COORDINATION CHEMISTRY OF METAL SURFACES AND METAL COMPLEXES

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Abstract - The coordination chemistry of two isomeric molecules, acetonitrile
and methyl isocyanide, has been characterized for (A) single crystal nickel
surfaces as a function of crystallography and surface composition, (B) nickel
catalyst surfaces and (C) molecular mononuclear and polynuclear metal complexes.
Conditions have been established for the catalytic isomerization of methyl
isocyanide to acetonitrile within these nickel surface and molecular complex
regimes. A comparison is made of the acetonitrile and methyl isocyanide chem-
istry between the surface and molecular complex areas.

INTRODUCTION

Our research addresses the intimate structural and stereochemical features of the inter-
actions and reactions of molecules with metal atoms constrained at the surfaces of metals
and within molecular mononuclear and polynuclear metal complexes (1,2). I believe that
there is a fundamental set of coordination chemistry principles applicable to all metal
complex and all metal chemistry; there should be no discontinuities in the applicability of
the principles. Certainly, differences in features of the chemistry must be present as the
regimes of surface chemistry, molecular metal cluster chemistry and molecular mononuclear
metal chemistry are traversed but the differences should be explicable in terms of state
differences such as differences in nuclearity, metal atom coordination number and degree of
coordination saturation (1). We have sought an experimental characterization of the
similarities and differences of the chemistry within these regimes--and an understanding
of these similarities and of the differences.

I describe here the results from a study of the metal atom chemistry of two isomeric mole-
cules, acetonitrile and methyl isocyanide, with respect to (A) metal surfaces of well defined
crystallography and composition, (B) metal catalysts and (C) metal clusters and mononuclear
metal complexes. First described is the acetonitrile and methyl isocyanide coordination
chemistry of metal single crystals under ultrahigh vacuum conditions whereby the crystal-
lographic and surface compositional effects on chemistry can be precisely established.
Secondly, the chemistry of these isomeric molecules on "real" surfaces of less well defined
crystallography and composition is described. Finally, the structural, stereochemical and
chemical features of the two isomeric molecules on surfaces are compared with established
features of molecular metal acetonitrile and methyl isocyanide complexes. To this point,
the characterized metal chemistry is that of nickel and platinum. The catalytic isomeriza-
tion of methyl isocyanide to acetonitrile on nickel surfaces is defined in terms of requisite
crystallographic and compositional features of the surface.

EXPERIMENTAL

All studies with metal single crystals were performed in a Varian bakeable, ultrahigh vacuum
chamber, with a base pressure of 10^{-10} to 10^{-11} torr. The chamber was equipped with low-
energy electron diffraction, retarding-field Auger electron spectroscopy and a quadrupole
mass spectrometer (with the capability to scan and store data from different mass ion
currents in rapid succession) accessories. Platinum and nickel single crystals were spark-
cut from single crystal rods, oriented by Laue back X-ray reflections, polished and then
cleaned by oxygen and by ion sputtering. Platinum crystals after high temperature O_2
treatments were cleaned with acid to remove calcium impurities. The nickel and platinum
crystals after cleaning were free of the common impurities of C, S, Ca, O and P as judged
by Auger electron spectroscopy. Controlled introduction of carbon atoms on the nickel
surface was by treatment of the crystal with either benzene or methyl isocyanide at elevated
temperatures. Nickel and platinum crystal blanks with the front face (only) covered with a
gold microcrystalline layer (~0.0002 inches thick) were prepared by procedures described
elsewhere (3,4). Experiments with "real" surfaces at low or ambient pressures included Raney

nickel, nickel from hydrogen reduction of nickel oxide, nickel foil and a nickel(111) surface (with the sides and back covered with gold--only the (111) surface was exposed). Isomerization of methyl cyanide to acetonitrile was quantitatively assessed by gas chromatographic analysis. Blank experiments for the catalytic isomerization employed quartz fragments; no significant isomerization was observed up to temperatures of ~300°C in the blank experiments.

Mononuclear and polynuclear nickel and platinum complexes were prepared by standard procedures (5,6).

RESULTS AND DISCUSSION

Ultrahigh vacuum studies of nickel and platinum single crystals (4)

Acetonitrile chemisorption on nickel(111) is primarily a reversible process; the majority of acetonitrile molecules chemisorbed on this initially clean nickel surface desorbed with a maximum at ~85-90°C. Some irreversible decomposition (<5%) occurred as evidenced by Auger spectroscopic analysis of the surface following the thermal desorption experiment whereby the presence of nitrogen and carbon were established. At 20°C, a significant fraction of the acetonitrile molecules chemisorbed on the Ni(111) surface was ordered. Low-energy electron diffraction experiments showed a well defined 2x2 chemisorbed layer, a unit cell twice the size of the (111) metal surface unit cell and rotationally in correspondence of the surface metal atom unit cell (7). The simplest interpretation of the diffraction data is that there is coordination of the acetonitrile nitrogen atom to every other nickel atom with the CN vector normal or nearly normal to the metal surface. This orientation of the acetonitrile molecule with the CH₃ group maximally distal to the surface nickel atoms is consistent with the nearly complete thermal reversibility of the chemisorption process (7).

The presence of carbon on the nickel(111) surface did not significantly alter the acetonitrile chemistry; the only detectable difference was an apparent decrease in the sticking coefficient and a decrease in the saturation coverage with increasing surface carbon contamination. With increase in carbon surface concentration, there was no change in the temperature maximum for the acetonitrile thermal desorption process. Also, this chemistry was nondetectably altered in going from the (111) close-packed surface to the stepped 9(111)x(111) surface. Only a minor difference was detected in the acetonitrile chemistry between the (111) surface and a stepped and kinked 7(111)x(310) surface; the extent of reversibility on the more irregular surface seemed to be slightly lower than on the close-packed surface. In any case, the thermal desorption temperature maximum did not shift from 85-90°C in going from the close-packed surface to the stepped and kinked surface.

Chemisorption of acetonitrile was defined as a molecular or nondissociative process by labeling experiments. Chemisorption of a mixture of CD₃CN and CH₃C¹⁵N yielded in the thermal desorption experiment only these two labeled molecules. No cross-labeled molecules were detected by mass spectrometric analysis of the desorbed molecules. Thus, no reversible C-H, C-N or C-C bond breaking (assuming mobility for molecular fragments) occurred for chemisorbed acetonitrile on nickel within the time scale (minutes) and the temperature range of 20-90°C of these experiments. Chemisorption of acetonitrile on the Pt(111) surface was quite analogous to the nickel surface chemistry (8). In this case, the thermal desorption temperature was similar ~80-90°C; however, the sticking coefficient and coverage at saturation was much lower than for nickel. Polycrystalline gold was virtually identical to the Pt(111) surface in behavior toward acetonitrile except that the sticking coefficient was lower still.

Methyl isocyanide was much more strongly bound on the nickel surfaces than was acetonitrile as evidenced by a very high sticking coefficient and by an essentially complete thermal irreversibility of the chemisorption process from the close-packed (111) surface and also the stepped 9(111)x(111) and stepped-kinked 7(111)x(310) surfaces. Attempted thermal desorption of methyl isocyanide from the close-packed surface led to a trace desorption of a molecule of mass 41 (CH₃NC or CH₃CN) at 90°C, major hydrogen (H₂) desorption beginning at ~100°C, and nitrogen (N₂) desorption above 500°C. However, this methyl isocyanide chemistry was very sensitive to surface composition. Sulfur contamination did not perceptably affect the CH₃NC surface chemistry but the presence of surface carbon atoms dramatically affected the chemistry. Carbon surface atoms derived from either benzene or CH₃NC totally altered the surface behavior of methyl isocyanide. In the presence of surface carbon atoms (0.05 to 0.30 of a monolayer), the thermal behavior of CH₃NC changed to a reversible process with desorption of molecules of mass 41 (CH₃NC or CH₃CN) for both the (111) and 9(111)x(111) surfaces. Mass spectrometry cannot distinguish between CH₃NC or CH₃CN but for reasons discussed below the molecules released in the thermal desorption process are believed to be acetonitrile. Firstly, the desorption temperature for the close-packed or stepped Ni-C-CH₃NC surface is 85-90°C which is the desorption temperature for the CH₃CN molecule from either the clean or carbon contaminated nickel surfaces (Note a). For desorption of

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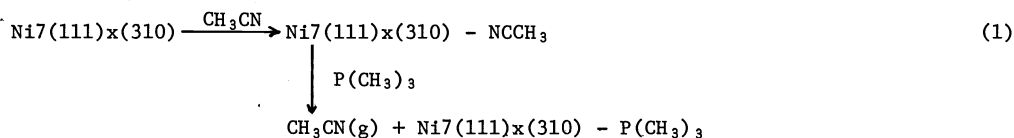Note a: Ni(111), Ni9(111)x(111), and Ni7(111)x(310).

the CH₃NC molecule to occur at this same temperature as for CH₃CN would be more than an unusual coincidence since it would be a very low desorption temperature in a relative (to CH₃CN) sense. We expect CH₃NC to be much more strongly bound than CH₃CN on these metal surfaces; and, in fact, the thermal desorption maxima for CH₃CN and CH₃NC on Pt(111) differ significantly and, respectively, are ~80-90 and ~170°C (8). Secondly, the catalytic isomerization of CH₃NC to CH₃CN on a nickel surface has been established (see below).

The isomerization reaction on the nickel surfaces is intramolecular as shown by the absence of cross-labeled molecules in the thermal desorption experiment with Ni(111)-C-CD₃NC-CH₃N¹³C. Surface carbon atoms were not exchanged with CH₃NC in the isomerization and thermal desorption processes: Acetonitrile evolved in the thermal desorption experiment from Ni(111)-¹³C-CH₃NC had not detectably incorporated ¹³C from surface ¹³C carbon atoms.

Thermal desorption experiments with methyl isocyanide from the carbon contaminated stepped-kinked Ni7(111)x(310)-C surface was substantially different from the close-packed and stepped Ni-C surfaces. A large desorption maximum for mass 41 at 85-90°C was again present but there was a smaller though substantial second maximum at ~150°C. Clearly, the presence of kink sites (although low in concentration) did alter the behavior on the carbon containing nickel surface. The first and obvious question is "Which molecule desorbs in the 150°C range?". This question could not be answered in a rigorous fashion but for reasons discussed in the following section the desorbing molecules in the 150°C range are believed to be the isomerized species, acetonitrile. Both the 85-90°C and 150°C processes were fully molecular and intramolecular in character. The molecules released thermally from a Ni7(111)x(310)-C-CD₃NC-CH₃N¹³C surface were only CD₃CN and CH₃¹³CN; no significant degree of reversible C-H, C-C or C-N bond breaking process occurred between 25°C and the 90 and 150°C desorption temperatures (again assuming mobility for any molecular fragment).

Finally, we note that trimethylphosphine, (CH₃)₃P, a molecule that is very strongly bound to the nickel surface readily displaced acetonitrile from the nickel surfaces (equation 1) but

$$\text{Ni7(111)x(310)} \xrightarrow{\text{CH}_3\text{CN}} \text{Ni7(111)x(310)} - \text{NCCH}_3 \tag{1}$$

$$\downarrow \text{P(CH}_3)_3$$

$$\text{CH}_3\text{CN(g)} + \text{Ni7(111)x(310)} - \text{P(CH}_3)_3$$

did not displace CH₃NC from either the clean or carbon containing nickel surfaces. Thus, CH₃NC does not isomerize on chemisorption on the Ni-C surfaces at 25°C but at some higher temperature, somewhere between 25 and 90°C.

Catalytic isomerization of methyl isocyanide

When liquid methyl isocyanide was heated in a sealed vessel and in contact with nickel metal, no isomerization was observed up to 180°C and isocyanide was nearly quantitatively recovered. In all these instances, there was darkening of the nickel surface suggestive of a polymerization of the isocyanide on the surface. In sharp contrast, with passage of the isocyanide at short contact times through a bed of high surface area nickel metal, e.g., Raney nickel, isomerization proceeded smoothly at 150-200°C without discoloration of the nickel surface. Thirty percent conversions per pass at ~1 mm pressure were observed at ~180°C. Substitution of the metal by finely divided quartz particles gave an inert system--inert to ~280°C. Hence, nickel metal does catalyze the isomerization of methyl isocyanide to acetonitrile. However, we were unsuccessful in effecting catalytic isomerization with nickel at temperatures of 90-100°C--the temperature that methyl isocyanide desorbs from a nickel surface to give acetonitrile. Apparent temperature differences between the ultrahigh vacuum experiments and the catalyst experiments may only reflect differences that arise from the very short contact times necessarily used in the catalytic experiment in order to minimize surface polymerization reactions. Surface oxygen contamination appears to have a deleterious effect on the isomerization process (ultrahigh vacuum studies are in progress to establish precisely the role of oxygen in this nickel surface chemistry). Nickel foil (acid etched before use) and nickel metal obtained by hydrogen reduction of the oxide both contained substantial surface oxygen and both were inactive as catalysts for the isocyanide isomerization reaction up to 200°C.
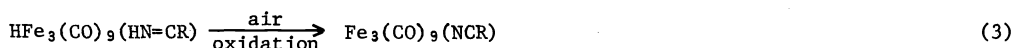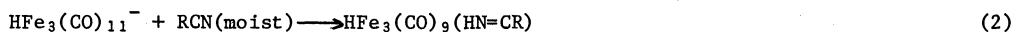

Molecular cluster acetonitrile and alkyl isocyanide chemistry

Acetonitrile is typically a weak field ligand in transition metal chemistry. This invariably is the case for mononuclear metal complexes and these complexes, like W(CO)₃(NCCH₃), are excellent synthesis intermediates because of the ready dissociation of the acetonitrile ligand. Such chemistry also prevails for molecular metal clusters with but one exception which is discussed below. Generally, acetonitrile is a weaker ligand than carbon monoxide in molecular zerovalent or low-valent metal complex chemistry. In this thermochemical context, there is a precise correspondence between the nickel and platinum surface chemistry

and molecular metal coordination chemistry. Acetonitrile is quantitatively displaced from
the nickel and platinum surfaces by carbon monoxide.

The mode of acetonitrile (or any alkyl cyanide) bonding to transition metals in mononuclear
or polynuclear complexes, with one exception, simply comprises a σ bond between the nitrile
nitrogen atom and a single metal atom (9). Although side, π bonding of nitriles has been
been claimed, none is structurally established for acetonitrile or a simple alkyl isocyanide
(9). Unlike carbon monoxide, acetonitrile is not known to form two electron bridge bonds
between two or three metal atoms. Thus, it is tempting to characterize, by analogy, the
acetonitrile chemisorption state on Ni(111) and Pt(111) as nitrogen direct bonding to single
metal atoms. However, these surface states represent coordinately unsaturated states whereas
all known molecular cluster-acetonitrile complexes are coordinately saturated; hence, there
is a reasonable probability that for Ni(111)-NCCH$_3$ and Pt(111)-NCCH$_3$ the nitrogen atom lies
in a three-fold site and interacts with three metal atoms. Nonetheless, none of the avail-
able data is consistent with a bonding of both the nitrile nitrogen and carbon atoms to
surface metal atoms; the acetonitrile CN vector must be nearly normal to the nickel and
platinum surfaces.

The one exceptional case of a nitrile in which the nitrogen and carbon atoms are bonded to
several metal atoms is the molecular metal cluster Fe$_3$(CO)$_9$(NC-n-C$_3$H$_7$) (10). Interestingly,
this cluster has not been prepared directly from the nitrile but by an indirect two-step
synthesis outlined in equations 2 and 3 below:

$$HFe_3(CO)_{11}^- + RCN(moist) \longrightarrow HFe_3(CO)_9(HN=CR) \qquad (2)$$

$$HFe_3(CO)_9(HN=CR) \xrightarrow[\text{oxidation}]{\text{air}} Fe_3(CO)_9(NCR) \qquad (3)$$

This structurally defined cluster (10) has the nitrogen and carbon atoms bound to the iron
triangle as shown in 1. It will be interesting to compare the chemistry of acetonitrile on

C-N	1.26Å
^{2}Fe-C	2.08Å
^{2}Fe-N	1.97Å
^{1}Fe-N	1.80Å

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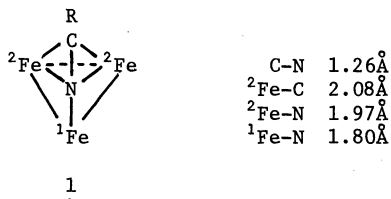
the Ni(111) surface with the Fe(111) surface--a study now in progress in our laboratories.

Alkyl isocyanides are relatively strong field ligands in transition metal chemistry; the
molecules are both good σ donor and π acceptor ligands and typically the isocyanides readily
displace carbon monoxide from mononuclear or polynuclear metal carbonyl complexes. Since
methyl isocyanide is strongly bound on both the Ni(111) and Pt(111) surfaces, the thermo-
chemical features of CH$_3$CN and CH$_3$NC chemisorption on these surfaces are fully analogous to
that of molecular coordination compounds. Available surface data do not define the stereo-
chemical character of methyl isocyanide bonding to the nickel and platinum surfaces. In
molecular cluster chemistry, alkyl isocyanide binding is established for two electron-two
center carbon-metal interactions, 2, and for two electron-three center metal-carbon-metal
bridging interactions, 3, as in Pt$_3$(CNR)$_6$ (11). In addition, there is one example of an

M-CNR

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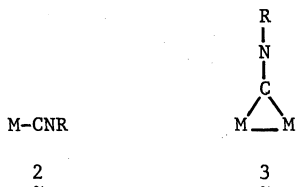
alkyl isocyanide ligand bound through both the carbon and nitrogen atoms to three metal
atoms. In Ni$_4$[CNC(CH$_3$)$_3$]$_7$, three of the isocyanide ligands are bridging ligands about the
enlarged face of the compressed nickel tetrahedron as shown in Fig. 1 (12). This type of
multicenter and multielectron binding of the isocyanide ligand, or one very similar to it,
is probably the mode of binding for methyl isocyanide on the Ni(111) surface. The irrevers-
ible character of the binding of methyl isocyanide on the nickel surface in contrast to the
weak and thermally reversible chemisorption of acetonitrile on nickel is partially ascribed
to the stronger binding of the isocyanide but the key factor is probably the stereochemical
feature that places the NC vector more or less parallel to the surface to bring the methyl
hydrogen atoms in close proximity to the surface nickel atoms thereby facilitating
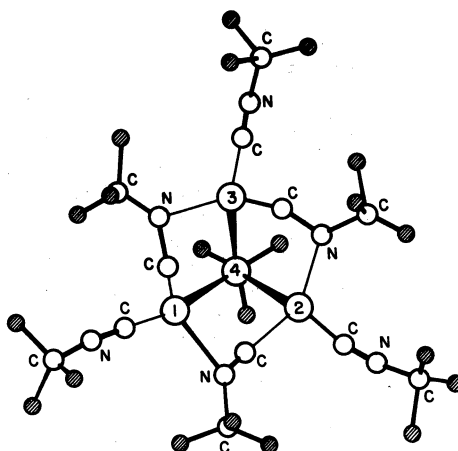
Fig. 1. A representation of the structure of $Ni_4[CNC(CH_3)_3]_7$ is viewed here along the three-fold axis of the compressed Ni_4 tetrahedron. The unique apical nickel atom is labeled 4, and the basal nickel atoms are numbered 1 through 3. The three isocyanide ligands that bridge the basal edges of the tetrahedron are effectively four-electron donors whereas the four terminally bound isocyanide ligands are two-electron donors. Because there was a disorder in the crystal used in the crystallographic study, a precise characterization of the unique bridging isocyanide ligand atom positions was not feasible. The apical to basal nickel-nickel distances are very short, ~2.34Å. Hydrogen atoms of the tert-butyl groups are not depicted.

irreversible C-H bond breaking processes. Contrasts in the CH_3 group position for CH_3CN and CH_3NC chemisorption states on nickel are depicted in Fig. 2.
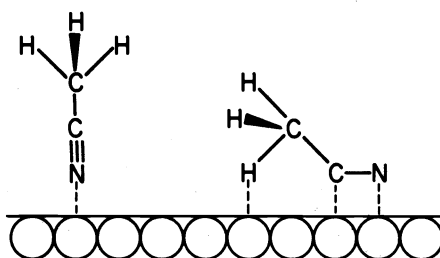
SURFACE BONDING

Fig. 2. To the left is a representation of the probable orientation of acetonitrile molecules bound to a nickel or platinum (111) surface--note the relatively large distance between the methyl group hydrogen atoms and the nickel surface atoms. To the right is a formal representation of the μ_2-binding of methyl isocyanide on the nickel(111) surface whereby the methyl group hydrogen atoms closely approach the surface nickel atoms.

The role of carbon atoms in transforming the nickel surface chemistry of methyl isocyanide from a tightly bonded and thermally irreversible state to one in which isomerization and thermal liberation of the isomer acetonitrile prevails cannot be delineated on a molecular basis with the available data. Nevertheless, the profound affect of the carbon atoms at low coverages, 0.05 to 0.25 of a monolayer, suggests that it is not short range or steric but long range and electronic in character. No such specific alteration in molecular coordination chemistry of CH_3NC has been reported.

Vibrational (high resolution electron energy loss spectroscopy) studies of the CH_3CN and CH_3NC chemisorption states on nickel surfaces, now planned for investigations as a function of temperature, crystallography, and surface composition, may resolve some of the stereochemical features of this surface chemistry.

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