CHEMCOMM
Communication
www.rsc.org/chemcomm

Mixed-valence, tetranuclear cobalt(III, IV) complexes: preparation and properties of $[Co_4O_4(O_2CR)_2(bpy)_4]^{3+}$ salts

Katerina Dimitrou,[a] Angelica D. Brown,[a] Thomas E. Concolino,[b] Arnold L. Rheingold[b] and George Christou*[a]

[a] *Department of Chemistry, Indiana University, Bloomington, IN 47405, USA.*
E-mail: christou@indiana.edu
[b] *Department of Chemistry, University of Delaware, Newark, DE 19716, USA*

Received (in Cambridge, UK) 2nd March 2001, Accepted 1st June 2001
First published as an Advance Article on the web 27th June 2001

Cyclic voltammetric examination of $[Co_4O_4(O_2CR)_2(bpy)_4](ClO_4)_2$ cubane complexes 1 (R = various; bpy = 2,2′-bipyridine) in MeCN reveals a one-electron reversible oxidation in the range 0.68–0.86 V *vs.* ferrocene; the one-electron oxidized clusters can be obtained in analytical purity by either controlled potential electrolysis to give $[Co_4O_4(O_2CR)_2(bpy)_4](ClO_4)_3$ 2 or oxidation with $(NH_4)_2Ce(NO_3)_6$ to give $[Co_4O_4(O_2CR)_2(bpy)_4][Ce(NO_3)_6]$ 3.

The ability of hard oxide (O^{2-}) ions to stabilize unusually high metal oxidation states has long been recognized in such textbook species as MnO_4^- and CrO_4^{2-}. More recently, some interesting new examples have been identified in which bridging O^{2-} ions stabilize rare oxidation states of Fe and Cu in non-mononuclear chemistry: apart from their intrinsic importance, such species offer insights into the mode of action of certain metalloenzymes. Thus, the $Fe^{III}Fe^{IV}$ oxidation level, thought to correspond to species X of ribonucleotide reductase,[1,2] has been obtained in oxide-bridged Fe_2 complexes,[2,3] whereas a $2Fe^{IV}$ species is believed to be species Q of methane monooxygenase.[1] Similarly, the $[Cu_2(\mu\text{-}O)_2]^{2+}$ core ($2Cu^{III}$) has been structurally characterized,[4,5] as well as a related species containing the $[Cu_3(\mu_3\text{-}O)_2]^{3+}$ core ($2Cu^{II}$, Cu^{III}).[6] Such species offer valuable insights into Cu-mediated O_2-activation biochemistry. We have now discovered that the cubane $[Co_4(\mu_3\text{-}O_4)_4]^{4+}$ core containing $4Co^{III}$ can be oxidized to a $3Co^{III}$, Co^{IV} form, and we describe the preparation and characterization of several such novel species.

As reported previously,[7] the D_{2d} symmetry complex $[Co_4O_4(O_2CR)_2(bpy)_4](ClO_4)_2$ **1** (R = Me; bpy = 2,2′-bipyridyl) can be prepared by deprotonating $[Co_2(OH)_2(O_2CMe)_3(bpy)_2](ClO_4)$ with Li_2O_2 in DMSO. A series of $[Co_4O_4(O_2CR)_2(bpy)_4](ClO_4)_2$ **1** complexes has now been prepared by ligand substitution with RCO_2H in refluxing MeCN, and electrochemical examination of these $[Co_4O_4]^{4+}$ complexes by cyclic voltammetry (CV) reveals irreversible reductions at $\leqslant -1.4$ V *vs.* ferrocene and a reversible one-electron oxidation at *ca.* 0.7 V *vs.* ferrocene. The CV scan for the R = $C_6H_4NO_2$-4 complex is shown in Fig. 1, and the oxidation potentials as a function of R group are listed in Table 1. The peak separations are comparable with that of the ferrocene/ferrocenium couple used as an internal reference (Fig. 1). Controlled potential coulometry at 0.90 V *vs.* ferrocene for the R = C_6H_4Me-4 and C_6H_4OMe-4 species gave 0.9–1.0 e^-/Co_4 transferred, confirming a one-electron oxidation process. The CV are thus consistent with oxidation to $[Co_4O_4(O_2CR)_2(bpy)_4]^{3+}$, which would contain $3Co^{III}$,Co^{IV} if the oxidation were metal-based. Metal/bpy complexes can often exhibit bpy-based reversible reductions but not oxidations.[8]

Analytically-pure oxidized clusters† were prepared in bulk by two methods: (i) controlled potential electrolysis in MeCN or MeCN–CH_2Cl_2 containing 0.4 M $LiClO_4$ at 0.90–1.00 V *vs.* ferrocene, which caused precipitation of $[Co_4O_4(O_2CR)_2(bpy)_4](ClO_4)_3$ **2** in $\geqslant$ 85% yield as microcrystalline powders; and (ii) oxidation with $(NH_4)_2Ce(NO_3)_6$ in MeCN, which caused precipitation of sparingly soluble microcrystalline $[Co_4O_4(O_2CR)_2(bpy)_4][Ce(NO_3)_6]$ **3**.‡ Complexes **2** can be recrystallized from MeCN–Et_2O. EPR spectra at 5 and 75–100 K of the R = C_6H_4Me-4 and C_6H_4OMe-4 derivatives as powders (**3**) or MeCN–toluene (1 : 1) glasses (**2**) show a broad (*ca.* 800 G) signal at g = 2.20 with no resolved hyperfine, consistent with a $S = \frac{1}{2}$ species and a Co-based oxidation. Solid-state magnetic susceptibility studies at room temperature on the same two derivatives of **2** gave $\mu_{\text{eff}} \approx 2.2\ \mu_B$, consistent with one unpaired electron. ^1H NMR spectra show paramagnetically shifted and broadened signals for **2**, again consistent with $S = \frac{1}{2}$ oxidized clusters whereas complexes **1** are diamagnetic. Comparison of the spectra for **1** and **2** (R = C_6H_4Me-4), for example, show that only four bpy and three carboxylate signals are observed and that the bpy signals are much more shifted on oxidation than the carboxylate signals,

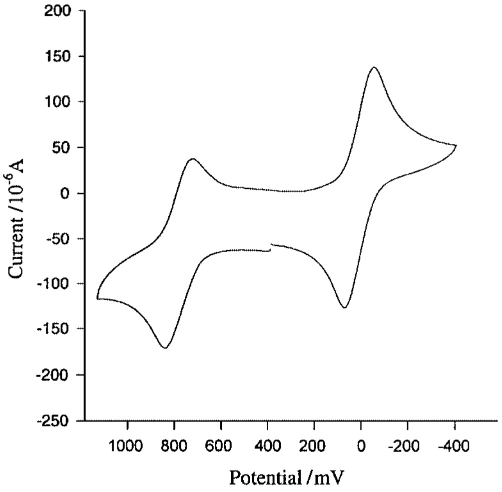

Fig. 1 Cyclic voltammogram at a glassy carbon electrode of **1**; R = $C_6H_4NO_2$-4 (1 mM) in MeCN containing 0.1 M $NBu^n{}_4PF_6$ and ferrocene as an internal standard ($E_{1/2}$ = 0.00 V).

Table 1 Cyclic voltammetric data for the oxidation of $[Co_4O_4(O_2CR)_2(bpy)_2](ClO_4)_2$ **1** complexes in MeCN[ab]

R	$E_{1/2}{}^c$/V	R	$E_{1/2}{}^c$/V
Me	0.69	C_6H_4OMe-4	0.68
CH=CHMe	0.70	$C_6H_3(OMe)_2$-2,4	0.68
Ph	0.70	C_6H_4Cl-4	0.72
C_6H_4Me-4	0.70	$C_6H_4NO_2$-4	0.77
C_6H_4Et-4	0.69	C_6F_5	0.86
$C_6H_4Bu^t$-4	0.67		

[a] In volts *vs.* the ferrocene/ferrocenium couple as an internal standard; ±0.01 V. [b] Glassy carbon working, Pt wire auxiliary, and SCE reference electrodes; 0.1 M $NBu^n{}_4PF_6$ supporting electrolyte. [c] $E_{1/2}$ is the midpoint of the forward (anodic) and reverse (cathodic) peak potentials.

DOI: 10.1039/b102008k

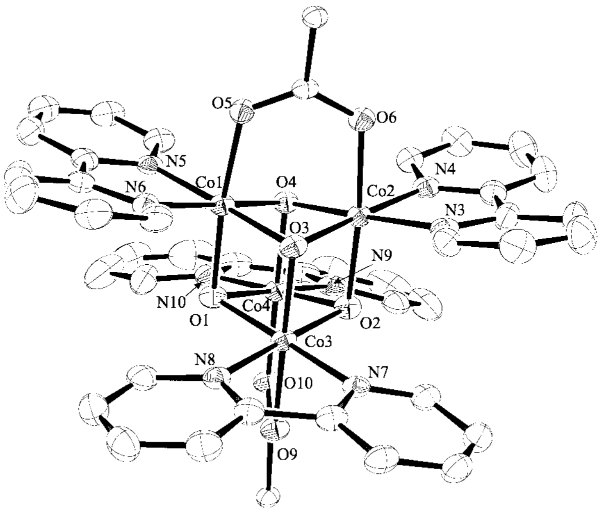

Fig. 2 ORTEP plot of the cation of **2** (R = $C_6H_4NO_2$-4) at the 40% probability level; for clarity, only the *ipso*-C atom of the carboxylate group is shown. Selected distances (Å): Co(1)···Co(2) 2.641(1), Co(1)···Co(3) 2.872(1), Co(1)···Co(4) 2.874(1), Co(2)···Co(3) 2.855(1), Co(2)···Co(4) 2.861(1), Co(3)···Co(4) 2.662(1), Co(1)–O(1) 1.903(4), Co(1)–O(3) 1.882(4), Co(1)–O(4) 1.876(3), Co(2)–O(2) 1.900(4), Co(2)–O(3) 1.877(4), Co(2)–O(4) 1.871(4), Co(3)–O(1) 1.902(4), Co(3)–O(2) 1.878(4), Co(3)–O(3) 1.886(4), Co(4)–O(1) 1.894(4), Co(4)–O(2) 1.882(4), Co(4)–O(4) 1.899(4).

consistent with greater spin delocalization onto the former groups. On the ^{1}H NMR timescale, therefore, the oxidized clusters retain D_{2d} symmetry, which is consistent with electronic delocalization, or detrapping that is fast on the ^{1}H NMR timescale.

The crystal structure‡ of complex **2** (R = $C_6H_4NO_2$-4) was obtained at –100 °C. The cation (Fig. 2) has no crystallographic symmetry, but has virtual D_{2d} symmetry. There is a $[Co_4O_4]$ cubane with a bpy at each Co and a RCO_2^- group bridging two opposite faces; the virtual S_4 axis passes through the latter. Three independent ClO_4^- groups confirm the 3+ charge of the cation. Examination of the bond distances shows that the four Co ions are all equivalent, indicating electronic delocalization and a $Co^{3.25+}$ oxidation state description, even in the solid state at −100 °C. The anisotropic thermal parameters of core Co and O atoms do not appear abnormally large, arguing against a static disorder of a trapped-valence $3Co^{III},Co^{IV}$ system. Protonation of a core O^{2-} ion (and a resulting $4Co^{III}$ description) is ruled out by the absence of Co–O bond lengthening as seen previously[9] in the genuinely protonated species $[Co_4O_3(OH)(O_2CR)_2(bpy)_4]^{3+}$ and $[Co_4O_2(OH)_2(O_2CR)_2(bpy)_4]^{4+}$. Comparison of the structure of **2** (R = $C_6H_4NO_2$-4) with that of **1** (R = C_6H_4Me-4) indicates no significant difference: the largest variation is in the Co–O (carboxylate) distances (average 1.942 Å for **2** *vs*. 1.955 Å for **1**) but these and all the other Co–X distances are statistically the same within the 3σ criterion.

The combined results indicate that the diamagnetic $[Co_4O_4]^{4+}$ core can be oxidized to a paramagnetic (S = ½) $[Co_4O_4]^{5+}$ core that is electronically delocalized, as might be expected for mixed-valence, low-spin Co^{III} (t_{2g}^6), Co^{IV} (t_{2g}^5) species. Cobalt(IV) is still a rare oxidation state, and isolated, well characterized examples that are stable at room temperature are few and all mononuclear,[10] but the combined results above establish that stable $[Co_4O_4]^{5+}$ clusters can be accessed which formally contain $3Co^{III}$, Co^{IV}. Such species could prove useful as a new family of strong oxidizing agents soluble in organic solvents, particularly since their oxidizing strength can be tuned by appropriate choice of organic ligands.

This work was supported by the National Science Foundation.

Notes and references

† The complexes analysed satisfactorily. Calc. (found) for $[Co_4O_4(O_2CC_6H_4Me\text{-}4)_2(bpy)_4](ClO_4)_3\cdot H_2O$: C, 44.51 (44.31); H, 3.20 (3.34); N, 7.42 (7.44); Cl, 7.04 (7.59). $[Co_4O_4(O_2CC_6H_4OMe\text{-}4)_2(bpy)_4](ClO_4)_3\cdot 3/2CH_2Cl_2$: C, 41.79 (41.78); H, 2.99 (3.15); N, 6.78 (6.93); Cl, 12.87 (12.18). $[Co_4O_4(O_2CC_6H_4Me\text{-}4)_2(bpy)_2][Ce(NO_3)_6]\cdot 2H_2O$: C, 38.59 (38.34); H, 2.89 (2.69); N, 11.25 (11.26). $[Co_4O_4(O_2CC_6H_4OMe\text{-}4)_2(bpy)_4][Ce(NO_3)_6]\cdot MeCN\cdot 2H_2O$: C, 39.19 (38.95); H, 2.96 (2.92); N, 12.19 (12.15). Electronic spectra in MeCN for the R = C_6H_4Me-4 complexes: **1**; 556 (sh), 414 (10800), 293 (65800). **2**; 520 (sh), 332 (sh), 314 (sh), 302 (47100).

‡ *Crystal data* for $[Co_4O_4(O_2CC_6H_4NO_2\text{-}4)_2(bpy)_4](ClO_4)_3\cdot MeCN\cdot 3H_2O$: $C_{56}H_{49}Cl_3Co_4N_{11}O_{27}$, M = 1650.16, triclinic, $P\bar{1}$, a = 11.6330(2), b = 14.1304(2), c = 20.7165(2) Å, α = 91.8195(6), β = 95.8450(8), γ = 110.1203(4)°, V = 3172.78(4) Å^3, Z = 2, D_c = 1.727 g cm^{-3}, λ = 0.71073 Å, T = −100 °C, 4 < 2θ < 50°, $R(R_w)$ = 0.0846 (0.2279) for refinement on F^2 using all 10537 unique reflections. The structure was solved and refined using SHELXTL-97. All non-hydrogen atoms were refined anisotropically. Three independent ClO_4^- ions were located, each at 100% occupancy. Hydrogen atoms were included as fixed atom contributors. No disorder problems were encountered.

CCDC reference number 161550. See http://www.rsc.org/suppdata/b1/b102008k/ for crystallographic data in CIF or other electronic format.

1 B. J. Wallar and J. D. Lipscomb, *Chem. Rev.*, 1996, **96**, 2625 and references therein.
2 H. Zheng, S. J. Yoo, E. Munck and L. Que, Jr., *J. Am. Chem. Soc.*, 2000, **122**, 3789 and references therein.
3 H.-F. Hsu, Y. Dong, L. Shu, V. G. Young, Jr. and L. Que, Jr., *J. Am. Chem. Soc.*, 1999, **121**, 5230.
4 J. A. Halfen, S. Mahapatra, E. C. Wilkinson, S. Kaderli, V. G. Young, Jr., L. Que, Jr., A. D. Zuberbühler and W. B. Tolman, *Science*, 1996, **271**, 1397; W. B. Tolman, *Acc. Chem. Res.*, 1997, **30**, 227; S. Mahapatra, V. G. Young, S. Kaderli, A. D. Zuberbühler and W. B. Tolman, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 130.
5 V. Mahadevan, Z. Hou, A. P. Cole, D. E. Root, T. K. Lal, E. I. Solomon and T. D. P. Stack, *J. Am. Chem. Soc.*, 1997, **119**, 11 996.
6 A. P. Cole, D. E. Root, P. Mukherjee, E. I. Solomon and T. D. P. Stack, *Science*, 1996, **273**, 1848; D. E. Root, M. J. Henson, T. Machonkin, P. Mukherjee, T. D. P. Stack and E. I. Solomon, *J. Am. Chem. Soc.*, 1998, **120**, 4982.
7 K. Dimitrou, K. Folting, W. E. Streib and G. Christou, *J. Am. Chem. Soc.*, 1993, **115**, 6432.
8 C. A. Crawford, J. H. Matonic, J. C. Huffman, K. Folting, K. R. Dunbar and G. Christou, *Inorg. Chem.*, 1997, **36**, 2361; P. S. Braterman, J.-I. Song, F. M. Wimmer, S. Wimmer, W. Kaim, A. Klein and R. D. Peacock, *Inorg. Chem.*, 1992, **31**, 5084, and references therein.
9 K. Dimitrou, A. D. Brown, K. Folting and G. Christou, *Inorg. Chem.*, 1999, **38**, 1834.
10 F. C. Anson, T. J. Collins, R. J. Coots, S. L. Gipson and T. G. Richmond, *J. Am. Chem. Soc.*, 1984, **106**, 5037; E. K. Byrne and K. H. Theopold, *J. Am. Chem. Soc.*, 1987, **109**, 1282; J. W. Quail and G. A. Rivett, *Can. J. Chem.*, 1972, **50**, 2447; M. Koikawa, M. Gotoh, H. Okawa, S. Kida and T. Kohzuma, *J. Chem. Soc., Dalton Trans.*, 1989, 1613; J.-P. Barbier, B. M. Ondo and R. P. Hugel, *J. Chem. Soc., Dalton Trans.*, 1985, 597; Y. Yamamoto, E. Toyota and H. Konno, *Bull. Chem. Soc. Jpn.*, 1991, **64**, 1398.