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# Synthesis and characterization of a decacobalt carbonyl cluster with two semi-interstitial phosphorus atoms

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**A paramagnetic cobalt carbonyl cluster, $[Co_{10}P_2(CO)_{23}H]^{2-}$, containing two partially-encapsulated phosphorus atoms is synthesized through the reaction of $[Co_6(CO)_{15}]^{2-}$ and $[Co(CO)_4]^-$ with $PBr_3$ in THF.**

The magnetic character of clusters with direct metal–metal bonding often arises from molecular orbitals whose unpaired electrons are delocalized over the entire metal framework.[1] To further probe the magnetism in such systems, we have begun to explore routes to high-nuclearity cobalt carbonyl clusters with a large magnetic moment. Here, one would ideally like to obtain clusters sizable enough to contain interior cobalt atoms with an environment similar to that in cobalt metal. To date, however, the largest pure cobalt carbonyl cluster is still $[Co_6(CO)_{16}]$,[2] for which all of the Co moments are effectively quenched by the surface CO ligands.

To increase cluster nuclearity, atoms such as C, N, Si, P, and Ge have been employed as nucleation centers.[3] The ensuing structures are, at least to some extent, dictated by the radius of the incorporated heteroatom. Thus, for example, while a N atom is readily accommodated at the center of a trigonal prismatic $Co_6$ cluster,[4] the larger radius P atom requires a significantly expanded metal cage. Consequently, nuclearities greater than six have been achieved in clusters such as $[Co_9P(CO)_{21}]^{2-}$ and $[Co_{10}P(CO)_{22}]^{3-}$, in which a single P atom is fully encapsulated within a mono- or bicapped square antiprism of Co atoms.[5] As a possible means of further increasing nuclearity in this system, we have attempted reactions utilizing a lower Co : P ratio, in hope of generating clusters containing more than one P center. Herein, we report the synthesis of the first such species: a paramagnetic $[Co_{10}P_2(CO)_{23}H]^{2-}$ cluster with a unique structural arrangement featuring two semi-interstitial phosphorus atoms.

Preparation of the cluster proceeds with use of $PBr_3$ as a source of phosphorus. A solution of $PBr_3$ (40 μL, 0.42 mmol) in 10 mL of THF was added to a solution of $[Et_4N][Co(CO)_4]$ (240 mg, 0.80 mmol) and $[Et_4N]_2[Co_6(CO)_{15}]$ [6] (210 mg, 0.20 mmol) in 30 mL of THF. This mixture was stirred for 14 h and filtered. The dark brown filtrate was then reduced to dryness *in vacuo*, and the residue was washed with successive aliquots of water and 2-propanol, extracted into THF, and precipitated with ether. The resulting solid was recrystallized twice by diffusing ether vapor into a THF solution, yielding 65 mg (10%) of pure $[Et_4N]_2[Co_{10}P_2(CO)_{23}H]$ (**1**) as a dark brown microcrystalline solid.† Brown–black block-shaped crystals suitable for X-ray analysis were obtained by layering isopropyl ether onto an acetone solution of **1**.‡

The cluster assembly process was probed *via* infrared spectroscopy. In THF, $[Co_6(CO)_{15}]^{2-}$ reacts with $[Co(CO)_4]^-$, gradually decomposing to give additional $[Co(CO)_4]^-$ and an unidentified cobalt species. On the other hand, treatment of $[Co_6(CO)_{15}]^{2-}$ with $PBr_3$ in the absence of $[Co(CO)_4]^-$ quickly produces the triangular cluster $[Co_3P(CO)_9]$.[7] Addition of $PBr_3$ to a THF solution of $[Co_6(CO)_{15}]^{2-}$ and $[Co(CO)_4]^-$ results in the immediate disappearance of the CO stretching bands for $[Co_6(CO)_{15}]^{2-}$ and the gradual emergence of new peaks associated with $[Co_{10}P_2(CO)_{23}H]^{2-}$. These observations suggest that two molecules of $[Co_3P(CO)_9]$ may aggregate through interactions with the excess $[Co(CO)_4]^-$ to give the diphosphorus cluster. Adventitious water, possibly associated with the $PBr_3$, is the most likely source of hydrogen in the reaction.

As shown in Fig. 1, the $[Co_{10}P_2(CO)_{23}H]^{2-}$ cluster exhibits a core structure in which each of the two phosphorus centers is coordinated by seven cobalt atoms, four of which comprise an intervening square. The coordination environment about either phosphorus can be described as deriving from a monocapped square antiprism, such as that present in $[Co_9P(CO)_{21}]^{2-}$,[5] through the removal of two adjacent vertices. A very similar coordination mode has been observed in $[Fe_3(CO)_9P(Au(PPh_3))_4]^-$;[8] however, the only other cobalt carbonyl cluster known to contain this type of "semi-interstitial" phosphorus is $[Co_6P(CO)_{16}]^-$, in which the $\mu_6$ central atom is even further exposed.[9] The Co–Co bonds in $[Co_{10}P_2(CO)_{23}H]^{2-}$ are of two types: six with a bridging carbonyl ligand and a mean distance of 2.54(4) Å, and nine with no bridging carbonyl group and a mean distance of 2.67(3) Å. The separation of 2.802(2) Å between the two phosphorus atoms is substantially less than the sum of the $P^{3-}$ radii, suggesting a reduced ionic charge and perhaps the presence of a weak P–P bonding interaction. In all, the $Co_{10}P_2$ cluster core approximates $C_{2h}$ symmetry, with a two-fold rotation axis penetrating atoms Co5 and Co7.

The symmetry of the cluster core is destroyed by the arrangement of its outer ligands. The two-fold rotation axis and inversion center are negated by the presence of a carbonyl

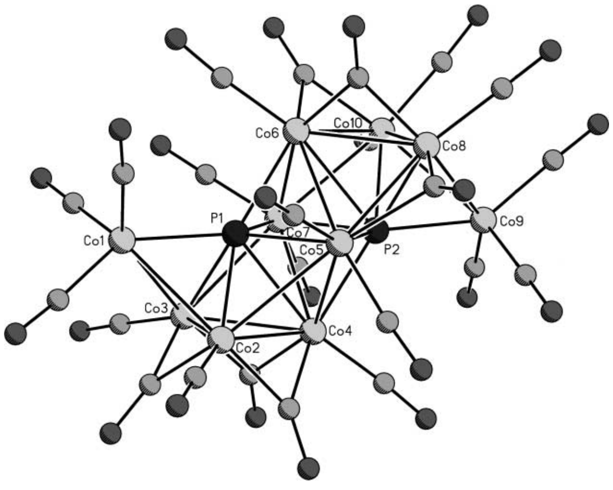

**Fig. 1** Structure of the $[Co_{10}P_2(CO)_{23}H]^{2-}$ cluster in **1**. Progressively darker shades of gray represent Co, C, O and P, respectively. Selected interatomic distances (Å): Co1–Co2 2.642(1), Co1–Co3 2.6769(9), Co2–Co3 2.501(1), Co2–Co4 2.5086(9), Co2–Co5 2.843(1), Co3–Co4 2.533(1), Co3–Co7 2.740(1), Co4–Co7 2.665(1), Co4–Co5 2.6972(9), Co5–Co8 2.608(1), Co5–Co6 2.723(1), Co6–Co10 2.5287(9), Co6–Co8 2.535(1), Co6–Co7 2.6046(9), Co7–Co10 2.654(1), Co8–Co9 2.656(1), Co8–Co10 2.697(1), Co9–Co10 2.669(1), Co1–P1 2.214(2), Co2–P1 2.270(2), Co3–P1 2.260(2), Co4–P1 2.480(2), Co5–P1 2.344(2), Co6–P1 2.265(2), Co7–P1 2.335(1), Co4–P2 2.273(2), Co5–P2 2.336(2), Co6–P2 2.505(2), Co7–P2 2.269(2), Co8–P2 2.281(2), Co9–P2 2.183(2), Co10–P2 2.293(2), mean Co–C($\mu_2$) 1.93(9), mean Co–C($\mu_1$) 1.78(2), mean C($\mu_2$)–O 1.177(5), mean C($\mu_1$)–O 1.144(8), P1 ··· P2 2.802(2).

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bridge along the Co2–Co3 bond but not along the opposing Co8–Co10 bond. In addition, the presence of a carbonyl group spanning the Co5–Co8 bond (albeit asymmetrically, with Co5–C = 2.152(6) Å and Co8–C = 1.802(6) Å) but not the Co7–Co10 bond negates a potential mirror plane, lowering the overall symmetry to $C_1$. The hydride ligand could not be located in the crystal structure, but possibly bridges between atoms Co2 and Co5, which, at a separation of 2.843(1) Å, are joined by the longest Co–Co bond in the cluster.

The cyclic voltammogram for an acetonitrile solution of **1** is displayed in Fig. 2. A quasireversible redox process is apparent at $E_{1/2} = -0.731$ V ($\Delta E_p = 154$ mV) *versus* SCE, corresponding to the $[Co_{10}P_2(CO)_{23}H]^{2-/3-}$ couple. A second reduction occurs at −1.098 V; however, the return wave is significantly diminished, indicating an irreversible process. These features are sustained in repeated cycles, and remain essentially unchanged upon increasing the scan rate to 500 mV $s^{-1}$. At more positive potentials, no reversible oxidation chemistry occurs.

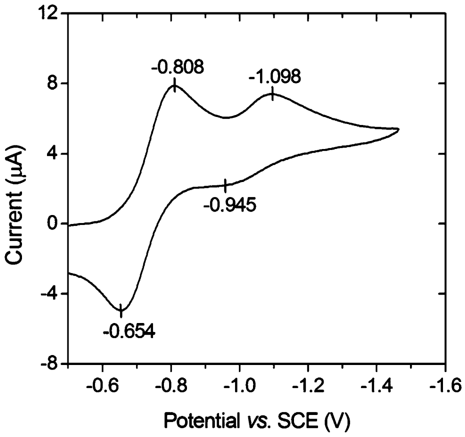

**Fig. 2** Cyclic voltammogram of **1** in acetonitrile, recorded at a platinum electrode with 0.1 M $Bu_4NPF_6$ as the electrolyte. The scan rate was 100 mV $s^{-1}$, and ferrocene was used as an internal reference.

Magnetic susceptibility data for compound **1** were collected in the temperature range 5–295 K (see Fig. 3). These data were fit using the equation $\chi_M = C/(T - \theta) + \chi_0$, resulting in a Curie constant of $C = 0.38$ cm$^3$ K mol$^{-1}$, a Weiss constant of $\theta = -11$ K, and a temperature independent paramagnetism (TIP) parameter of $\chi_0 = 2480 \times 10^{-6}$ cm$^3$ mol$^{-1}$. A similar Curie–Weiss behaviour with $\theta$ of −11 K has been reported for $[Rh_5Ni_6(CO)_{21}H_x]^{3-}$.[10] The TIP term originates from the Van Vleck contribution associated with an energy gap between occupied and unoccupied states. As the cluster size increases, the energy gap decreases, leading to a larger TIP. The observed value falls into a reasonable range for high-nuclearity metal carbonyl clusters.[11] The effective magnetic moment of 1.74 $\mu_B$ calculated from $C$ indicates that one unpaired electron is delocalized over the cluster.

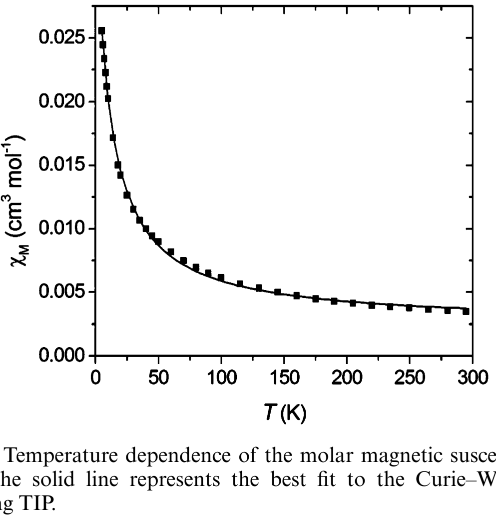

**Fig. 3** Temperature dependence of the molar magnetic susceptibility of **1**. The solid line represents the best fit to the Curie–Weiss law including TIP.

The EPR spectra of a solution of **1** in acetonitrile were recorded over the temperature range 4–50 K. As the temperature is lowered, the intensity of an isotropic singlet with $g = 2.05$ grows; analogous spectra have been observed for C-centered cobalt carbonyl clusters bearing one unpaired electron.[12] No hyperfine structure associated with coupling to the Co ($I = 7/2$) or P ($I = 1/2$) atoms is evident in the spectra. Thus, both the magnetic moment and the EPR data are indicative of an $S = 1/2$ ground state, which is most reasonably reconciled by assuming the presence of a single hydride ligand in the cluster.[10,13]

In summary, the synthesis of the first sizable cobalt carbonyl cluster incorporating two phosphorus atoms has been accomplished. The semi-interstitial nature of these phosphorus centers suggests the possibility of adding four more cobalt atoms to generate a peanut-like cluster, in which two monocapped square antiprisms are fused through a square face. Ultimately, it is hoped that significantly greater cobalt cluster nuclearities can be achieved, leading to higher-spin molecules.

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## Notes and references

† Elemental analysis of **1**: $C_{39}H_{41}Co_{10}N_2O_{23}P_2$: Calc.: C, 30.0; H, 2.65; N, 1.80. Found: C, 29.79; H, 2.65; N, 1.82. IR: $\nu_{max}$/cm$^{-1}$ (MeCN) 2062w (CO), 2023vs (CO), 2014s (CO), 2007s (CO), 1971mw (CO), 1802w (CO). UV-vis: $\lambda_{max}$/nm (MeCN) 206 ($\varepsilon$/l mol$^{-1}$ cm$^{-1}$ 1080000), 255 (169000), 330 (sh, 36400), 450 (sh, 15800), 600 (740), 710 (570). ES$^+$-MS: (MeCN) *m*/*z* 578 ($[\mathbf{1} - 2Et_4N - 5CO]^{2-}$).

‡ Crystallographic data of **1**: $C_{39}H_{41}Co_{10}N_2O_{23}P_2$: $M = 1556.98$, triclinic, space group $P\bar{1}$, $a = 10.0788(2)$, $b = 11.8610(4)$, $c = 22.9170(8)$ Å, $\alpha = 82.243(1)$, $\beta = 79.064(1)$, $\gamma = 86.405(1)$°, $V = 2663.30(14)$ Å$^3$, $T = 155$ K, $Z = 2$, $\mu$(Mo-K$\alpha$) = 3.168 mm$^{-1}$, 13547 reflections collected, 8563 unique ($R_{int} = 0.0462$). Refinement on $F^2$ gave $R_1 = 0.0445$ [8562 data with $I > 2\sigma(I)$] and $wR_2 = 0.1160$ (all data). CCDC reference number 205220. See http://www.rsc.org/suppdata/dt/b3/b302383d/ for crystallographic data in CIF or other electronic format.

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