Pergamon

PII: S0277–5387(96)00498–6

Polyhedron Vol. 16, No. 12, pp. 2109–2112, 1997

0277–5387/97 $17.00+0.00

The chemistry of cobalt acetate—III. The isolation and crystal structure characterisation of the mixed valence octacobalt oligomer, $[Co_8(O)_4(CH_3CO_2)_6(OMe)_4]Cl_4(OH_n)_4 \cdot 6H_2O$ ($n = 1$ or 2), derived from the preparation of cobalt(III) acetate

James K. Beattie,* Trevor W. Hambley, John A. Klepetko,
Anthony F. Masters* and Peter Turner

School of Chemistry, The University of Sydney, NSW, 2006, Australia

(Received 28 March 1996; accepted 9 October 1996)

Abstract—The mixed valence octacobalt oligomer, $[Co_8(O)_4(CH_3CO_2)_6(OMe)_4Cl_4(OH_n)_4]$ ($n = 1$ or 2), in which the Co_8O_8 core defines a helical array of three condensed, face-sharing Co_4O_4 cubanes, was isolated during the recrystallisation of crude "$[Co(OAc)_3]$" from methanol/dichloromethane/diethyl ether and its crystal structure determined. © 1997 Elsevier Science Ltd. All rights reserved.

Keywords: cobalt; acetate; structure; X-ray; octamer; mixed valence.

Cobalt carboxylates are the most widely used homogeneous catalysts in industry [1–10]. They find particular application in the oxidation of hydrocarbons, most noticeably the oxidation of *p*-xylene to terephthalic acid or dimethyl terephthalate, the largest industrial-scale use of homogeneous catalysts. Other industrially important oxidations catalysed by cobalt carboxylates include the oxidation of other methylbenzenes to their respective acids, of cyclohexane to cyclohexanol and cyclohexanone in the generation of adipic acid for nylon synthesis, the oxidation of butane, acetaldehyde or ethanol to acetic acid and in the production of dodecanoic acid and lauryl lactam from cyclododecane. The conversion of $[Co(OAc)_2]$ to a species presumed to be $[Co_3O(OAc)_6(AcOH)_3]$ by ozone improves the batch oxidation of butane and the Co^{III} clusters, $[Co_3O(OAc)_{6-n}(py)_3(OH)_n]^+$ ($n = 0,1$) have been shown to be catalyst precursors for the autoxidation of aromatic hydrocarbons [11]. The complexes are generally thought to be effective by increasing the decomposition rates of alkylhydroperoxide intermediates in hydrocarbon oxidations [5, 9]. In addition, "cobalt acetate" derivatives have been studied as potential structural models of biological systems [12,13].

Despite this interest, the constitution and structure of simple "$[Co(OAc)_3]$" are complex and incompletely established [14–24]. Although a trimeric structure was first proposed in 1929 [16], a variety of structural types including a monomer, dimers, trimers, mixed valence trimers and mixtures of these species has been suggested. This uncertainty is due in part to the amorphous nature of the "$[Co(OAc)_3]$" product and the different preparations employed by different experimenters (although the preparation of "well defined green octahedrons" was reported [15] in 1924). The use of pyridine as a ligand to aid in the isolation of crystalline derivatives [25] was a significant advance which led to the determination of the crystal structures of dinuclear, hydroxy bridged and of trinuclear, oxo-centred, derivatives [11, 26]. Recently, an additional structural type, based on a Co_4O_4 cubane, was isolated using bipyridine as a ligand and the structure established crystallographically [12]. This material was not, however,

---

*Authors to whom correspondence should be addressed.

isolated from "cobalt acetate" preparations, but rather by the reaction of an isolated $Co_2(\mu\text{-}OH)_2$ dimer with lithium peroxide. The Co_4O_4 core had previously been observed in the cobalt(II) complexes $[Co_4(acac)_4(\mu\text{-}OMe)_4(CH_3OH)_4]$ [27], $[Co_4(\mu\text{-}OMe)_4(Cl_3C_6H_2O)_4(MeOH)_4]$ [28], $[Co_4((NO_2)_2C_6H_3O)_4(MeOH)_4]$ [29] and $[Co_4(thf)_{5.5}(\mu\text{-}O_2Bu^t{}_2C_6H_2)_4]$ [30] and in the mixed valence cobalt(II,III) complex, $[Co_4(acac)_4(\mu\text{-}OMe)_4(\mu\text{-}OAc)_2]$ [31], but had not been established in cobalt(III) compounds. The tetranuclear cobalt (II/III) complexes, $[Co_4L_2(\mu\text{-}OH)_4(\mu\text{-}OAc)_2]$, ($L = MeC_6H_2O(CHNC_6H_4O)_2$) and $[Co_4\{NH(C_2H_4OH)_2\}_2(NH(C_2H_4O)_2\}_4][ClO_4]_2$ have Co_4O_6 cores [32,33]. Unfortunately, however, in the context of the structure and composition of "$[Co(OAc)_3]$", all of these examples have been isolated from solutions to which other ligands have been deliberately added.

We report here the serendipitous isolation of an octanuclear complex following the recrystallisation of the green "$[Co(OAc)_3]$" prepared by ozonation of $[Co(OAc)_2]\cdot 4H_2O$ in acetic acid.

RESULTS AND DISCUSSION

Dark green, air sensitive crystals of $[Co_8(O)_4(OAc)_6(OMe)_4Cl_4(OH_n)_4]\cdot 6H_2O$ (**I** $\cdot 6H_2O$, $n = 1,2$) were isolated following the recrystallisation from methanol/dichloromethane/diethyl ether of the products of the reaction between cobalt(II) acetate tetrahydrate, acetic acid and ozone. The dichloromethane can be replaced as chloride source by LiCl, HCl or NH_4Cl. The yield of (**I**) was near quantitative. The octanuclear structure was established by single crystal X-ray crystallography. The corresponding bromide derivative can also be prepared by recrystallisation of "cobalt(III) acetate" from methanol/diethyl ether in the presence of HBr.

The structure is illustrated in Fig. 1, which also contains the atom numbering scheme. The formula, $[Co_8(O)_4(OAc)_6(OMe)_4Cl_4(OH_n)_4]$ ($n = 1,2$), is derived from the crystal structure—the data do not allow us to distinguish between coordinated hydroxyl and coordinated water as ligands on the terminal cobalt atoms. No counter ions could be detected in the lattice. Magnetic susceptibility measurements yield a room temperature magnetic moment of approximately 9.2 ± 0.2 BM (depending on the formulation). The structure can be described as a linear chain of three face-sharing Co_4O_4 cubes or as a Co_4O_4 cube capped on opposite faces by $Co_2(OMe)_2$ dimers. The Co_8 framework is aligned along the centre of a double helix of acetate ligands—each helix containing three ligands. Each cobalt atom is approximately octahedrally coordinated. This structural motif differs from that of $[Co_8(O)_4(PhCO_2)_{12}(dmf)_3(OH_2)]$ (**II**) [34], which also contains a central $[Co_4O_4]$ cubane unit. Although (**I**) and (**II**) both contain a cobalt atom coordinated to each of the bridging oxide ligands of a central $[Co_4O_4]$ cube, these cobalt atoms in (**II**) are not held relatively close together by bridging ligands as they are in (**I**). The cobalt–cobalt distances within the $[Co_4O_4]$ core of (**I**) differ. Those bridged by an acetate ligand are separated by 2.666(3) Å, the same distance as that (2.666(2) Å) between the cobalt atoms of the cubic $[Co_4O_4(O_2tol)_2(bpy)_2]^{2+}$ [12]. The remaining pairs of cobalt atoms of the $[Co_4O_4]$ core are separated by 2.848(4) Å (capped by the $[Co_2(OMe)_2]$ moiety) and 2.852(4) Å (across the unbridged "outside" of the structure). The cobalt atoms of the $[Co_2(OMe)_2]$ fragment are separated by 3.216(4) Å, a cobalt–cobalt distance intermediate between those in $[Co_3O(OAc)_6(py)_3]^+$ and $[Co_3O(OAc)_3(OH)_2(py_5)]^{2+}$ [26, 35]. The cobalt–cobalt distances between the $[Co_4O_4]$ and $[Co_2(OMe)_2]$ moieties are 2.861(3) Å (bridged by an acetate ligand) and 3.096(3) Å.

The isolation of (**I**) establishes a new structural form isolated from "$Co(OAc)_3$" solutions, the present compound providing a rare example of a $[M_8(\mu\text{-}O)_4]$ unit in a molecular metal complex and underscoring the rich chemistry of the deceptively simple but widely used "$[Co(OAc)_3]$".

EXPERIMENTAL

Chemicals

Cobalt(II) acetate tetrahydrate (Aldrich) and acetic acid (BDH) were of analytical reagent grade and were used as received. Methylene chloride (Prolab) was distilled over calcium hydride. Diethyl ether (Merck) was distilled from benzophenone ketyl over sodium wire. Ozone was generated using a Wallace and Tiernan laboratory ozonator (model BA.023012).

Synthesis

Cobalt(III) acetate was prepared from the reaction between cobalt(II) acetate tetrahydrate, acetic acid and ozone as described by Uemura, Spencer and Wilkinson [25] and was recrystallized slowly, over a period of several months, from methanol/dichloromethane/diethyl ether. Alternatively, the dichloromethane can be omitted and the cobalt(III) acetate recrystallized in the presence of an excess of LiCl, NH_4Cl, HCl or HBr to produce the appropriate halide containing octanuclear species near quantitatively.

Structure determination

Data were collected on an Enraf-Nonius CAD4 diffractometer with graphite monochromated Mo-K_α radiation. A dark green bipyramidal crystal of $[Co_8(H_xO)_8(OMe)_4(OAc)_6(Cl)_4]\cdot 6H_2O$, $C_{16}H_{24}Cl_4Co_8O_{28}$ having approximate dimensions of 0.25 × 0.23 × 0.23 mm was mounted in a glass capillary. Crystals of this material rapidly decompose when

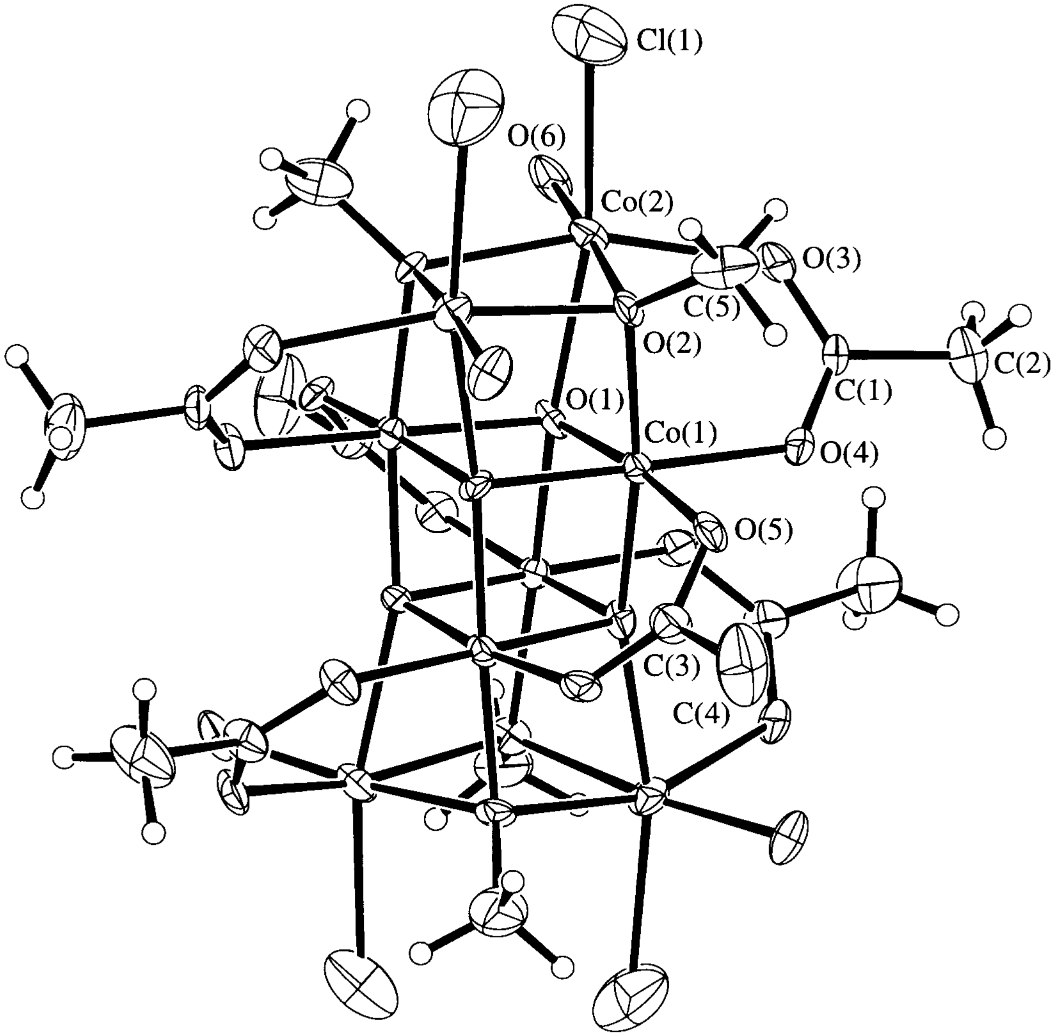

Fig. 1. Thermal ellipsoid plot of $[Co_8(O)_4(OAc)_6(OMe)_4Cl_4(OH_n)_4]$ ($n = 1, 2$) drawn at the 25% probability level. Selected interatomic distances (Å) and angles ( ): Co(1)—Co(1) 2.666(3), 2.848(4), 2.852(4), Co(1)—Co(2), 2.861(3), 3.096(3), Co(2)—Co(2) 3.216(4), Co(1)—O(1) 1.878(8), 1.890(8), 1.906(7), Co(1)—O(2)(OMe) 1.904(8), Co(1)—O(4)(OAc) 1.935(8), Co(1)—O(5)(OAc) 1.914(9), Co(2)—(O1) 2.133(8), Co(2)—O(2)(OMe) 2.083(9), 2.111(8), Co(2)—O(3)(OAc) 2.130(9), Co(2)—O(6)(OH_n) 2.061(9), Co(2)—Cl 2.358(7), Co(1)—O(1)—Co(1) 89.6(3), 97.2(4), 98.4(4), Co(1)—O(1)—Co(2) 90.4(3), 99.9(4), 166.2(4), Co(1)—O(2)—Co(2) 91.6(4), 100.8(3), Co(2)—O(2)—Co(2) 100.1(4).

removed from the mother liquor. Several crystals were examined and all were found to be twinned. However, one crystal had a dominant twin component that could be indexed. Cell constants obtained from a least-squares refinement against the setting angles of 25 reflections in the range $16.24 < 2\theta < 24.02°$ corresponded to an *F*-centered orthorhombic unit cell. The systematic absences determine the space group to be *F*ddd (#70). Approximately half of the *hk*0 reflections were classified as observed, presumably as a consequence of the twinning. A solution obtained in *F*2dd did not refine satisfactorily.* The data were corrected for Lorentz and polarization effects. An empirical absorption correction based on the azimuthal scans of the reflections was also applied to the

---

*The reflection statistics strongly indicated a centrosymmetric lattice, however the systematic absences to 50° 2θ suggested the non-centrosymmetric space group *F*2dd with 43 of the 110 *0kl* $k+l$ 4n reflections being classified as observed. However, the $I/\sigma(I)$ for these reflections is only 5.2 compared to the data set average of 15.1. This suggested that the *0kl* reflections arise from a flaw or perhaps twin in the crystal. The absences to 25° 2θ are consistent with *F*ddd, with only 1 of the 40 *0kl* reflections being observed ($I/\sigma(I)$ – 0.6). A solution can be obtained in *F*2dd, but refinement of the solution reveals extensive correlation and inverting the structure has no impact on the *R* values, suggesting centric symmetry or at least pseudo centricity. The crystals decay rapidly on removal from the mother solution. A crystal was mounted in a capillary, even so there was 16% decay during the collection. The cause of the decay is not certain.

data. The structure was solved using SHELXS86 and expanded using Fourier techniques. With the exception of the isotropically refined oxygen atoms of the water molecules, the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the refinement at calculated positions with group isotropic temperature factors. Hydrogens were not attached to the water molecules to atom O(6) or the C4 methyl residue. The complex was generated from the $C_5H_5Co_2O_6$ asymmetric unit by three mutually orthogonal 2-fold axes. The C3 and C4 acetate backbone carbons reside on one of the two-fold axes. All calculations were performed as described previously [35] using the teXsan crystallographic software package of Molecular Structure Corporation. Atomic coordinates, interatomic lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data centre.

Crystal data

$C_{16}H_{24}Cl_4Co_8O_{28}$, $M = 1277.63$, orthorhombic, space group *F*ddd (No. 70), $a = 28.859(6)$, $b = 30.119(9)$, $c = 13.925(4)$ Å, $V = 12104(5)$ Å^3, $Z = 8$, $D_c = 1.402$ g cm^3, μ(Mo-K_α) = 23.735 cm^{-1}, $F(000) = 5024$. Final R (Rw) = 0.092 (0.081) for 1683 unique observed [$F_0 > 3.0\sigma(F_0)$], absorption-corrected intensities with $1 < 2\theta < 50°$.

Acknowledgements—We thank the Australian Research Council for financial support. J.A.K. thanks the University of Sydney for a Postgraduate Scholarship.

REFERENCES

1. A. E. Shilov, *Activation of Saturated Hydrocarbons by Transition Metal Complexes*. D. Reidel, Dordrecht (1984).
2. C. A. Tolman, J. D. Druliner, M. J. Nappa and N. Herron, in *Activation and Functionalization of Alkanes* (Edited by C. L. Hill), Vol. p. 303. Wiley-Interscience, New York (1989).
3. R. A. Sheldon and J. K. Kochi, *Oxidation and Combustion Reviews* 1973, **5**, 226.
4. R. A. Sheldon and J. K. Kochi, *Adv. Catal.* 1976, **25**, 272.
5. J. V. Zeile Krevor, in *Selective Hydrocarbon Activation Principles and Progress* Edited by J. A. Davies, P. L. Watson, A. Greenberg and J. F. Liebman, p. 19. VCH, New York (1990).
6. *Dioxygen Activation and Homogeneous Catalytic Oxidation* Edited by L. I. Simandi, Vol. 66. Elsevier, Amsterdam (1991).
7. *Catalytic Oxidations with Hydrogen Peroxide as Oxidant* (Edited by G. Strukul). Kluwer, Dordrecht (1992).
8. B. C. Gates, *Catalytic Chemistry*. Wiley-Interscience, New York (1992).
9. G. W. Parshall and S. D. Ittel, *Homogeneous Catalysis*. Wiley-Interscience, New York (1992).
10. *The Activation of Dioxygen and Homogeneous Catalytic Oxidation* Edited by D. H. R. Barton, A. E. Martell and D. T. Sawyer. Plenum, N.Y. (1993).
11. C. E. Sumner, Jr and G. R. Steinmetz, *J. Am. Chem. Soc.* 1985, **107**, 6124.
12. K. Dimitrou, K. Folting, W. E. Streib and G. Christou, *J. Am. Chem. Soc.* 1993, **115**, 6432.
13. K. S. Hagen, R. Lachiotte and A. Kitaygorodskiy, *J. Am. Chem. Soc.* 1993, **115**, 12617.
14. Copaux, *Ann. Chim. Phys.* 1905, **6**, 548.
15. C. Schall and H. Markgraf, *Trans. Am. Electrochem. Soc.* (*C.A.* 18 (1924) 944) 1924, **45**, 161.
16. C. Schall and C. Thieme-Weidtmarkter, *Z. Electrochem.* (*C.A.* 23 (1929) 4412) 1929, **35**, 337.
17. J. A. Sharp and A. G. White, *J. Chem. Soc.* 1952, 110.
18. M. Mori, K. Kyumo and M. Shibata, *Nippon Kagaku Zasshi* 1956, **77**, 1434.
19. E. Koubek and J. Edwards, *J. Inorg. Nucl. Chem.* 1963, **25**, 1401.
20. S. S. Lande, C. D. Falk and J. K. Kochi, *J. Inorg. Nucl. Chem.* 1971, **33**, 4101.
21. J. J. Ziolkowski, F. Pruchnik and T. Szymanska-Buzar, *Inorg. Chim. Acta* 1973, **7**, 473.
22. G. H. Jones, *J. Chem. Soc., Chem. Commun.* 1979, 536.
23. G. H. Jones, *J. Chem. Res.* (*M*) 1981, 2801.
24. A. B. Blake, J. R. Chipperfield, S. Lau and D. E. Webster, *J. Chem. Soc., Dalton Trans.* 1990, 3719.
25. S. Uemura, A. Spencer and G. Wilkinson, *J. Chem. Soc., Dalton Trans.* 1973, 2565.
26. C. E. Sumner, Jr, *Inorg. Chem.* 1988, **27**, 1320.
27. J. A. Bertrand, A. P. Ginsberg, R. I. Kaplan, C. E. Kirkwood, R. L. Martin and R. C. Sherwood, *Inorg. Chem.* 1971, **10**, 240.
28. Y. A. Simonov, G. S. Matuzenko, M. M. Botoshanskii, M. A. Yampol'skaya, N. V. Gerbeleu and T. I. Malinovskii, *Russian J. Inorg. Chem.* 1982, **27**, 231.
29. Y. A. Simonov, V. K. Bel'skii, G. S. Matuzenko and N. V. Gerbeleu, *Krystalogrfiya* 1984, **29**, 82.
30. M. M. Olmstead, P. P. Power and G. A. Sigel, *Inorg. Chem.* 1988, **27**, 580.
31. J. A. Bertrand and T. C. Hightower, *Inorg. Chem.* 1973, **12**, 206.
32. B. F. Hoskins, R. Robson and D. Vince, *J. Chem. Soc., Chem. Commun.* 1973, 392.
33. J. A. Bertrand, E. Fujita and D. G. Vanderveer, *Inorg. Chem.* 1979, **18**, 230.
34. K. Dimitrou, K. Folting, W. E. Streib and G. Christou, *J. Chem. Soc., Chem. Commun.* 1994, 1385.
35. J. K. Beattie, T. W. Hambley, J. A. Klepetko, A. F. Masters and P. Turner, *Polyhedron* 1996, **15**, 2141.