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Received May 25, 1976

Synthesis and Structural Characterization of a New Type of Metal Cluster System, $Ni_8(CO)_8(\mu_4\text{-}PC_6H_5)_6$, Containing a Completely Bonding Metal Cube. A Transition Metal Analogue of Cubane, C_8H_8

Sir:

We wish to report the preparation and structural analysis of $Ni_8(CO)_8(\mu_4\text{-}PC_6H_5)_6$ which not only establishes the completely bonding metal cube as a basic structural unit in transition metal chemistry but also provides the first example of a $M_8L_8(\mu_4\text{-}X)_6$ type of metal cluster system. This work was a result of systematic studies designed to produce new transition metal cluster systems (with different MO electronic configurations) containing bridging main group ligands from the preformed metal cluster $[Ni_3(CO)_3(\mu_2\text{-}CO)_3]_n{}^{2-}$ ($n = 2$,[1] 3[2]) and $[Pt_3(CO)_3(\mu_2\text{-}CO)_3]_n{}^{2-}$ ($n = 2, 3, 4, 5$)[3] dianions.

The synthesis of $Ni_8(CO)_8(\mu_2\text{-}PC_6H_5)_6$ was accomplished by the addition of 0.28 g (1.6 mmol) of $C_6H_5PCl_2$ to a suspension of 0.85 g (1.0 mmol) of $[NMe_4]_2[Ni_3(CO)_3(\mu_2\text{-}CO)_3]_2$ in 40 ml of dry THF.[4] The mixture immediately changed from a bright orange-red to a deep purple color. After 1.5 h of stirring under N_2, the solvent was removed under vacuum and the residue washed three times with 15-ml portions of hexane. About 75 mg (ca. 20% yield based on P) of black plate-like crystals of $Ni_8(CO)_8(\mu_4\text{-}PC_6H_5)_6$ were separated by the slow diffusion of heptane into a saturated toluene solution. Dark-red octahedral-shaped crystals of another compound also were isolated, but their unstable nature (as well as small yield) has prevented adequate characterization to date. Attempts to separate the compounds by elution from a silica gel column were unsuccessful due to extensive decomposition. The infrared spectrum for $Ni_8(CO)_8(\mu_4\text{-}PC_6H_5)_6$ in CS_2 exhibited a very sharp carbonyl stretching frequency at 2020 cm^{-1}. Its proton NMR spectrum (JEOL MH-100) in CS_2 (with Me_4Si as internal standard) showed sharp resonances characteristic of a diamagnetic compound with overlapping phenyl resonances centered at δ 7.5.

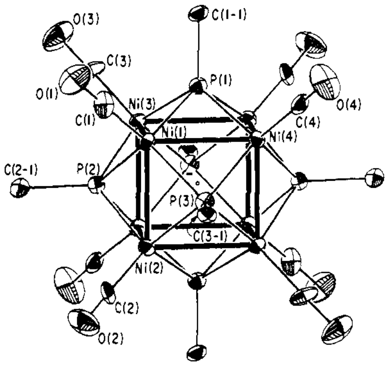

Figure 1. View of the $Ni_8(CO)_8(\mu_4\text{-}PC_6H_5)_6$ fragment of the phenylphosphido-bridged molecule. All atoms are represented by 25% thermal ellipsoids. The phenyl rings have been omitted for clarity. The entire molecule possesses crystallographic $C_i - \bar{1}$ symmetry, while the fragment ideally conforms to cubic O_h symmetry.

An x-ray structural determination[5,6] revealed the existence of $Ni_8(CO)_8(\mu_4\text{-}PC_6H_5)_6$ as a discrete molecule which with the neglect of the phenyl rings ideally conforms to cubic O_h symmetry, although an inversion center is the only crystallographically required molecular symmetry element. The molecular configuration (Figure 1) consists of a cube of nickel atoms with each square tetranickel face symmetrically capped by a phenylphosphido ligand. The additional coordination of one terminal carbonyl group, which is directed outward along one of the nickel cube's body-diagonals, results in a tetrahedral-like ligand environment of one carbonyl and three phosphorus atoms about each nickel atom. Each nickel atom then attains a noble-gas electronic configuration through a two-electron donation from the terminal carbonyl ligand, a one-electron donation from each of the three phenylphosphido ligands, and electron-pair Ni-Ni bonds with the three adjacent nickel atoms. This completely bonding (electron precise) homonuclear metal cube may be considered to be the first transition metal analogue of the C_8H_8 hydrocarbon[7] denoted as "cubane". Three octacopper cubane complexes, the $[Cu_8(i\text{-}MNT)_6]^{4-}$, $[Cu_8(DED)_6]^{4-}$, and $[Cu_8(DTS)_6]^{4-}$ tetraanions, have previously been found from structural analyses[8a-c] to possess a $[M_8(\mu_2 - X)_{12}]^{4-}$ type structure based upon a metal cube with edge-bridged X ligands. This geometry arises from the 12 sulfur atoms of the six bidentate sulfur ligands in each tetraanion being arranged in a distorted icosahedral array such that each Cu(I) is trigonally coordinated to three sulfur atoms from different ligands with a sulfur atom linked to two copper atoms along each of the 12 octacopper cube edges. Whereas a conformity to the EAN rule by each Cu(I) would effectively correspond to a two-thirds electron-pair Cu-Cu bond along each of the 12 cube edges, an alternative bonding model suggested from MO calculations[8d] involves no net Cu-Cu interactions.[9]

The Ni_8P_6 core in $Ni_8(CO)_8(\mu_4\text{-}PC_6H_5)_6$ may be viewed as the result of the interpenetration of a nonbonding P_6 octahedron by a bonding Ni_8 cube. The Ni atoms are ca. 2.6 Å apart, while the P···P distance along any of the three octahedral axes is 4.9 Å. The result is that each phosphorus atom lies approximately 1.1 Å out of its square Ni_4 face. This octametal-hexaligand architecture has a reciprocal structural relationship to the hexametal-octaligand $[Mo_6Cl_8]^{4+}$ type structure,[10] which may be viewed to evolve from a bonding

Mo_6 octahedron interpenetrating a nonbonding Cl_8 cube with the Mo–Mo and Cl···Cl distances being such that the molybdenum atoms project by only 0.1 Å outside the nonbonding Cl_8 cube.

Three other compounds, in addition to $Ni_8(CO)_8(\mu_4\text{-}PC_6H_5)_6$, are now known to possess pentacoordinate phosphorus or arsenic atoms bonded to four transition metal atoms. These are $Co_4(CO)_8(\mu_2\text{-}CO)_2(\mu_4\text{-}PC_6H_5)_2$,[11] its arsenic analogue $Co_4(CO)_8(\mu_2\text{-}CO)_2(\mu_4\text{-}AsC_6H_5)_2$,[12] and the $[Co_4(CO)_8(\mu_2\text{-}CO)(\mu_2\text{-}H)(\mu_4\text{-}PC_6H_5)_2]^-$ monoanion.[13] In each case, a square-pyramidal coordination is observed for either the phosphorus or arsenic atoms with four metals comprising the basal plane and with a phenyl ligand at the apex.

Prominent structural features for $Ni_8(CO)_8(\mu_4\text{-}PC_6H_5)_6$ include the following: (1) the electron-pair Ni–Ni distances vary from 2.636 (3) to 2.681 (3) Å[14] with the mean value of 2.648 Å being similar to the mean electron-pair Co–Co (unbridged) distance of 2.697(2) Å observed[11] in $Co_4(CO)_8(\mu_2\text{-}CO)_2(\mu_4\text{-}PC_6H_5)_2$; (2) the Ni–P distances range from 2.172 (5) to 2.192 (5) Å with the mean value of 2.183 Å being comparable with the mean value of 2.242 Å for the corresponding distances in $Co_4(CO)_8(\mu_2\text{-}CO)_2(\mu_4\text{-}PC_6H_5)_2$; (3) the P atoms lie ca. 1.1 Å out of their respective Ni_4 planes with Ni–P–Ni angles of range 74.1 (2)–76.1 (2)° and of mean value 75°. The corresponding mean Co–P–Co angle for the unbridged edges of $Co_4(CO)_8(\mu_2\text{-}CO)_2(\mu_4\text{-}PC_6H_5)_2$ is 74°; (4) the P–Ni–P bond angles are of range 103.4 (2)–105.7 (2)° and mean value 105°, while the P–Ni–CO bond angles are of range 107.6 (6)–121.9 (6)° and mean value 114°; (5) the four crystallographically independent carbonyl groups are nearly linear, with an Ni–C–O range of 171 (2)–179 (2)° (The Ni–C and C–O average distances of 1.78 and 1.14 Å, respectively, are in agreement with expected values.); (6) the mean P–C (phenyl) bond length of 1.81 (2) Å is identical with that found in $Co_4(CO)_8(\mu_2\text{-}CO)_2(\mu_4\text{-}PC_6H_5)_2$ and is consistent with the assignment of a single P–C bond; (7) all distances and bond angles within the three crystallographically independent phenyl rings are within experimental error of normal values. Consideration of interplanar angles indicates that two of the phenyl rings, $C_6H_5(1)$ and $C_6H_5(3)$, are only 15.5° away from being parallel to each other and that they both lie nearly in the P(1), P(3), P(1′), P(3′) plane. The third ring, $C_6H_5(2)$, lies approximately in the P(2), P(3), P(2′), P(3′) plane and is nearly pendicular to both $C_6H_5(1)$ and $C_6H_5(3)$.

The $Ni_8(CO)_8(\mu_4\text{-}PC_6H_5)_6$ molecule belongs to a relatively small class of organometallic complexes containing a nickel polyhedron. Other structurally analyzed systems include $Ni_4[P(C_2H_4CN)_3]_4(\mu_2\text{-}CO)_6$,[15a] $Ni_4[CNC(CH_3)_3]_7$,[15b] $Ni_4(CO)_4(CF_3C_2CF_3)_3$,[15c] the $[Ni_3(CO)_3(\mu_2\text{-}CO)_3]_2{}^{2-}$ dianion,[1a] the $[Ni_5(CO)_9(\mu_2\text{-}CO)_3]^{2-}$ dianion,[15d] and the $[Ni_3(CO)_3(\mu_2\text{-}CO)_3]_3{}^{2-}$ dianion.[2]

Work is presently underway to examine the physical and chemical properties of the $Ni_8(CO)_8(\mu_4\text{-}PC_6H_5)_6$ molecule and to attempt the preparation of related metal cluster systems.

Acknowledgments. We wish to thank the National Science Foundation (No. GP-19175X) for their financial support. The use of the UNIVAC 1110 computer at the Academic Computing Center, University of Wisconsin (Madison), was made available through partial support of the National Science Foundation and the Wisconsin Alumni Research Foundation administered through the University Research Committee.

Supplementary Material Available: A listing of atomic coordinates (3 pages). Ordering information is available on any current masthead page.

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Received March 29, 1976