The structures of bare and deuterated Co₁₉*

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Abstract

The structures of bare Co₁₉ and deuterated Co₁₉D_m clusters are examined by the chemical probe method, and earlier assignments of bare Co₁₉ as an fcc octahedron are reconsidered. New experimental measurements of the reactivity of Co₁₉ with ammonia, nitrogen, and deuterium are presented, and together with earlier measurements of the reactivity with water suggest that bare Co₁₉ has an hcp structure (D_{3h} symmetry). The adsorption of deuterium on Co₁₉ is found to proceed in steps, leading to successive saturation levels at Co₁₉D₄, Co₁₉D₁₄, and Co₁₉D₁₈. Using binding rules derived from earlier studies of larger cobalt and nickel clusters, possible D-atom binding sites on Co₁₉D_m (both fcc and hcp) are proposed.

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I. INTRODUCTION

In previous publications,^{1,2,3} we suggested that the Co_{19} cluster has the geometrical structure of an fcc octahedron. This was based primarily on the fact that Co_{19} saturates with the adsorption of six ammonia molecules at 20 °C, the assumption being that the molecules bind to each of the six apex atoms on the octahedron. As has previously been demonstrated,^{3,4,5} low-coordinate nickel or cobalt atoms are the preferred sites for adsorption of ammonia, water, or molecular nitrogen on small clusters, and the six apex atoms on the octahedron have a metal coordination of four compared to the other surface atoms which have a coordination of seven. In these earlier studies, however, the possibility of adsorbate-induced structural change was not addressed, and other structures consistent with the ammonia uptake data were not fully considered. In particular, a hexagonal-close-packed Co_{19} structure (D_{3h} symmetry)⁶ also has six apex atoms that could bind NH_3 molecules and result in saturation at the $\text{Co}_{19}(\text{NH}_3)_6$ level. In this paper we will reconsider the structure of Co_{19} and, in addition, discuss possible configurations of the deuterium atoms on the deuterated Co_{19}D_m species, based on new experimental observations.

II. EXPERIMENTAL RESULTS

Clusters are made by the pulsed-laser vaporization/inert gas condensation method and then pass into a flow-tube reactor (FTR) where various gaseous reagents can be added. After reacting for ~1 msec, the clusters exit through a nozzle at the end of the FTR, are formed into a molecular beam, and are transported to a laser-ionization reflectron time-of-flight mass spectrometer for detection. The cluster temperature

(i.e., the temperature of the FTR) can be varied from -160 to 150 °C. See Ref. 5(a) for further details of the experimental procedure.

In Fig. 1, the uptake of ammonia by Co_{19} as a function of ammonia pressure is shown at four temperatures of the FTR: 20, 50, 100, and 150 °C. The uptake is measured by the average number $\bar{m}$ of NH_3 molecules adsorbed on the cluster, determined from an intensity-weighted average of product peak heights in the mass spectra. The extended plateau at $\text{Co}_{19}(\text{NH}_3)_6$ at 20 °C becomes a change in slope at $\bar{m} = 6$ at 150 °C. Although at 150 °C saturation at $\text{Co}_{19}(\text{NH}_3)_6$ is not evident in the uptake data, the distribution of $\text{Co}_{19}(\text{NH}_3)_m^+$ peak intensities in the mass spectra clearly shows a significant decrease in the binding energy following the adsorption of six NH_3 molecules. Such a decrease suggests there are six primary NH_3 binding sites on the cluster.⁵ The uptake of ammonia at 150 °C, which occurs entirely under equilibrium conditions, shows no evidence for structural changes (i.e., no unusual distributions of the $\text{Co}_{19}(\text{NH}_3)_m^+$ peaks in the mass spectra) over the coverage range from the bare cluster to $\text{Co}_{19}(\text{NH}_3)_6$, suggesting that the adsorption of six NH_3 molecules does not induce a change from the structure of the bare Co_{19} cluster.⁷

Another molecule that has been successfully used to probe cluster structure is nitrogen.^{5,8} However, the binding of N_2 to cobalt clusters is quite weak,⁸ and very low temperatures must be used to saturate the clusters. At these temperatures, a number of cobalt clusters, including Co_{19} , have several isomers. This is illustrated in Fig. 2, where the adsorption of nitrogen on Co_{19} at -160 °C is shown at low nitrogen pressures. The bar plots give the intensities of the $\text{Co}_{19}(\text{N}_2)_m^+$ ion signals observed in the mass spectra for two nitrogen pressures. The adsorption of nitrogen at this low temperature and pressure is kinetically

controlled⁹ and results in a wide distribution of $\text{Co}_{19}(\text{N}_2)_m$ products for each isomer. However, the upper plot appears to show saturation of one isomer at the $\text{Co}_{19}(\text{N}_2)_6$ level, analogous to the saturation level for ammonia. The lower plot shows that at higher nitrogen pressures this isomer does indeed saturate at $m = 6$, but its reduced intensity relative to the other isomers indicates that N_2 adsorption is causing a conversion to isomers having a larger number of N_2 binding sites. Nevertheless, the apparent saturation at $\text{Co}_{19}(\text{N}_2)_6$ is consistent with N_2 molecules, like NH_3 molecules, preferring to bind to the low-coordinate apex sites on an fcc or hcp cluster.

Further evidence that Co_{19} is either fcc or hcp comes from a comparison of nitrogen binding strengths to other cobalt clusters. A previous study⁸ of the reaction of cobalt clusters with nitrogen showed that Co_6 , Co_{13} , Co_{19} , and Co_{20} bind nitrogen either very weakly or not at all. It was concluded that Co_{13} has either an fcc or hcp structure and that Co_6 is an octahedron, which can be considered part of either an fcc or hcp lattice. It thus appears generally true that cobalt clusters with fcc or hcp structures bind N_2 weakly compared to other structures. Since Co_{20} seems to have an even weaker bond for N_2 than does Co_{19} , we assume it also has either an fcc or hcp structure. In contrast, cobalt clusters with icosahedral structure appear to bind N_2 much more strongly. The experimental evidence⁸ suggests that Co_{13} converts at relatively low nitrogen coverages to an icosahedron, which appears to have the highest N_2 adsorption energy of any Co_n cluster studied.¹⁰

The reaction of cobalt clusters with D_2 also provides some structural information. Earlier studies¹¹ of the kinetics of the $\text{Co}_{19} + \text{D}_2 \rightarrow \text{Co}_{19}2\text{D}$ chemisorption reaction gave a linear rate plot¹² at 20 °C, which suggests that only a single Co_{19} isomer is present at room

temperature. At lower temperatures, however, the rate plots are nonlinear, indicating that more than one Co_{19} isomer is present in the FTR, a result consistent with the nitrogen reaction studies. The room temperature studies^{11,13} showed that Co_{19} and Co_{20} were particularly unreactive, with the Co_{20} rate constant being about 25% smaller than that of Co_{19} . We will return below to a discussion of the significance of this result.

As in the case of ammonia and nitrogen, the saturation of Co_{19} by deuterium has structural implications. In Fig. 3 we show three mass spectra resulting from the addition of deuterium to Co_{19} at -40°C and the D_2 pressures indicated. It is evident that deuterium coverage does not increase continuously with increasing deuterium pressure, but "jumps" from one level to another. Since these reactions are kinetically controlled, these results indicate that there are barriers to D_2 chemisorption, and that each level of coverage is the result of reactions with increasingly higher barriers. The three levels of saturation that are observed are Co_{19}D_4 , $\text{Co}_{19}\text{D}_{14}$, and $\text{Co}_{19}\text{D}_{18}$. D_2 adsorption above the $\text{Co}_{19}\text{D}_{18}$ level does occur, but additional levels of saturation are not apparent. Although adsorbate-induced structural changes in the Co_{19} cluster cannot be ruled out, such changes cannot be inferred from the bimodal distributions seen in Fig. 3 (e.g., a peak at Co_{19}^+ and $\text{Co}_{19}\text{D}_4^+$, but not at $\text{Co}_{19}\text{D}_2^+$), since these distributions reflect the kinetics of D_2 addition, not equilibrium conditions.¹⁴ It should be noted that since deuterium adds in units of D_2 , the observed saturation at Co_{19}D_4 , for example, is consistent with the presence of four or five binding sites.

III. DISCUSSION

The three levels of D_2 adsorption seen in Fig. 3 are consistent with either the fcc or hcp structure for Co_{19} if we assume the following D-atom binding rules: (1) D atoms do not bind to atop sites; (2) bridge and three-fold sites have roughly equivalent binding energies; (3) a triangular arrangement of three cobalt atoms can bind only one D atom, whether it be in a bridge or three-fold site; (4) two adjacent three-fold sites that share a common edge cannot simultaneously bind D atoms; and (5) all atoms on the cluster's surface other than the apex atoms can bind to up to three D atoms. These rules were derived in a recent study¹⁵ of D-atom binding to cobalt and nickel clusters in the 55-147 atom size range, where they successfully explained the observed deuterium saturation levels on closed-shell or closed-subshell icosahedral clusters. The rules are applied as follows to explain the $Co_{19}D_4$, $Co_{19}D_{14}$, and $Co_{19}D_{18}$ species. The first species has each cobalt atom in the cluster, other than the apex atoms, binding to only a single D atom. (This actually predicts a $Co_{19}D_5$ species, which as discussed above is not inconsistent with the experimental data.) The second has the maximum coverage possible with apex atoms binding to only a single D atom. The third has apex atoms binding to two D atoms. Likely D-atom configurations for these species are shown in Fig. 4 for the fcc and hcp structures. In the case of the fcc octahedron, the $Co_{19}D_5$ cluster corresponds to placing two D atoms in the centers of opposing faces of the octahedron (top and bottom in Fig. 4) and three additional D atoms on alternate bridge sites around the central hexagonal ring of atoms. For the $Co_{19}D_{14}$ cluster one D atom is in the center of each face of the octahedron and each apex atom has one bridging D atom. For $Co_{19}D_{18}$ the single atoms on the upper and lower close packed faces are replaced by sets of three atoms, such that all six apex atoms then bind to two D atoms. The configurations of D atoms on

the hcp clusters are determined in an analogous way.¹⁶ A possible alternate configuration for an fcc Co_{19}D_4 species would have four D atoms in the centers of four of the faces of the octahedron that do not share a common edge. As for Co_{19}D_5 , this configuration has each surface atom in the cluster other than the apex atoms binding to a single D atom.

While the observed deuterium saturation levels on Co_{19} point to fcc and hcp structures (they are inconsistent, for example, with the double icosahedral structure found for Ni_{19}), they cannot distinguish between them. Some additional analysis is needed for this. Both structures have the same number of nearest neighbor metal-metal interactions, i.e., the interactions within a close-packed plane and the interactions between adjacent planes. They differ in the secondary interactions between non-adjacent planes. In the hcp structure, the upper and lower close-packed triangular surfaces are more favorably oriented for interaction. For example, if some expansion of the upper and lower triangular faces occurs, the three pairs of apex atoms (see Fig. 4) can move closer together, increasing the net bonding between the atoms. Since such additional bonding cannot occur in the fcc structure, the hcp structure might be expected to have somewhat greater stability.

Experimental evidence against the fcc structure comes from a comparison of the chemical properties of Co_{19} with those of Co_{20} . Briefly summarized, these are that Co_{20} binds ammonia,¹⁷ nitrogen (as mentioned above), and water³ more weakly than Co_{19} , that Co_{19} has six clear primary ammonia binding sites while Co_{20} has no clear ammonia saturation level, and (as mentioned above) that Co_{20} has a rate constant for dissociative chemisorption of D_2 that is about 25% smaller than that of Co_{19} . To correlate these properties with structure we consider three possible structures, shown in Fig. 5, for Co_{20} , based on fcc and/or hcp

packing. These are: the hcp 19-atom cluster with an additional atom [shaded in Fig. 5(a)] added to one of the three four-fold sites; the fcc octahedron with an atom added to one face [Fig. 5(b)]; and a cluster derived from a 19-atom fcc tetrahedron by rearranging the four three-coordinate atoms to produce the largest number of metal-metal bonds [Fig. 5(c)].¹⁸ (The 20-atom tetrahedron itself is not considered likely since it has four fewer metal-metal bonds than the hcp structure. Also, it should provide four strong ammonia binding sites rather than the six sites observed experimentally.) Structure 5(b) is clearly inconsistent with the ammonia, nitrogen, and water binding results, since the shaded atom is only three-coordinate and should bind these reagents more strongly than any atom in the fcc octahedron. Also this structure should have a clear ammonia saturation at $m = 7$, which is not seen. The 5(c) structure has the same number of nearest neighbor metal-metal bonds as 5(a), and has a single four-coordinate atom on its surface [the shaded atom in Fig. 5(c)]. Since the fcc octahedron has six four-coordinate atoms, a decrease in the adsorption of ammonia, nitrogen and water would be expected for 5(c). However, this sequence, octahedron $\rightarrow$ 5(c), is inconsistent with the deuterium reactivity results. Calculations by Jellinek¹⁹ on Ni_{13} in both fcc and hcp structures have shown that D_2 dissociates more readily on four-fold sites than on three-fold sites. Since the octahedron has no four-fold sites, and 5(c) has two, an increase in D_2 reactivity would be expected, rather than the decrease that is seen. In fact, if we assume that the three four-fold sites on the Co_{19} hcp cluster are the active sites for D_2 chemisorption, then adding a 20th Co atom to one of these sites to form 5(a) would be expected to cause a roughly 1/3 reduction in the rate of D_2 chemisorption. This is certainly within experimental error of the measured 25% decrease. The hcp Co_{20} cluster

formed in this way would also be expected to have a reduced capacity for equilibrium adsorption of ammonia, nitrogen or water at low coverage, since the number of four-coordinate atoms on the cluster is reduced from six for hcp Co_{19} to five for Co_{20} . Thus, the most likely sequence is a conversion from hcp Co_{19} to the hcp Co_{20} structure of Fig. 5(a). The structure of the deuterated Co_{19} cluster can be either fcc or hcp, since either structure is consistent with the observed pattern of D_2 uptake.

The analysis presented here is an attempt to correlate the experimental observations with reasonable assumptions about cluster structure. The apparent existence of additional structures below room temperature suggests that there may be several Co_{19} isomers of comparable energy at low temperatures. These probably include the three structures in Fig. 5 (without the darkly shaded atoms) as well as the double icosahedron. An accurate theoretical determination of the temperature dependence of Co_{19} free energies does not currently appear feasible, so experimental probes of cluster structure are important. Any theoretical modeling must accurately take into account directional bonding between the atoms in the cluster. Such bonding is probably more important for cobalt than for nickel, due to the increased influence of the d orbitals. Indeed, the change from the double icosahedron for Ni_{19} to the hcp structure for Co_{19} is most likely a consequence of this increase in the directional character of the metal-metal bonds. The challenge for theory is to accurately account for these effects.

¹S.J. Riley and E.K. Parks, in *Physics and Chemistry of Finite Systems: From Clusters to Crystals*, Vol. I, edited by P. Jena et al. (Kluwer, Dordrecht, 1992), p. 19.

²E.K. Parks, B.J. Winter, T.D. Klots, and S.J. Riley, *J. Chem. Phys.* **96**, 8267 (1992).

³E.K. Parks, T.D. Klots, B.J. Winter, and S.J. Riley, *J. Chem. Phys.* **99**, 5831 (1993).

⁴E.K. Parks, B.J. Winter, T.D. Klots, and S.J. Riley, *J. Chem. Phys.* **94**, 1882 (1991).

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- ⁶The hcp Co₁₉ cluster can be obtained from the octahedron by rotating one of the outer close-packed triangular surfaces by 60°.
- ⁷The additional adsorption above the Co₁₉(NH₃)₆ level can, in principle, be due to the binding of ammonia to weaker sites on the Co₁₉(NH₃)₆ cluster. However, for all four temperatures shown in Fig. 1 the mass spectra reveal that at coverages above the Co₁₉(NH₃)₆ level the adsorption of ammonia induces a change in the cluster's structure to one with a larger number of NH₃ binding sites; see Ref. (2) for results at 20 °C.
- ⁸J. Ho, E.K. Parks, L. Zhu, and S.J. Riley, *Chem. Phys.* (in press).
- ⁹In this temperature and pressure region, molecules adsorb, but do not desorb during the time the clusters spend in the FTR. Thus, the distribution of products is determined by the *number* of cluster-molecule collisions, rather than the thermodynamics of the adsorption process. A bar plot is shown for the Co₁₉(N₂)_m⁺ ion signal due to peak congestion in the mass spectra.
- ¹⁰The bare Ni₁₃ and Ni₁₉ clusters, whose structures are the icosahedron and double icosahedron, respectively (see Ref. 5), also show the strongest N₂ adsorption of all nickel clusters studied.
- ¹¹J. Ho, L. Zhu, E.K. Parks, and S.J. Riley, *J. Chem. Phys.* **99**, 140 (1993).
- ¹²On a rate plot, the logarithm of the bare cluster ion signal is plotted vs the deuterium pressure in the FTR. A linear rate plot implies that a single isomer is present in the FTR or that several isomers are present that rapidly interconvert. The latter possibility can only occur if the two isomers have close lying free energies and there are no significant barriers to structural interconversion.
- ¹³J. Ho, L. Zhu, E. K. Parks, and S. J. Riley, *Z. Phys. D*, **26**, 331 (1993).
- ¹⁴Bimodal distributions under equilibrium conditions usually imply that the adsorbed species is inducing a change in structure.
- ¹⁵E.K. Parks, G.C. Nieman, and S.J. Riley, *Surf. Sci.* (submitted)
- ¹⁶In the case of the hcp Co₁₉D₅ structure, an alternate possibility to the configuration shown in Fig. 4 is to place the three atoms around the central close-packed plane in the three elongated four-fold sites
- ¹⁷A comparison of the ammonia uptake plots for Co₁₉ and Co₂₀ at 100 and 150 °C and low ammonia pressure shows lower coverages for Co₂₀ than for Co₁₉; unpublished results from this laboratory.
- ¹⁸The 19-atom cluster that would result from removing the shaded atom in Fig. 5(c) is not considered a likely candidate for Co₁₉ since it would not have six primary ammonia binding sites.
- ¹⁹J. Jellinek and Z. B. Güvenç in *Physics and Chemistry of Finite Systems; From Clusters to Crystals*, Vol. I, edited by P. Jena et al. (Kluwer, Dordrecht, 1992), p. 405.

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Figure Captions

- Fig. 1 Ammonia uptake plots for Co_{19} at four temperatures of the flow-tube reactor.
- Fig. 2 Bar plots of the intensity of $\text{Co}_{19}(\text{N}_2)_m^+$ peaks in the mass spectra at two nitrogen pressures with the flow-tube reactor at -160°C .
- Fig. 3 Mass spectra of $\text{Co}_{19}\text{D}_m^+$ at three deuterium pressures with the flow-tube reactor at -40°C .
- Fig. 4 Configurations of D atoms (black circles) on fcc and hcp Co_{19} that are consistent with the Co_{19}D_m saturation levels observed experimentally.
- Fig. 5 Three possible structures for Co_{20} obtained by adding a single Co atom (dark shading) to the symmetrical Co_{19} structures.

$\text{Co}_{19}\text{D}_m^+$

-40 °C

Fig. 3

fcc

Co_{19}D_5

$\text{Co}_{19}\text{D}_{14}$

$\text{Co}_{19}\text{D}_{18}$

hcp