Inorg. Chem. **1989**, *28*, 2022–2024

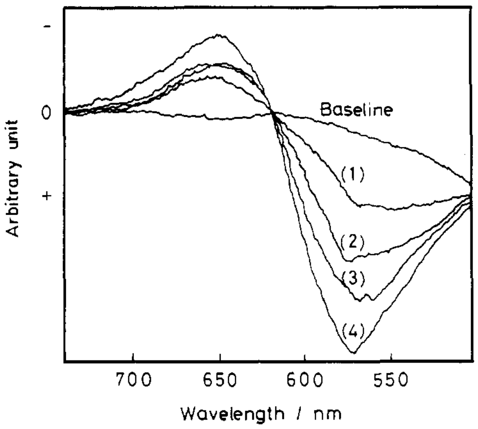

Figure 3. CD spectral changes in the course of the photoreduction of $Co(acac)_3$ at various conversions: (1) 13%; (2) 23%; (3) 31%; (4) 40%.

with detection of acetaldehyde as its hydrazone derivative from the reaction mixtures by the use of (2,4-dinitrophenyl)hydrazine.[9] Turnover numbers (converted mol of Co^{III}/mol of catalyst) achieved were 38.6 and 30.0 for Δ- and Λ-$Co(acac)_3$, respectively, after 1 h, indicating also that the reaction proceeded catalytically.[10]

The photochemical reactions obeyed the pseudo-first-order kinetics as shown in Figure 2, which depicts the pseudo-first-order plots of Δ- and Λ-$Co(acac)_3$ photoreduction catalyzed by $[Ru((-)\text{-mncb})_3]^{2+}$ in ethanol/water (7:3 v/v), though an induction period of ca. 10 min existed. The reaction rates ($10^2 k_{obs}$) are 1.23 ± 0.04, 1.46 ± 0.03, and 1.10 ± 0.02 min^{-1} for the racemic, Δ, and Λ forms of $Co(acac)_3$, respectively, and the rate constants ratio (k_Δ:k_Λ) obtained is 1.33. CD spectral changes of the reaction solution in the photoreduction of *rac*-$Co(acac)_3$ determined in the same solvent system are shown in Figure 3; the absorptions at λ_{max} 574 and 647 nm increased with photoirradiation. The CD spectral changes suggest the predominant consumption of the Δ isomer of the substrate by the catalyst with accumulation of the Λ isomer. The enantioselectivities evaluated from the CD spectral changes are 1.32 ± 0.02,[11] which not only remained constant during the reaction within experimental error but also were consistent with the value from the enantiomer rate ratio (k_Δ:k_Λ).

It is concluded that the present ruthenium complex having chiral positions in the ligands without molecular asymmetry recognizes the enantiomeric complexes of $Co(acac)_3$ with a selectivity (Δ:Λ) of 1.33 as an enantiomer rate ratio. The stereoselection of $Co(acac)_3$ by chiral ruthenium complexes, which has hitherto been reported to be the enantiomer rate ratio 1.08 with Δ-$[Ru(bpy)_3]^{2+}$,[1a] was improved by $[Ru((-)\text{-mncb})_3]^{2+}$ possessing an efficient chiral ligand. In addition, catalytic and enantioselective reduction proceeded, suggesting that photoracemization of the chiral ligands of $[Ru((-)\text{-mncb})_3]^{2+}$ hardly occurred. It is also noted that the selectivity evaluated from the enantiomers' reaction rates is consistent with that from the quenching rate ratio. This experimental finding suggests that the stereoselectivity observed in the present reaction would result from the close contact between the ruthenium catalyst and the cobalt complex during the formation of the encounter complex.

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(11) The value is calculated from the equation $\ln [\Delta_0/(\Delta_0 - \Delta)]/\ln [\Lambda_0/(\Lambda_0 - \Lambda)]$ (Δ_0, Λ_0 = initial concentrations of the Δ or Λ isomer; Δ, Λ = reacted concentrations of the Δ or Λ isomer evaluated from CD spectra).

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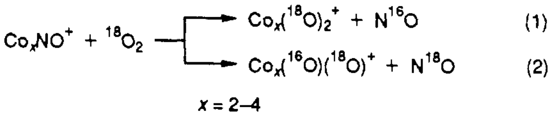
Received November 28, 1988

Facile Oxygen Exchange by Cobalt Cluster Oxide Ions with Water-^{18}O in the Gas Phase

Dissociative chemisorption (molecular activation) of small molecules such as CO, NO, N_2, H_2, etc. is a requisite process for heterogeneous catalysis and surface chemistry.[1] It is of interest, therefore, to understand the factors that facilitate dissociative chemisorption on transition-metal clusters. Gas phase ion techniques are particularly promising in this regard since distinct ion clusters can be selected and studied; however, distinguishing dissociative chemisorption from molecular chemisorption is quite challenging. We recently demonstrated that dissociative chemisorption of nitric oxide can be distinguished from molecular chemisorption for small bare cationic cobalt clusters by monitoring the oxygen isotopic distribution for reaction with dioxygen-^{18}O[2] (processes 1 and 2). This method proved useful in distinguishing dissociative from molecular chemisorption of NO on these clusters; however, it is limited to very simple systems (i.e., systems with only one ligand). As a consequence we have investigated a number of other methods that would distinguish dissociative chemisorption of nitric oxide from molecular chemisorption for complex, multiligated clusters. These efforts led us to consider the potential of water-^{18}O as a probe of metal cluster oxide character since oxygen exchange with water has been observed on metal oxide surfaces.[3-9]



$$Co_xNO^+ + {}^{18}O_2 \longrightarrow Co_x({}^{18}O)_2^+ + N^{16}O \qquad (1)$$

$$Co_xNO^+ + {}^{18}O_2 \longrightarrow Co_x({}^{16}O)({}^{18}O)^+ + N^{18}O \qquad (2)$$

$x = 2–4$

All experiments were performed by using a Nicolet FTMS-1000 Fourier transform mass spectrometer equipped with a 5.08-cm cubic-trapping cell and a 3.0-T superconducting magnet.[10] The theory, instrumentation, and methodology of conventional ion cyclotron resonance (ICR)[11] and Fourier transform mass spectrometry (FTMS)[12,13] have been discussed at length elsewhere. The cobalt cluster oxide cations were generated by reaction of cobalt cluster carbonyl nitrosyl ions, generated from electron impact on $Co(CO)_3NO$,[14] with dioxygen[15] followed by collisional activation (CA)[16,17] and isolation of the desired $Co_xO_y^+$ ion.[12]

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Argon was used as the collision gas for CA at a pressure of ~1 × 10^{-5} Torr and also served to collisionally cool the $Co_xO_y^+$ ions prior to study. The pressure of water-^{18}*O* was ~3.0 × 10^{-8} Torr to ensure that the clusters were thermalized prior to reaction. Water-^{18}*O* was obtained from MSD Isotopes with >98 atom % purity.

The oxygen-equivalent clusters ($Co_2O_2^+$, $Co_3O_3^+$, $Co_4O_4^+$) react with water-^{18}*O*, yielding facile oxygen exchange (process 3), with all oxygen atoms undergoing sequential exchange. These exchanges yield pseudo-first-order kinetics, indicating that excited-state ions are not responsible for the exchange process.

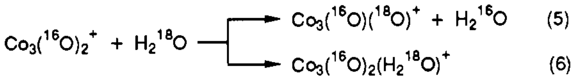
$$Co_x(^{16}O)_x^+ \underset{-H_2{}^{16}O}{\overset{+H_2{}^{18}O}{\rightleftharpoons}} Co_x(^{16}O)_{x-1}(^{18}O)^+ \underset{-H_2{}^{16}O}{\overset{+H_2{}^{18}O}{\rightleftharpoons}} Co_x(^{16}O)_{x-2}(^{18}O)_2^+ \ldots \quad (3)$$

$$x = 2\text{–}4$$

If excited states were responsible for the above exchange, then quenching of the excited states by numerous thermalizing collisions with the argon buffer gas would result in only a fraction of the ion population undergoing exchange, yielding nonlinear kinetics. The rate constants for oxygen exchange for $Co_2(^{16}O)_2^+$, $Co_2(^{16}O)(^{18}O)^+$, and $Co_3(^{16}O)_3^+$ are (9.3 ± 2.8) × 10^{-10}, (5.2 ± 1.6) × 10^{-10}, and (1.0 ± 0.3) × 10^{-9} cm^3 $molecule^{-1}$ s^{-1}, respectively.[18,19] Comparison with the calculated collision rates[20] yield reaction efficiencies, k_{obs}/k_{coll}, of 0.55 (0.67), 0.30 (0.33), and 0.61 (0.75), respectively, for $Co_2(^{16}O)_2^+$, $Co_2(^{16}O)(^{18}O)^+$, and $Co_3(^{16}O)_3^+$ (reaction efficiencies for statistical distribution of the label are given in parentheses). With $Co_4O_4^+$, facile condensation (process 4) competes with the oxygen-exchange process. This facile condensation suggests that the product of reaction 4 exists in a deep potential well and, as a consequence, is long lived and stabilized by either infrared radiative stabilization[21,22] or by collisional stabilization with argon (on average ~6 ms/collision).

$$Co_4O_4^+ + H_2{}^{18}O \rightarrow Co_4(O)_4(H_2{}^{18}O)^+ \qquad (4)$$

Oxygen exchange involving the oxygen-deficient clusters (Co_2O^+ and $Co_3O_2^+$) was investigated in order to probe the effect of oxygen on the oxygen isotopic exchange process. No exchange was observed for Co_2O^+ with water-^{18}*O*; however, $Co_3O_2^+$ undergoes facile sequential exchange as well as competitive condensation (processes 5 and 6).



$$Co_3(^{16}O)_2^+ + H_2{}^{18}O \rightarrow \begin{cases} Co_3(^{16}O)(^{18}O)^+ + H_2{}^{16}O & (5) \\ Co_3(^{16}O)_2(H_2{}^{18}O)^+ & (6) \end{cases}$$

The isotopic oxygen exchanges described above may proceed by initial water coordination followed by reversible migration of hydrogen to "oxide" oxygen, generating a dihydroxyl species (process 7) that ultimately eliminates water. Such a mechanism

$$Co_x(O)_x(H_2O)^+ \rightleftharpoons Co_x(O)_{x-1}(OH)_2^+ \qquad (7)$$

is supported by surface chemistry, where stable surface hydroxyls have been generated from reaction of surface oxides with water at low temperatures[3-6] and, upon heating, recombination forming water occurs.[7-9] Calculations reveal a low barrier for this process, involving an FeO–water system.[23] It is believed that hydroxyl formation involving surface oxides exposed to water is facilitated by strong hydrogen-bonding interactions between water hydrogens and an adjacent surface oxide oxygen atom.[24]

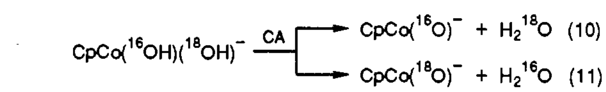
An alternative mechanism involving direct insertion of an oxygen atom into an O–H bond of water (process 8) may also be

$$Co_x(O)_x^+ + H_2O \rightleftharpoons Co_x(O)_{x-1}(OH)_2^+ \qquad (8)$$

involved. If this process were exclusively responsible for oxygen atom exchange, then CA of the isotopomer ions formed in reactions 4 and 6 should yield equal amounts of water-^{16}*O* and water-^{18}*O* eliminations. Both $Co_4(^{16}O)_4(H_2{}^{18}O)^+$ and $Co_3(^{16}O)_2(H_2{}^{18}O)^+$, formed in reactions 4 and 6, respectively, yield elimination of water as the initial fragmentation upon CA with a *statistical* distribution of label, indicating that the oxygen atoms are completely scrambled prior to fragmentation. These CA results provide support for the hydrogen atom migration mechanism (process 7); however, they do not eliminate process 8 as a contributing mechanism. In addition, these CA results imply low barriers for oxygen atom scrambling since it is facile.[25] If process 7 is indeed important, then hydrogen atom migration involving other hydrogen-bonding compounds such as NH_3 may also be accessible. Indeed, $Co_2O_2^+$ reacts with ammonia exclusively by process 9, providing additional

$$Co_2O_2^+ + NH_3 \rightarrow Co_2ONH^+ + H_2O \qquad (9)$$

support for the hydrogen atom migration mechanism (process 7).[26] In a related study, Wang and Squires,[27] employing a flowing afterglow apparatus,[28] observed isotopic oxygen atom exchange with $CpCo^{16}O^-$ (Cp = cyclopentadienyl) and water-^{18}*O* upon CA of the adduct (processes 10 and 11).



$$CpCo^{16}O^- + H_2{}^{18}O \longrightarrow CpCo(^{16}OH)(^{18}OH)^- \xrightarrow{CA} \begin{cases} CpCo(^{16}O)^- + H_2{}^{18}O & (10) \\ CpCo(^{18}O)^- + H_2{}^{16}O & (11) \end{cases}$$

Absence of oxygen exchange for Co_2O^+ with water-^{18}*O* is intriguing. This may be due to an unfavorable barrier to hydrogen migration generating a dihydroxyl or the possibility that formation of the dihydroxyl may simply be endothermic. Alternatively, the inert behavior of Co_2O^+ may be a consequence of the overall geometry of the oxide (terminal or bridging oxygen in the cluster), where a terminal oxide is required for the exchange process to occur. It is interesting to note that metal surfaces containing higher oxide coverages facilitate hydroxyl formation upon exposure to water.[3] These limited results suggest that a similar trend may be valid for transition-metal cluster oxide ions.

Oxygen exchange involving the related oxygen compound CH_3OH with $Co_2O_2^+$ was investigated in order to probe the dynamics of methyl migration. In this system reversible hydrogen migration as depicted in process 12 may indeed be facile;[29] however, methyl migration or initial "oxide" insertion into the CH_3–O bond is required in order for oxygen scrambling to occur. Absence

$$Co_2(^{18}O)_2(CH_3{}^{16}OH)^+ \rightleftharpoons Co_2(^{18}O)(^{18}OH)(^{16}OCH_3)^+ \qquad (12)$$

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(18) The ionization gauge was calibrated for water by monitoring the proton-transfer reaction

$$HCO^+ + H_2O \rightarrow CO + H_3O^+$$

which has a reported rate constant 2.5 × 10^{-9} cm^3 $molecule^{-1}$ s^{-1} (±30%) (Adams, N. G.; Smith, D.; Grieb, D. *Int. J. Mass Spectrom. Ion Phys.* **1978**, *26*, 405).

(19) The rate constant for exchange involving the mixed isotopomer $Co_2(^{16}O)(^{18}O)^+$ was obtained by first isolating it by using double-resonance techniques followed by monitoring the exchange reaction.

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of oxygen exchange suggests unfavorable barriers for either process.

Observation of facile oxygen exchange (process 3) suggests that water-^{18}O may be employed as a sensitive probe for oxide character in transition-metal cluster ion complexes (i.e., to distinguish dissociative from molecular chemisorption for simple oxides such as NO, CO, and CO_2). Co_3NO^+ serves as a model since we have previously demonstrated that it contains NO dissociatively chemisorbed on the cluster.[2] Competitive oxygen exchange and condensation are observed (processes 13 and 14) with water-^{18}O.

$$\mathrm{Co_3(N^{16}O)^+ + H_2{}^{18}O} \longrightarrow \begin{cases} \mathrm{Co_3(N^{18}O)^+ + H_2{}^{16}O} & (13)\\ \mathrm{Co_3(N^{16}O)(H_2{}^{18}O)^+} & (14)\end{cases}$$

CA of the water adduct $Co_3(N^{16}O)(H_2{}^{18}O)^+$ yields elimination of water as the primary fragmentation process with a statistical $H_2{}^{16}O/H_2{}^{18}O$ distribution, indicating that the oxygen atoms are rapidly interconverting. These results confirm that NO is dissociatively chemisorbed on Co_3^+.

The above results demonstrate the potential of water-^{18}O as a sensitive probe for metal oxide character in transition-metal cluster ion complexes. We are currently exploring the scope of this method for probing oxide character in a variety of transition-metal cluster ion systems. This technique may prove to be a powerful and nondestructive method for probing the structure of complex transition-metal cluster ions in the gas phase.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

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Received December 19, 1988

Soluble Polychalcogenide Chemistry of Indium. Synthesis and Characterization of $[In_2Se_{21}]^{4-}$, the First Indium Polyselenide

Compared to transition-metal polychalcogenide chemistry, the corresponding chemistry of group III metals is virtually unexplored.[1a,b] For example, in contrast to a number of monochalcogenide compounds,[1c] no In/polychalcogenide species are known to date. As part of our continuing efforts to characterize late-transition-metal/- and main-group-metal/chalcogen chemistry, we and others recently reported the new series of $[M(Q_4)_2]^{2-}$ complex anions[2] (where M = Zn, Cd, Hg, Ni, Pd and Q = Se, Te) and their use as precursors to intermetallic solids. We also reported the unusual $[Ag(Se_4)]_n{}^{n-}$, a one-dimensional inorganic polymer.[3] We expected that at least the softer, heavier members of group III elements (i.e. In, Tl) would form analogous, stable chalcogenide complexes. The pnictide and chalcogenide binary and ternary compounds of group III metals (i.e. Al, Ga, In) are technologically important due to their promising electronic and optoelectronic properties.[4,5] Among the chalcogenides, In_2Se_3, InSe, and $CuInSe_2$ are noteworthy for their photovoltaic properties.[6] It has been recognized that, apart from the conventional high-temperature routes to such materials, molecular precursor methods are highly desirable.[7] From this perspective as well as the fact that heavier group III metals exhibit interesting structural chemistry,[8] we report here the synthesis, molecular structure, and properties of the first In/polychalcogenide complex, the Se-rich $[In_2Se_{21}]^{4-}$ (I).

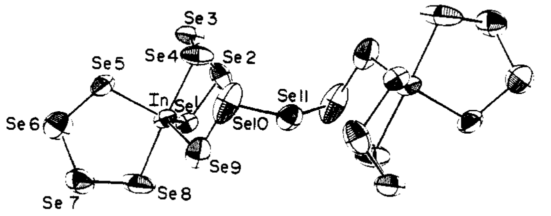

Figure 1. ORTEP projection and atom-labeling scheme of $[In_2(Se_4)_4(Se_5)]^{4-}$. Atom Se(11) is positionally disordered around a crystallographic inversion center. Only one of the Se(11) positions is shown. Individual indium–selenium bond distances are In–Se(1) = 2.663 (4) Å, In–Se(4) = 2.729 (6) Å, In–Se(5) = 2.622 (4) Å, In–Se(8) = 2.734 (6) Å, and In–Se(9) = 2.615 (5) Å. Bond distances within the $Se_4{}^{2-}$ ligands are Se(1)–Se(2) = 2.330 (7) Å, Se(2)–Se(3) = 2.334 (5) Å, Se(3)–Se(4) = 2.349 (6) Å, Se(5)–Se(6) = 2.311 (8) Å, Se(6)–Se(7) = 2.289 (7) Å, and Se(7)–Se(8) = 2.337 (5) Å. Corresponding angles are Se(1)–Se(2)–Se(3) = 100.9 (2)°, Se(2)–Se(3)–Se(4) = 99.1 (2)°, Se(5)–Se(6)–Se(7) = 102.5 (2)°, and Se(6)–Se(7)–Se(8) = 102.7 (3)°.

I was prepared according to eq 1. Slow addition of a dimethylformamide (DMF) solution of anhydrous $InCl_3$ (0.10 g,

$$2\mathrm{InCl_3} + 5\mathrm{Na_2Se_5} + 4\mathrm{Ph_4PCl} \rightarrow [\mathrm{Ph_4P}]_4[\mathrm{In_2Se_{21}}] + 10\mathrm{NaCl} \qquad (1)$$

0.452 mmol) to a mixture of Na_2Se_5[9] (0.50 g, 1.132 mmol) and Ph_4PCl (0.34 g, 0.908 mmol) in DMF caused an immediate color change from deep green to brown. Following 40 min of stirring at room temperature and removal of NaCl by filtration, the solution was diluted with ether to incipient crystallization. Within 2 days brown crystals of $[Ph_4P]_4In_2Se_{21}$ are reproducibly obtained in ca. 75% yield. Anal. Calcd for $C_{96}H_{80}P_4In_4Se_{21}$: C, 35.51; H, 2.47; In, 7.08; Se, 51.12. Found: C, 35.04; H, 2.48; In, 6.86; Se, 50.89. Care must be taken to exclude traces of water and oxygen. Although the optimum stoichiometric ratio of In^{3+}:$Se_5{}^{2-}$ is 2:5, lower yields of $[In_2Se_{21}]^{4-}$ were obtained even when the ratio was 1:2 or 1:3. This, coupled with the fact that $[In_2Se_{21}]^{4-}$

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