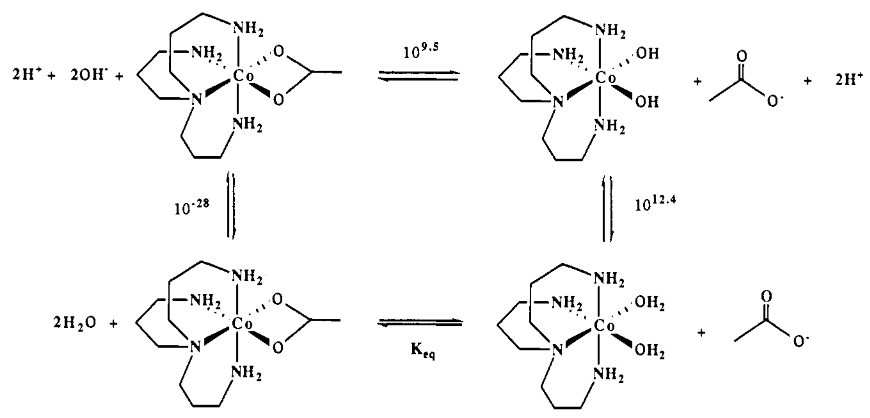
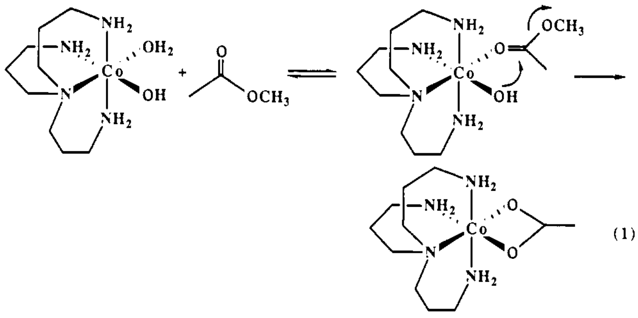
Scheme II



of **2**. Two equiv of NaOH are consumed in forming $[(trpn)Co(OH)_2]^+$ and NaOAc from **2** (Scheme II). The midpoint of the titration curve is at pH = 7.6 when the initial concentration of **2** is 1 mM. Therefore, the equilibrium constant for displacement of acetate from **2** with 2 equiv hydroxide is $10^{9.5}$ M^{-1} (Scheme II). Since $K_w = 10^{-14}$ and the pK_{a1} and pK_{a2} values of $[(trpn)Co(OH_2)_2]^{3+}$ are 4.8 and 7.6, respectively,[11b] the equilibrium constant for formation of **2** from $[(trpn)Co(OH_2)_2]^{3+}$ and NaOAc can be obtained from the cycle in Scheme II ($K_{eq} = 10^{6.1}$ M^{-1}). Due to the tight association of NaOAc to $[(trpn)Co(OH_2)_2]^{3+}$, there is considerable product inhibition during $[(trpn)Co(OH_2)(OH)]^{2+}$-catalyzed hydrolysis of methyl acetate below pH 7.6.

The rate constant for dissociation of acetate from **2** at pH 7.6 was measured by the pH stat method ($k = 2.3 \times 10^{-2}$ s^{-1}). Since the turnover time (30 min) of the catalyst is much greater than the half-life (30 s) for dissociation of acetate from **2**, the rate-determining step in the catalytic cycle (Scheme I) should not be the dissociation step. Therefore the rate-determining step should be either the complexation step or the ester bond cleavage step (eq 1).[16] Interestingly, the second-order rate constants for formation of **2** from $[(trpn)Co(OH_2)(OH)]^{2+}$ and methyl acetate (5.5×10^{-3} M^{-1} s^{-1}), *p*-nitrophenyl acetate (7.4×10^{-3} M^{-1} s^{-1}), or acetylcholine (4.0×10^{-3} M^{-1} s^{-1}) are comparable (at pH 7.0, 25 °C), indicating that complexation of the ester to the cobalt complex is the rate-determining step.[17]



(1)

The water rate for methyl acetate hydrolysis is very slow (3.16×10^{-10} s^{-1} at 25 °C, half-life = 70 years).[18] We have demonstrated for the first time, efficient catalytic hydrolysis of methyl acetate and acetylcholine in neutral water at 25 °C. The rate-determining step in the catalytic cycle is complexation of the ester to the catalyst. A key four-membered ring intermediate $[(trpn)Co(OAc)]^{2+}$ in the catalytic cycle has been isolated for the first time. The stability of the four-membered ring intermediate is highly sensitive to the tetraamine ligand structure.

Acknowledgment. We thank Suzanne Lilker for preliminary work. This work was supported by the Natural Sciences and Engineering Research Council of Canada.

Supplementary Material Available: Figures of ^{13}C NMR spectra of carboxyl carbon (2 pages).[14] Ordering information is given on any current masthead page.

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[16] Direct intermolecular metal–hydroxide mechanism can be ruled out since monoaquo metal complexes are not active.[7]

[17] The second-order rate constants were obtained from the rate of formation of **2**. In a typical kinetic experiment, methyl acetate (0.1 M) was allowed to react in a buffered solution (pH 7, 0.02 M collidine; ionic strength 0.1 M with $NaClO_4$) of $[(trpn)Co(OH_2)(OH)]^{2+}$ (10 mM) at 25 °C. Formation of **2** was monitored by following the increase in the visible absorption at λ_{max} for **2** (531 nm).

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Reversible Redox Processes in Main-Group/Transition-Metal Clusters: The $[Sb_2Co_4(CO)_{10}(\mu\text{-}CO)]^{-/2-}$ Couple

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Elaborate theories have developed over the past 20 years to aid in understanding structure and bonding in small metal clusters.[1-7] Dahl and co-workers have performed numerous studies focusing on the geometric effects caused by changes of electronic configurations in various metal clusters.[8] They have found that many

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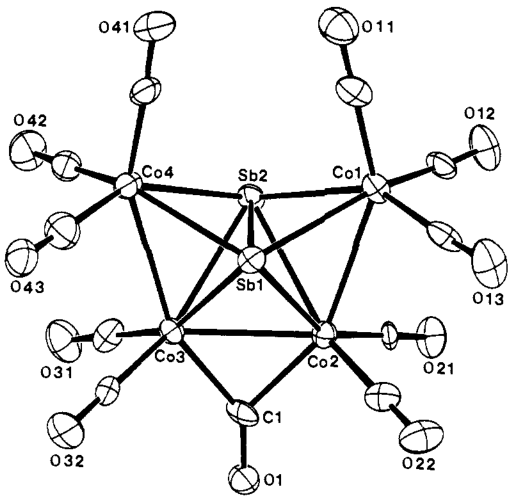

Figure 1. ORTEP diagram of **1** showing 30% thermal probability ellipsoids and atom labeling. The carbonyl carbon atoms are labeled according to their respective oxygen atoms. Selected bond distances (Å) are as follows: Sb1–Sb2 = 2.911 (1), Sb–Co(av) = 2.640 [range = 2.605 (2) to 2.692 (2)], Co1–Co2 = 2.725 (3), Co2–Co3 = 2.510 (3), Co3–Co4 = 2.694 (3). Corresponding distances (Å) for **2** are as follows: Sb1–Sb2 = 2.882 (2), Sb–Co (av) = 2.642 [range = 2.616 (4) to 2.676 (4)], Co1–Co2 = 2.716 (5), Co2–Co3 = 2.646 (5), Co3–Co4 = 2.717 (5).

such molecules can gain or lose valence electrons without breakdown of their central cluster frameworks. Here we report results of the reversible one-electron reduction of $[Sb_2Co_4(CO)_{10}(\mu\text{-}CO)]^-$, **1**, to $[Sb_2Co_4(CO)_{10}(\mu\text{-}CO)]^{2-}$, **2**, along with the crystal structures of their $[PPN]^+$ salts. These molecules, which do not obey any current electron-counting formalism, are related by a reversible one-electron redox cycle in which the molecular framework is maintained.

The reaction of $SbCl_3$ with $NaCo(CO)_4$ (1:3 ratio) in dilute aqueous HCl forms a dark green precipitate which infrared data indicate may be $SbCo_3(CO)_{12}$ through comparisons with infrared spectra of known $BiCo_3(CO)_{12}$.[9] This unstable compound begins to decompose immediately upon dissolution in tetrahydrofuran, forming after several hours a dark precipitate from which **1** and **2** were isolated as their $[PPN]^+$ or $[Et_4N]^+$ salts.[10,11]

The framework of **2** is the same found for **1**. The core geometry consists of a Sb_2Co_2 tetrahedron with a bridging carbonyl ligand between the two cobalt atoms. Each cobalt atom possesses two terminal carbonyl ligands, and two $Co(CO)_3$ groups cap the Sb_2Co faces of the parent tetrahedron. The metal framework thus may be described either as a bicapped tetrahedron or as a monocapped trigonal bipyramid. Such cluster geometries have been reported for a number of compounds[12–14] including the paramagnetic bismuth homologue, $[Bi_2Co_4(CO)_{10}(\mu\text{-}CO)]^-$, **3**.[15] Like **3**, **1** is paramagnetic (ESR signal at $g = 2.032$ at 12 K). An electron precise tetrahedron, i.e., $[Sb_2Co_2(CO)_4(\mu\text{-}CO)]^{2-}$, possesses 12 skeletal electrons.[3,5] In the normal situation, each capping unit supplies no additional skeletal electrons to the cluster.[5,12–14] Teo has allowed for the possibility of four extra electrons to be introduced.[6] In the present case, six electrons in fact are added by the capping $Co(CO)_3$ units in **2**. We have previously shown[16] that the eight additional electrons in a tricapped tetrahedral derivative of $[Bi_4\{Fe(CO)_3\}_3]^{2-}$ are accommodated by using the three members of a low-lying, empty t_1 set of the tetrahedron, and one combination of capping $Fe(CO)_3$ orbitals is left nonbonding. Extended Hückel calculations[17] on **1** and **2** reveal that $[Sb_2Co_2(CO)_4(\mu\text{-}CO)]^{2-}$ is indeed isolobal[1] to an electron precise tetrahedron and that the three components of empty t_1 ($b_2 + b_1 + a_2$ in C_{2v} symmetry) are utilized by the two capping $Co(CO)_3$ units. Hence, an 18 skeletal electron count is stable. Alternatively, **2** may be viewed as an *arachno*-dodecahedron or a *nido*-pentagonal bipyramid. Both formulations presuppose no direct Sb–Sb bonding. However, the Sb–Sb distances of 2.911 (1) Å in **1** and 2.882 (2) Å in **2** are only slightly longer than those reported for Sb_7^{3-} [range 2.693 (4) to 2.880 (4) Å][18] and Ph_4Sb_2 [2.837 (1) Å].[19] Our calculations also support the existence of substantial Sb–Sb bonding with overlap populations of 0.483 and 0.526 in **1** and **2**, respectively. For reference, the corresponding value in H_4Sb_2 is 0.686.

The most significant structural change upon reduction is the 0.136 Å increase in the Co2–Co3 distance [from 2.510 (3) to 2.646 (5) Å in **1** and **2**, respectively]. The other distances show much smaller differences. Thus, it is plausible that the HOMO in **2** is an antibonding orbital primarily localized on Co2–Co3. This is consistent with our calculations. The HOMO is an orbital of a_2 symmetry (Co2–Co3 π^*) which is 60% on Co2, Co3, 12% on Co1, Co4, and 0.3% on Sb1, Sb2. The Co2–Co3 overlap population drops from 0.066 in **1** to 0.012 in **2**. For comparison, the Co1–Co2 overlap population is 0.091 in **1**, 0.082 in **2**, and 0.055 in $Co_2(CO)_8$ where the Co–Co distance is 2.524 (2) Å.[20]

A cyclic voltammogram[21] of **1** displays a reversible one-electron reduction ($E_{1/2} = -0.54$ V, $\Delta E_p = 70$ mV) for the $Sb_2Co_4^{1-/2-}$ couple. **1** is reduced to **2** using cobaltocene or sodium naphthalenide, and **2** is oxidized to **1** upon treatment with $[Cu(MeCN)_4][BF_4]$.

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Supplementary Material Available: An ORTEP diagram of **2** and tables listing atomic positional and thermal parameters and intramolecular bond distances and angles for $[PPN][Sb_2Co_4(CO)_{10}(\mu\text{-}CO)]$ and $[PPN]_2[Sb_2Co_4(CO)_{10}(\mu\text{-}CO)]$ (42 pages); tables of observed and calculated structure factors (47 pages). Ordering information is given on any current masthead page.

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(10) IR of $[Et_4N]$**1** (ν_{CO} in tetrahydrofuran) 2010 (s), 1995 (ms), 1975 (m), 1802 (w, bridging CO) cm^{-1}; IR of $[PPN]_2$**2** (ν_{CO} in CH_2Cl_2) 1975 (s), 1950 (ms), 1925 (m), 1740 (w, bridging CO) cm^{-1}. Anal. $[Et_4N]$**1** ($C_{19}H_{20}NO_{11}Co_4Sb_2$) C; H: calcd, 2.20; found, 2.35; N: calcd, 1.53; found, 1.70.

(11) X-ray Crystal Data. [PPN]**1**: $C_{47}H_{30}NO_{11}P_2Co_4Sb_2$, FW = 1325.93, orthorhombic, *Pbca* (no. 61), $a = 18.408$ (3) Å, $b = 33.038$ (7) Å, $c = 16.301$ (3) Å, $V = 9914$ (3) Å^3, $Z = 8$, no. observed $[I > 3\sigma(I)] = 3729$, no. variables = 352, $2\theta_{max} = 55°$, $T = -80$ °C, $R = 0.053$, $R_w = 0.063$, $S = 1.20$, Rigaku AFC5S diffractometer, Mo Kα radiation. $[PPN]_2$**2**: $C_{83}H_{60}N_2O_{11}P_4Co_4Sb_2$, FW = 1864.52, triclinic, $P\bar{1}$ (no. 2), $a = 15.618$ (3) Å, $b = 19.333$ (4) Å, $c = 15.124$ (3) Å, $\alpha = 93.44$ (2)°, $\beta = 113.66$ (2)°, $\gamma = 69.60$ (1)°, $V = 3903$ (2) Å^3, $Z = 2$, no. observed $[I > 6\sigma(I)] = 3087$, no. variables = 451, $2\theta_{max} = 50°$, $T = 23$ °C, $R = 0.046$, $R_w = 0.057$, $S = 1.39$. Both solved using SHELXS86 and refined using TEXSAN (v. 2.0) structure analysis package.

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(21) Cyclic voltammogram: 1 mM $[PPN][Sb_2Co_4(CO)_{10}(\mu\text{-}CO)]$ in 0.1 M $[Bu_4N][ClO_4]/CH_2Cl_2$ (20 mV/s); glassy carbon working electrode; Ag/AgCl reference electrode; Pt auxiliary electrode.