the groups of Puddephatt[15] and Schmidbaur[16] have reported recently new interesting examples containing the elusive $Pd(\mu_4\text{-}O)$[15] and $Au_4(\mu_4\text{-}O)$[16] cluster moieties.

In conclusion, this work describes the synthesis and X-ray diffraction of the first complex containing a $Co_4(\mu_4\text{-}O)$ group bridged by carbamato ligands. The facile formation of **1** from $[Co_2(CO)_8]$ and tmpo is a surprisingly easy access to a $Co_4(\mu_4\text{-}O)$ cluster; attempts to generalize this chemistry with different

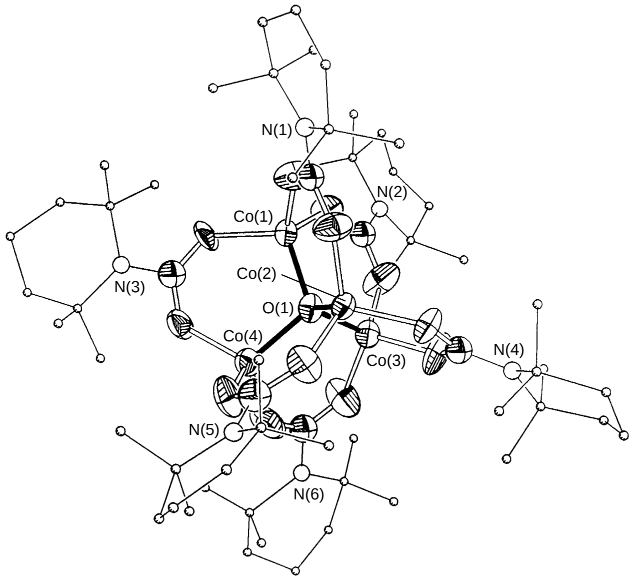

Fig. 1 Molecular structure of **1**; selected distances (pm) and angles (°): Co(1)–O(1) 193.2(11), Co(2)–O(1) 195.5(10), Co(3)–O(1) 195.2(9), Co(4)–O(1) 193.4(9); Co(1)–O(1)–Co(4) 111.9(5), Co(4)–O(1)–Co(3) 107.8(4), Co(4)–O(1)–Co(2) 108.2(5), Co(1)–O(1)–Co(3) 108.4(5), Co(1)–O(1)–Co(2) 110.3(4), Co(3)–O(1)–Co(2) 110.2(5).

metal carbonyls and oxidizing nitroxyl radicals are under current investigation.

Footnotes

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† *Crystal data* for **1**: $C_{60}H_{108}Co_4N_6O_{13}$, M = 1357.24, monoclinic, space group $P2_1/n$, a = 2083.8(5), b = 2964.7(7), c = 2540.7(6) pm, β = 114.20(1)°, U = 14.317(6) nm^3, Z = 8, Mo-Kα radiation (λ = 71.073 pm), D_c = 1.259 g cm^{-3} Crystal dimensions: 0.5 × 0.4 × 0.3 mm (blue prism). Data were measured on a Siemens P4 automatic diffractometer with a highly oriented graphite crystal monochromated Mo-Kα radiation using ω scans. The structure was solved by direct methods and refined using absorption corrected data to give R_1 = 0.0802 for 7092 independent observed reflections [$I > 2\sigma(I)$ and 897 parameters. Only the N, O and Co atoms were refined with anisotropic displacement parameters. The crystal structure has been determined and refined in the monoclinic system with X-ray data obtained from a merohedrally twinned crystal, volume ratio 23/5. The twin element can be a twofold rotation axis along c* or a mirror plane in the b*c*-plane of the reciprocal lattice (SHELXL-93; TWIN −100 0 − 10 101 or TWIN −100 010 101). The monoclinic P-lattice can be transformed to an orthorombic C-lattice a = 2083, 8(5), b = 4634.7(10), c = 2964.7(8) pm, but no solution is available in this system.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/475.

‡ ^{17}O NMR (C_6H_6–C_6D_6, ref. H_2O), δ 79 (μ_4-O), 279 ($\mu_2O_2CNC_9H_{18}$).

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