Interaction of Carbon Dioxide with Transition-Metal-Substituted Heteropolyanions in Nonpolar Solvents. Spectroscopic Evidence for Complex Formation

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Tetraheptylammonium salts of various transition-metal-substituted heteropolyanions with α-Keggin ($[XW_{11}O_{39}M]^{n-}$), α-Wells−Dawson ($[P_2W_{17}O_{61}M]^{m-}$), and Weakley and Finke structures ($[P_2W_{18}O_{68}Co_4]^{10-}$) were investigated with respect to their reactivity with CO_2 in nonpolar solvents. It was found that copper(II)- and manganese(III)-substituted heteropolyanions do not react with CO_2. Germano- and silicotungstates with the α-Keggin structure do form complexes with CO_2 when substituted with Co(II), Ni(II), and Mn(II). In contrast, boro- and phosphotungstates substituted with Co(II), Ni(II), and Mn(II) are unreactive. The α_2 isomers of Wells−Dawson phosphotungstates show reactivity similar to that of α-Keggin silicotungstates—i.e., Co(II), Ni(II), and Mn(II) derivatives do react with CO_2. On the other hand, the α_1 isomer of the Co(II)-substituted Wells−Dawson anion does not react with CO_2, and neither does the Weakley and Finke cobaltotungstate. When reactions do occur, they are completely reversible. An excess of water decomposes the complexes. Traces of water are, however, necessary for the reactions to take place. The CO_2 adducts were characterized by UV/vis, IR, and ^{13}C NMR. The IR data could be explained as originating either from CO_2 complexes with a direct η^1 metal−carbon bond or from bicarbonato complexes. IR spectra with isotopically enriched $^{13}CO_2$ and $C^{18}O_2$ support the presence of a η^1 metal−carbon bond. The ^{13}C NMR spectra indicate the presence of two different kinds of paramagnetic CO_2 complexes after the reaction of α-$[SiW_{11}O_{39}Co]^{6-}$ with CO_2 (chemical shifts 792 and 596 ppm at 26 °C). The variable-temperature experiments are consistent with the chemical exchange between these two species. UV/vis, IR, and NMR studies in the presence of controlled amounts of water or ethanol suggest the existence of H-bonding in the CO_2 complexes, similar to that reported in the past for complexes between heteropolyanions and dioxygen.

Introduction

In 1984 Pope and Katsoulis reported that transition-metal-substituted heteropolyanions (TMS HPA's) of tungsten[1] are readily transferable into nonpolar solvents such as benzene and toluene, where they lose water coordinated to the substituted transition metal, and become very reactive toward addition of small molecules to that empty site.[2] Reactivity with SO_2 and O_2 was observed. More recently, Anson and Toth demonstrated that TMS HPA's can serve as electrocatalysts and multiple-electron reservoirs in a one-step reduction of nitrite anion to ammonia in aqueous solutions,[3] indicating that these complexes are capable of storage and one-step transfer of at least six electrons. Other relevant work in the area of TMS HPA reactivity with various compounds in nonpolar solvents has been reviewed by Hill and Prosser-McCartha.[4] Electrochemical properties of polyoxometalates as potential electrocatalysts in homogeneous solutions, and when they are attached to electrode surfaces, have been reviewed recently by Sadakane and Steckhan.[5]

This paper reports the first data concerning the interaction of TMS HPA's in nonpolar solvents with carbon dioxide, a ligand of great current interest because of its potential as a C-1 feedstock and substrate for solar energy storage, as well as for its alleged role in atmospheric warming (the "greenhouse" effect).[6] In this regard the fixation of CO_2 under mild conditions by transition-metal complexes and its conversion into useful chemical compounds are areas of great importance in inorganic chemistry. The most desirable objective is to transform carbon dioxide into its highly reduced products by a multielectron route, with methane being the ultimate goal. One approach to reach

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this goal is to use compounds containing transition metals that could act as both electrocatalysts and electron reservoirs, thus providing a means to simultaneously deliver multiple electrons necessary in multielectron reductions.

A number of transition-metal complexes, both in solution and on electrode surfaces, have been shown to be effective in the electrocatalytic reduction of carbon dioxide.[7] All of those complexes significantly decrease the overpotential for reduction of CO_2 by up to 1 V (as compared to 1-e reduction to CO_2^- radical) and yield various multielectron reduction products. Some of those complexes form stable complexes with CO_2. Others coordinate CO_2 only under the conditions of electrochemical experiments. Known electrocatalysts yield primarily carbon monoxide and formate anion as the major products of the CO_2 reduction.[7] Sullivan et al. did detailed mechanistic work on a series of bipyridine complexes of transition metals and made several suggestions concerning the design of new electrocatalysts that would be capable of reducing CO_2 past the CO and formate step.[8] Their major recommendation is to use as electrocatalysts "electron reservoir" complexes, i.e., compounds capable of storing multiple electrons.

The report by Anson and Toth[3] indicating electrocatalytic and electron-reservoir capabilities of HPA's, and the report by Pope and Katsoulis demonstrating reactivity of TMS HPA's in nonpolar solvents with small molecules,[2] prompted us to investigate whether TMS HPA's in nonpolar solvents could activate CO_2 and serve as electrocatalysts in its multielectron reduction. This paper reports our findings concerning the reactivity of TMS HPA's with carbon dioxide in nonpolar solvents. Their electrocatalytic activity with respect to carbon dioxide reduction is presently being investigated in our laboratory.

Background

Heteropolyanions. HPA's are polyanionic, condensed oligomeric aggregates of transition-metal ions, usually in their d^0 electronic configuration, and oxide ions, held together by metal−oxygen bonds.[1] The largest number of HPA's is formed by Mo(VI) and W(VI). Mo or W in an HPA are typically surrounded by six oxide ions, forming MO_6 octahedra. The most widely studied HPA's are those with the formulas $XM_{12}O_{40}{}^{m-}$ (M = W, Mo, X = P, Si, B, Ge, etc.) and $X_2M_{18}O_{62}{}^{n-}$ (M = W, Mo, X = P, As). The former adopt the so-called "Keggin" structure. (See Figure 1a). The structure has overall T_d symmetry and is based on a central XO_4 tetrahedron surrounded by 12 MO_6 octahedra arranged in 4 groups of 3 edge-shared octahedra, M_3O_{13}. These groups are linked together and to the central XO_4 tetrahedron by sharing corners. The $X_2M_{18}O_{62}{}^{n-}$ anions adopt the so-called "Wells-Dawson" structure (see Figure 1b,c). The structure can be viewed as containing two subunits (two XM_9 groups) of the Keggin structure, fused into a cluster of virtual D_{3h} symmetry. During the last 30 years many "modified" Keggin and Wells−Dawson anions have been reported. They are based upon the replacement of one of the 12 or 18 tungsten or molybdenum atoms by another octahedrally coordinated metal atom, Z. The first example of such compounds was reported by Simmons and Baker in 1962,[9] and an extensive investigation followed, which established unequivocally the large new general structural category of heteropolyanions.[10] Since then, numerous examples of "modified" Keggin and Wells−Dawson heteropoly complexes containing a variety of octahedral heteroelements have been described.[11] It has also been established that when the octahedral heteroatom is a first-row transition metal, its sixth outer coordination site is occupied by a water molecule,[10] which may be more or less deprotonated depending on the substituted metal, Z, and on the pH.[10,11e] The anions then can be formulated: $[XM_{11}O_{39}Z(H_2O)]^{m-}$ (Keggin structure) and $[X_2M_{17}O_{61}Z(H_2O)]^{n-}$ (Wells−Dawson structure). Two structural isomers exist for the latter structure, depending on the position where the transition metal is substituted. In the so-called α_2 and α_1 isomers the metal is substituted in the cap and belt of the Wells−Dawson structure, respectively[12] (see Figure 1b,c).

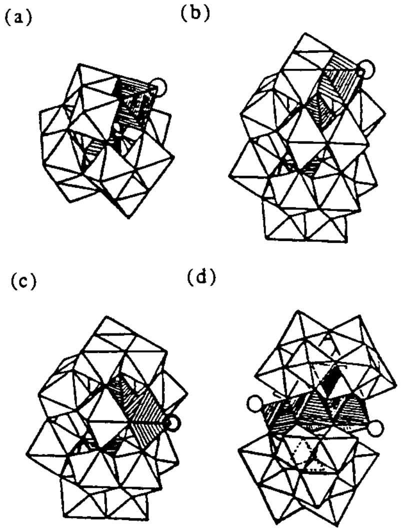

Figure 1. Polyhedral representations of transition-metal-substituted heteropolyanions examined in this study: (a) α-$[XW_{11}O_{39}Z(H_2O)]^{n-}$, X = P, Si, Ge, B and Z = Co^{2+}, Mn^{2+}, Ni^{2+}, Cu^{2+}, Mn^{3+}; (b) α_2-$[P_2W_{17}O_{61}Z(H_2O)]^{m-}$, Z = Co^{2+}, Mn^{2+}, Ni^{2+}, Cu^{2+}, Mn^{3+}; (c) α_1-$[P_2W_{17}O_{61}Z(H_2O)]^{m-}$, Z = Co^{2+}; (d) $[PW_9O_{27}Co^{II}{}_4O_{14}(H_2O)_2O_{27}W_9P]^{10-}$. Each vertex of a polyhedron locates an oxygen atom. A W atom is within each white octahedron. Each (shaded) tetrahedron contains heteroatom X. Each shaded octahedron contains the substituted transition metal, Z.

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Other transition-metal-substituted heteropolyanions containing *two* transition-metal-bound water molecules per heteropolyanion were reported by Weakley et al.[13] and by Finke et al.[14] One of these complexes containing cobalt has the formula $[PW_9O_{27}Co^{II}_4O_{14}(H_2O)_2O_{27}W_9P]^{10-}$ (see Figure 1d).

In 1984, Katsoulis and Pope[2] demonstrated that transition-metal-substituted heteropolyanions are easily transferred from water to a variety of nonpolar solvents by using tetraheptylammonium bromide as a phase-transfer agent. They reported that such polyanions show considerable (metalloporphyrin-like) reactivity in nonaqueous solvents. A major feature of the new chemistry is the facile loss of the coordinated water molecule(s), which leads to coordinatively unsaturated sites on the surface of the polyanion; e.g.

$$[SiW_{11}O_{39}Co(H_2O)]^{6-} \rightleftarrows [SiW_{11}O_{39}Co(\_)]^{6-} + H_2O$$

For metals such as Co(II) the process is readily detected spectroscopically. The "hydrated" complex and similar anions are pink or red, and the anhydrous complex and its analogues (with pentacoordinated Co(II)) are green. The anhydrous HPA's react easily with a variety of ligands, such as alcohols, acetonitrile, pyridine, chloride ion, *sulfur dioxide, and dioxygen*. The interaction with SO_2 and O_2 has been investigated in detail by Pope and Katsoulis. The IR evidence indicated a metal-to-sulfur bond in the complexes with SO_2.[2b,c] Multiple spectroscopic data were used to demonstrate that a weak dioxygen adduct is stabilized by a hydrogen-bonded water molecule.[2d]

The data reported in this paper demonstrate that TMS HPA's in nonpolar solvents react readily with carbon dioxide, forming complexes similar in certain characteristics to complexes with dioxygen reported by Pope and Katsoulis.

Experimental Section

Materials. HPLC grade nonpolar solvents toluene, dichloromethane, chloroform, and carbon tetrachloride were purchased from Aldrich. Toluene was distilled over sodium/benzophenone, and dichloromethane, chloroform, and carbon tetrachloride were distilled over calcium hydride. All solvents were stored under nitrogen, over molecular sieves. The water content in dried solvents was typically less than 1 mM. Potassium salts of transition-metal-substituted Keggin, Wells−Dawson, and Weakley and Finke complexes were prepared according to the methods published previously.[11−14] The IR and UV/vis spectra and cyclic voltammograms agreed with the data reported in the literature.[11−14] The phase transfer agent, tetraheptylammonium bromide, was obtained from Aldrich. Tetrabutylammonium bicarbonate ($TBAHCO_3$) was prepared according to the method described previously[15] by bubbling CO_2 gas through a methanolic solution of n-Bu_4NOH and then drying under vacuum at temperatures below 40 °C. The solution of this compound in toluene gave a ^{13}C NMR signal at 162 ppm, as expected for a bicarbonate.[16] "Bone dry" grade carbon dioxide gas (Linde, 99.8%) and extra dry nitrogen gas (Linde, 99.7%) were used without further purification. For the experiments that required drier conditions, CO_2 gas was dried over P_2O_5 and distilled into the reaction vessel under vacuum. Isotopically pure $^{13}CO_2$ and $C^{18}O_2$ were purchased from Cambridge Isotope Laboratories in 1.0 L "break seal" flasks.

Most experiments were carried out on Schlenk double-manifold lines, although certain experiments requiring extremely dry conditions (less than 10 mM water) were performed on a high-vacuum line with an oil diffusion pump.

Phase Transfer. A slight modification of the method introduced by Katsoulis and Pope[2] was used. Typically, an unbuffered 10 mM aqueous solution of the potassium salt of the heteropolyanion was shaken briefly with an equal volume of the stoichiometric amount of tetraheptylammonium bromide (THABr) in toluene. (The concentration of THABr solution was 10x mM, where x is the absolute value of the negative charge on the HPA.) Since all the HPA's were colored, it was easy to observe the complete transfer from the aqueous to the organic layer. After the two phases had been allowed to settle for 10 min, they were separated. The organic layer at this stage was determined, via coulometric Karl Fisher titration, to contain between 20 and 25 water molecules per heteropolyanion. Next, the wet toluene was removed by heating to 40 °C under vacuum, and the dry solvent (toluene, dichloromethane, chloroform, or carbon tetrachloride) was added using either the cannula technique on a Schlenk line (typically final water concentration was then 5 mM) or solvent distillation on the high-vacuum line (final water concentration as low as 1 mM was then possible). For the experiments with controlled amounts of water, water (or wet solvent) was added using gastight syringes or was distilled under vacuum into the reaction vessel.

Spectroscopy. UV/vis spectra were recorded using the HP 8452A diode array spectrophotometer. Vibrational spectra were run using a Nicolet Impact 410 FT IR spectrometer with KBr disks (for potassium salts) and 0.0050 cm AgCl windows (for 50 mM solutions of THA salts). The Bruker Avance 250 MHz spectrometer was used to record ^{13}C NMR spectra. The NMR samples were prepared on a high-vacuum line, by transferring $^{13}CO_2$ gas into HPA solutions in deuterated solvents, using 10 mm tubes with J. Young valves. The spectra reported in Figure 5 required 2000 scans.

Electrochemistry. Cyclic voltammetry was carried out on a PAR 273A potentiostat.

Water Measurements. Water was determined by coulometric Karl Fischer titration using a Metrohm 684 KF coulometer filled with Aquastar Coulomat single solution.

Magnetic Susceptibility. Magnetic susceptibility was measured in solution by the Evans NMR method, using a modification introduced by Kozik et al. in 1988.[17] As usually used, ^1H NMR chemical shifts are observed for a given H of a standard compound contained in solution in two coaxial NMR tubes, the outside of which also contains, in the solution, the compound of interest. Since the difference in chemical shifts depends on the difference in volume susceptibilities for the two solutions, the magnetic susceptibility of the subject compound is calculable. Frequent sources of inaccuracies involve neglect of corrections for density differences between the two solutions (especially important for solutions of heteropoly species) and neglect of differences in solvent concentrations. In this modification the unusual accuracy in determining the differences in susceptibilities results from placing a studied heteropoly compound in the outer tube and an equimolar solution of its diamagnetic standard in the inner. This setup eliminates the usual inaccuracies, as well as the relatively unpredictable diamagnetic corrections for the heteropoly species. This modification made possible the determination of excess diamagnetism of several two-electron-reduced heteropolyanions over their oxidized parents. In the present work the diamagnetic standard used was α-$[PW_{11}O_{39}Zn^{II}]^{5-}$. The ^1H NMR reference material was TMS.

Reactions of CO_2 with Heteropolytungstates. In a typical experiment, gaseous CO_2 was passed through the toluene, dichloromethane, chloroform, or carbon terachloride solution containing 0.01 M heteropolyanion. If the anion reacted with CO_2, a nearly instantaneous color change occurred for all complexes except those containing Mn(II) (which remained orange-yellow). The visible spectra of the complexes formed by TMS HPA's and CO_2 were recorded under a CO_2 atmosphere, using a specially designed UV/vis cell connected to

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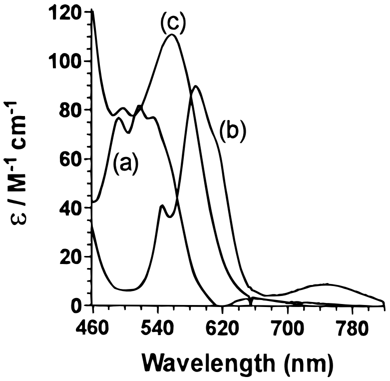

Figure 2. Visible spectra of tetraheptylammonium salts of (a) α-$[SiW_{11}O_{39}Co(OH_2)]^{6-}$, (b) α-$[SiW_{11}O_{39}Co(\_)]^{6-}$, and (c) α-$[SiW_{11}O_{39}Co(CO_2)]^{6-}$ in toluene.

the reaction flask. The experiment was repeated at 0.05 M HPA concentration, and the solution IR spectra were recorded using AgCl cells.

Results

A. General Observations. Reactivity of TMS HPA's with carbon dioxide in nonpolar solvents was investigated using a set of HPA's similar to, though more extensive than, the one used by Katsoulis and Pope in their work with sulfur dioxide and dioxygen.[2] Three kinds of structures were examined. The first two structures contain a single divalent or trivalent metal ion in place of a tungsten atom in the Keggin or the Wells−Dawson anion as a $MO_5(OH_2)$ octahedron, while the third structure contains two nonadjacent $CoO_5(OH_2)$ octahedra. All investigated complexes and their denotations in the following text are as follows: (A) metal-substituted Keggin silicotungstates $[SiW_{11}O_{39}M^{II}]^{6-}$ ($M^{II} = Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}$) and $[SiW_{11}O_{39}Mn^{III}]^{5-}$, denotations $SiW_{11}M^{II\,6-}$ and $SiW_{11}Mn^{III\,5-}$; (B) metal-substituted Keggin germanotungstates $[GeW_{11}O_{39}M^{II}]^{6-}$ ($M^{II} = Mn^{2+}, Co^{2+}, Ni^{2+}$), denotation $GeW_{11}M^{II\,6-}$; (C) metal-substituted Keggin phosphotungstates $[PW_{11}O_{39}M^{II}]^{5-}$ ($M^{II} = Mn^{2+}, Co^{2+}, Ni^{2+}$), denotation $PW_{11}M^{II\,5-}$; (D) cobalt-substituted Keggin borotungstate $[BW_{11}O_{39}Co^{II}]^{7-}$, denotation $BW_{11}Co^{II\,7-}$ (E) metal-substituted Wells−Dawson phosphotungstates α_2-$[P_2W_{17}O_{61}M^{II}]^{8-}$ ($M^{II} = Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}$), α_2-$[P_2W_{17}O_{61}Mn^{III}]^{7-}$, and α_1-$[P_2W_{17}O_{61}Co^{II}]^{8-}$, denotations α_2-$P_2W_{17}M^{II\,8-}$, α_2-$P_2W_{17}Mn^{III\,7-}$, and α_1-$P_2W_{17}Co^{II\,8-}$; (F) Weakley and Finke's phosphotungstocobaltate $[(PW_9O_{34})_2Co_4]^{10-}$, denotation $(PW_9)_2Co_4^{10-}$.

The evidence for complex formation was a color change and the appearance of two new vibrational frequencies, around 1675 and 1350 cm^{-1}, after carbon dioxide gas was bubbled through a solution of tetraheptylammonium salts of TMS HPA's in toluene, chloroform, dichloromethane, or carbon tetrachloride. The only exceptions were Mn(II) derivatives; for these, IR spectra alone were used, because the color change was not noticeable, owing to no spin-allowed transitions for a low-field d^5 electron configuration. Figures 2 and 3 show visible and IR spectra for cobalt-substituted silicotungstate, the compound for which more detailed studies described later were performed. For this compound the color changes are easily observed by eye. The "hydrated" complex is orange-red, the "dry" complex is green, and the "CO_2" complex is burgundy red. Table 1 summarizes the results of reactivity for TMS HPA's with carbon dioxide and the electronic spectra observed for hydrated, dry, and CO_2 complexes. In addition to the two vibrations around 1675 and 1350 cm^{-1} that are observed only for TMS HPA's which react with CO_2, the IR spectra of all tested compounds contain a strong signal around 2335 cm^{-1}, resulting from dissolved CO_2 gas.

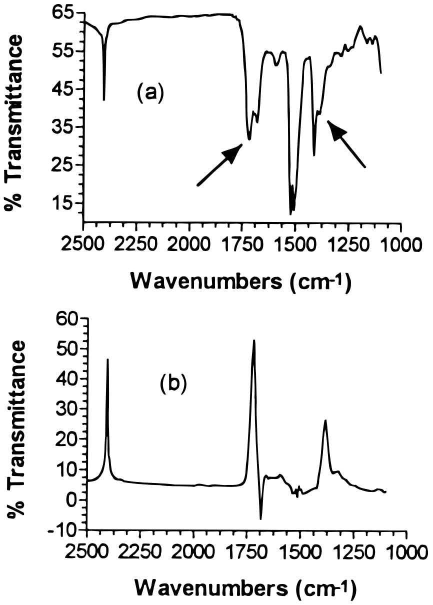

Figure 3. (a) Infrared spectrum of the tetraheptylammonium salt of α-$[SiW_{11}O_{39}Co(CO_2)]^{6-}$ in CCl_4. Two peaks marked with arrows appear after the CO_2 is bubbled, and they are assigned to vibrations of CO_2 complexed to cobalt. (b) Difference spectrum between α-$[SiW_{11}O_{39}Co(CO_2)]^{6-}$ and α-$[SiW_{11}O_{39}Co(-)]^{6-}$. The peak at 2335 cm^{-1} originates from CO_2 gas dissolved in the solvent.

When an excess of water is added to the heteropoly-CO_2 complexes, the UV/vis spectra change to these of the original hydrated complexes, matching the spectra immediately after the transfer from water to the nonpolar solvent. The same spectral change is observed when the heteropoly-CO_2 complexes are exposed to air for several hours.

The following reactivity patterns have been observed. Mn(II)-, Co(II)-, and Ni(II)-substituted Keggin silico- and germanotungstates ($SiW_{11}Mn^{II\,6-}$, $SiW_{11}Co^{II\,6-}$, $SiW_{11}Ni^{II\,6-}$, $GeW_{11}Mn^{II\,6-}$, $GeW_{11}Co^{II\,6-}$, $GeW_{11}Ni^{II\,6-}$) react with carbon dioxide, while Cu(II)- and Mn(III)-substituted silicotungstates ($SiW_{11}Cu^{II\,6-}$ and $SiW_{11}Mn^{III\,5-}$), a Co(II)-substituted borotungstate ($BW_{11}Co^{II\,7-}$), and all tested Keggin phosphotungstates ($PW_{11}Mn^{II\,5-}$, $PW_{11}Co^{II\,5-}$, and $PW_{11}Ni^{II\,5-}$) do not. Of all studied Wells−Dawson substituted phosphotungstates, α_2-$P_2W_{17}Mn^{II\,8-}$, α_2-$P_2W_{17}Co^{II\,8-}$, and α_2-$P_2W_{17}Ni^{II\,8-}$ do react, while α_2-$P_2W_{17}Cu^{II\,8-}$ and α_2-$P_2W_{17}Mn^{III\,7-}$ as well as the α_1 isomer of the Co(II) derivative do not. The only tested Weakley and Finke compound, $[(PW_9O_{34})_2Co_4]^{10-}$, was found not to react with CO_2.

For TMS HPA's that did form complexes with CO_2, the reactions were found to be completely reversible in all four investigated solvents. Bubbling nitrogen or evacuating the solutions yielded the original dry pentacoordinate spectra. Similar studies by Pope and Katsoulis concerning SO_2 and O_2 reactivity under the same conditions revealed that all of the listed compounds reacted with SO_2, but only two complexes ($[XW_{11}O_{39}Mn^{II}]^{6-}$, where X = Si, Ge) reacted with O_2.[2] In addition, reactions with SO_2 were found to be irreversible (except for the Weakley and Finke complex), while reactions with dioxygen were fully reversible.

When the solutions of complexes formed between heteropolyanions and CO_2 are heated, their colors revert to those of the original dry pentacoordinate species, indicating the loss of coordinated CO_2. This process is fully reversible, and the

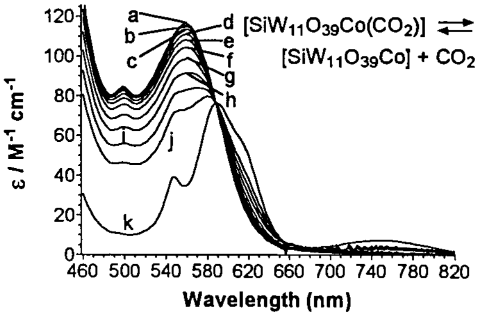

Figure 4. Visible spectra of α-$[SiW_{11}O_{39}Co(CO_2)]^{6-}$ in toluene vs temperature. Letters correspond to temperature (°C) and percent reacted, as follows: (a) 0 °C, 100%; (b) 10 °C, 99%; (c) 20 °C, 97%; (d) 30 °C, 94%; (e) 40 °C, 91%; (f) 50 °C, 87%; (g) 60 °C, 80%; (h) 70 °C, 71%; (i) 80 °C, 60%; (j) 90 °C, 47%; (k) unreacted.

colors of CO_2 complexes return when the solutions are cooled. Figure 4 demonstrates this thermochromic behavior for the $SiW_{11}Co-CO_2^{6-}$ complex. We discovered that it is possible to match the observed spectra with computer-generated linear combinations of observed spectra for the dry and CO_2 complex from Figure 2. The results of the computer fits are reported in Figure 4 as percentages of CO_2 complexes in the computer fit.

B. More Detailed Studies with α-$[SiW_{11}O_{39}Co^{II}]^{6-}$. More detailed studies were performed for the cobalt-substituted Keggin silicotungstate $SiW_{11}Co^{6-}$, owing to its very significant changes in UV/vis spectra on CO_2 complexation, very effective purification, and favorable electronic relaxation times for characterization by NMR of paramagnetic cobalt[18] in heteropoly complexes.[19]

1. Role of Water. Experiments performed on a high-vacuum line revealed that a certain amount of water is necessary for $SiW_{11}Co^{6-}$ to react with CO_2. To determine the exact amount of water required for the reaction, absorbance at 556 nm was monitored as a function of water concentration. Starting with a very dry solution with a water-to-HPA ratio of 1:10, water was continuously added to the solution until the absorbance value reached a maximum. Interestingly, the amount of required water changes with the concentration of $SiW_{11}Co^{6-}$. We tested solutions with HPA concentrations of 5, 10, 50, 100, and 200 mM. The required concentrations of water for full reaction were 8, 10, 30, 40, and 50 mM, respectively. Therefore, the ratio of water to HPA changes from 1.6:1 to 1:4 as the concentration of $SiW_{11}Co^{6-}$ increases from 5 to 200 mM.

It was also discovered that the reactions of $SiW_{11}Co^{6-}$ with CO_2 do take place in very dry solutions (ratio of H_2O to $SiW_{11}Co^{6-}$ less than 1:10), in the presence of methyl or ethyl alcohol. The electronic and IR spectra of CO_2 complexes prepared in the presence of alcohol are identical with the spectra recorded in the presence of the required amount of water.

2. Other Ligands. There is no reaction of $SiW_{11}Co^{6-}$ with dimethyl and diethyl carbonate. The visible spectra of $SiW_{11}Co^{6-}$ in these solvents are identical with those of the dry pentacoordinate species. Addition of water to these solutions leads to the hydrated species. In addition, $SiW_{11}Co^{6-}$ does not react with dry diethyl pyrocarbonate (acid anhydride of the monoethyl ester of carbonic acid). Addition of water to that solution leads to decomposition of the heteropoly complex. Another very important observation is that $SiW_{11}Co^{6-}$ does not react with tetrabutylammonium bicarbonate, even when a very large excess of $TBAHCO_3$ is used and the temperature is lowered to −80 °C.

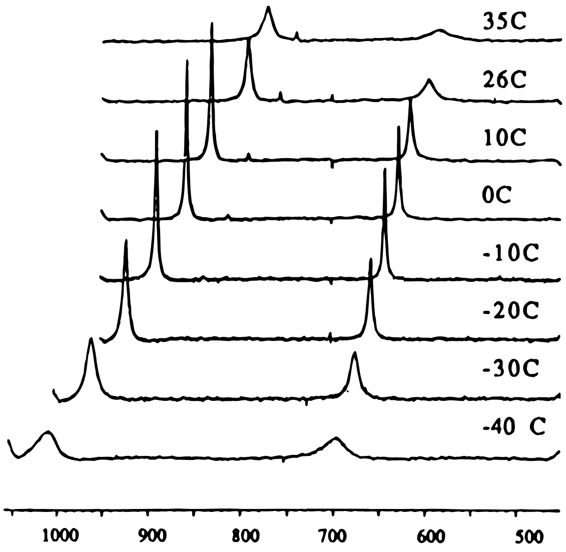

Figure 5. ^{13}C NMR spectra of 0.1 M α-$[SiW_{11}O_{39}Co(CO_2)]^{6-}$ in toluene at temperatures from −40 °C to +35 °C.

3. ^{13}C NMR Data. Figure 5 shows the low-field fragments (500−1000 ppm) of the ^{13}C NMR spectra for $SiW_{11}Co^{6-}$ in toluene, after the reaction with $^{13}CO_2$ in the presence of a small amount of water (H_2O:Co = 1:1) with temperatures ranging from −40 to 35 °C. Each spectrum has three new signals not seen before bubbling carbon dioxide. One peak at 125 ppm (not included in Figure 5) with a line width of less than 5 Hz is assigned as originating from $^{13}CO_2$ dissolved in the solvent.[16] Two other signals, whose chemical shifts and line widths are very sensitive to temperature, are shifted considerably downfield to 792 ppm ($\Delta_{1/2} = 400$ Hz) and 596 ppm ($\Delta_{1/2} = 1000$ Hz) at room temperature. These signals are assigned as originating from carbon atoms in a paramagnetic environment. The line widths of both signals decrease as the temperature increases from −40 to 0 °C (from 1550 to 200 Hz and from 1500 to 200 Hz for the downfield and upfield peaks, respectively), but that relationship inverts at higher temperatures. In the temperature range from 0 to 35 °C the line widths increase with temperature (from 200 to 800 Hz and from 200 to 1600 Hz for the downfield and upfield peaks, respectively). The downfield peak has a larger integration at all temperatures. The integration ratio of these two signals remains relatively constant in the temperature range from −40 to 10 °C ($I_1/I_2 = 1.3$), but it increases to almost 3.0 as the temperature increases to 35 °C. See Table 2 for the summary of these NMR data. Integration ratios and line widths are difficult to determine above 40 °C, owing to the significant decrease in signal-to-noise ratio caused by further increase in the line widths and the decomposition of the CO_2 complex to the dry complex. Adding water lowers the total integration of the signals, but the integration ratio is not affected.

The same spectra taken in the presence of methyl or ethyl alcohol have only two new signals; one at 125 ppm (dissolved CO_2) and one in the paramagnetic region, with a chemical shift of 770 ppm at room temperature. The chemical shift of the paramagnetic signal changes from 930 ppm at −30 °C to 745 ppm at 40 °C. The line width of this signal changes from 400 Hz at −30 °C to 650 Hz at 40 °C. As in the presence of water, the signal-to-noise ratio decreases considerably at temperatures above 40 °C.

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Table 1. Solution Visible Spectra (nm) of Heteropolyanion−Aquo, Dry Heteropolyanions, and Heteropolyanion−CO_2 Complexes in Toluene[a]

anion type	mol formula	hydrated heteropolyanion $MO_5(H_2O)$	dry heteropolyanion MO_5	complex with CO_2
α-Keggin silicotungstate	α-$[SiW_{11}O_{39}Co^{II}]^{6-}$	494 (55), 520 (59), 538 (59)[b]	548 (57), 586 (78), 617 (44) sh, 744 (7.1)[b]	502 (80), 556 (120) broad
	α-$[SiW_{11}O_{39}Mn^{II}]^{6-}$	no peaks obsd[b]	no peaks obsd[b]	no peaks obsd, complex forms[c]
	α-$[SiW_{11}O_{39}Ni^{II}]^{6-}$	700 (7), 704 (6) sh[b,d]	710 (5.1) v broad	708 (7); 760 (6.8) v broad
	α-$[SiW_{11}O_{39}Cu^{II}]^{6-}$	loss of water on transfer[b]	712 (17) broad[b]	no reacn
	α-$[SiW_{11}O_{39}Mn^{III}]^{5-}$	514 (156), 540 (140) sh	*e*	no reacn
α-Keggin germanotungstate	α-$[GeW_{11}O_{39}Co^{II}]^{6-}$	496 (56), 520 (60), 540 (60)	546 (40), 588 (78), 617 (45) sh, 750 (8)	494 (55), 576 (82) broad
	α-$[GeW_{11}O_{39}Mn^{II}]^{6-}$	no peaks obsd	no peaks obsd	no peaks obsd, complex forms[c]
	α-$[GeW_{11}O_{39}Ni^{II}]^{6-}$	750 (3) v broad	488 (3.5) sh, 732 (3.1) broad	712 (4.8), 790 (5.6)
α-Keggin phosophotungstate	α-$[PW_{11}O_{39}Co^{II}]^{5-}$	496 (87) sh, 518 (110), 542 (107), 604 (91)	530 (70) sh, 546 (80), 612 (76)[f]	no reacn
	α-$[PW_{11}O_{39}Mn^{II}]^{5-}$	no peaks obsd[b]	no peaks obsd[b]	no peaks obsd, no reacn[c]
	α-$[PW_{11}O_{39}Ni^{II}]^{5-}$	720 (1.5) v broad	no peaks obsd	no reacn[c]
α-Keggin borotungstate	α-$[BW_{11}O_{39}Co^{II}]^{7-}$	546 (39), 580 (37), 612 (27) sh	552 (51), 590 (80), 610 (75) sh, 764 (20)[b]	no reacn
Wells−Dawson phosphotungstate	α$_2$-$[P_2W_{17}O_{61}Co^{II}]^{8-}$	490 (52) sh, 520 (48), 540 (46)[b]	545 (60), 594 (70)[b]	562 (90) broad
	α$_1$-$[P_2W_{17}O_{61}Co^{II}]^{8-}$	500 (54) sh, 546 (50)	546 (55), 596 (96), 756 (17) broad	no reacn
	α$_2$-$[P_2W_{17}O_{61}Mn^{II}]^{8-}$	no peaks obsd	no peaks obsd	no peaks obsd, complex forms[c]
	α$_2$-$[P_2W_{17}O_{61}Ni^{II}]^{8-}$	698 (5) broad, 780 (4) sh	738 (6) broad	712 (8) broad, 786 (9) broad
	α$_2$-$[P_2W_{17}O_{61}Cu^{II}]^{8-}$	loss of water on transfer	700 (35) broad	no reacn
	α$_2$-$[P_2W_{17}O_{61}Mn^{III}]^{7-}$	458 (320)	*e*	no reacn
Weakley and Finke phosphotungstocobaltate	α-$[PW_9(O_{34})_2Co^{II}_4]^{10-}$	500 (60) sh, 560 (98) broad[b,g]	516 (54) sh, 550 (102), 576 (110) sh, 600 (116)[b,h]	no reacn

[a] Molar extinction coefficients are given in parentheses. [b] The same as reported in refs 2b,c. [c] Based on IR spectrum. [d] sh = shoulder. [e] No change in spectrum upon drying indicates no loss of water in toluene. [f] Mixture of six- and five-coordinate species, as reported also in ref 2b. [g] Two out of four cobalt atoms in the structure are $CoO_5(H_2O)$, and the other two are CoO_6. [h] Two out of four cobalt atoms in the structure are CoO_5, and the other two are CoO_6.

Table 2. ^{13}C NMR Data in Toluene for Complexes Formed between α-$[SiW_{11}O_{39}Co^{II}]^{6-}$ and CO_2 in the Presence of Water

temp (°C)	chem shift (ppm)		line width (Hz)		integration ratio I_1/I_2
	δ_1	δ_2	$(\Delta\nu_{1/2})_1$	$(\Delta\nu_{1/2})_2$	
35	765	583	800	1600	2.8
26	792	596	400	1000	1.6
10	833	616	250	380	1.3
0	861	630	200	200	1.3
−10	890	644	290	253	1.3
−20	930	660	370	300	1.3
−30	958	675	800	650	1.3
−40	1010	697	1550	1500	1.3

4. Vibrational Spectra with Isotopically Enriched $^{13}CO_2$ and $C^{18}O_2$. The vibrational frequency observed at 1347 cm^{-1} for the complex with natural abundance CO_2 was shifted to 1340 cm^{-1} for $^{13}CO_2$ and to 1331 cm^{-1} for $C^{18}O_2$, while the peak at 1673 cm^{-1} was shifted to 1633 and 1657 cm^{-1}, respectively.

5. Magnetic Susceptibility. Magnetic moments determined by Evans methods were 4.7, 4.6, and 4.6 for "hydrated", "dry", and "CO_2" complex, respectively.

Discussion

A. Reactions with CO_2. There is no doubt that certain transition-metal-substituted heteropolytungstates in nonpolar solvents form complexes with carbon dioxide. This statement is supported by changes in electronic and IR spectra and new ^{13}C NMR signals in the paramagnetic region for $SiW_{11}Co^{6-}$. The electronic spectra of new CO_2 complexes are similar to, but not identical with, those of aqua anions and are consistent with the attachment of the CO_2 ligand to the vacant coordination position.[2c] The reactions are fully reversible and are temperature-dependent. The temperature dependence of electronic spectra and the presence of the isosbestic point (see Figure 3) indicate the existence of two species at equilibrium: the dry pentacoordinate complex of the substituted transition metal and its hexacoordinate analogue, in which carbon dioxide fills the empty coordination site. It is possible to determine the percentages of both species at various temperatures by fitting the observed spectra with a linear combination of spectra for dry and CO_2 complexes. Excellent fits are obtained. The contribution of the CO_2 complex to the linear combinations at various temperatures is listed in the caption of Figure 4.

On the basis of reported data, it appears that no copper(II)- or manganese(III)-substituted HPA's react with CO_2, while the reactivity of cobalt(II), nickel(II), and manganese(II) complexes depends on the heteroatom and the geometry of the complex. Germano- and silicotungstates with the α-Keggin structure substituted with these three metals favor complex formation, while boro- and phosphotungstates are unreactive. However, α$_2$ isomers of Wells−Dawson phosphotungstates show reactivity similar to that of α-Keggin silicotungstates; i.e., cobalt(II), nickel(II), and manganese(II) derivatives do react with CO_2. On the other hand, the α$_1$ isomer of $P_2W_{17}Co$ behaves similarly to α-$PW_{11}Co$ and does not react with CO_2.

B. Structural Features of New Complexes. In general, reactions of transition-metal compounds with carbon dioxide can lead to many different types of structures: from classical carbonato (or bicarbonato) complexes to "real" CO_2 complexes. We have excluded any other complexes that would require oxidation state changes in the complexation, i.e., oxalates, formates, or other carboxylate complexes. We justify this conclusion by noting that there is no magnetic moment change for $SiW_{11}Co^{6-}$ after CO_2 complexation, indicating no change in the oxidation state for cobalt. Also excluded is the possibility that carbon dioxide does not bind to the transition metal but to the basic surface oxygen atoms, because neither unsubstituted

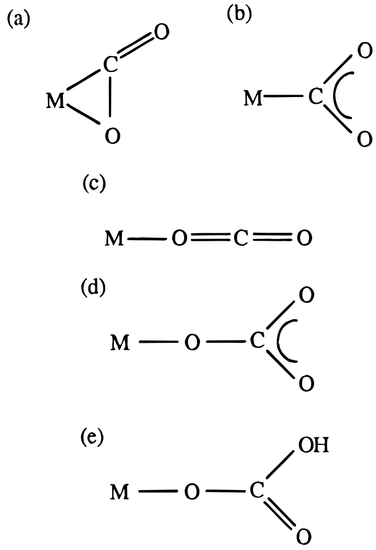

Figure 6. Possible binding modes with transition metals for CO_2 (a−c), monodentate carbonate (d), and bicarbonate complexes (e).

nor lacunary HPA's react with carbon dioxide, as indicated by no changes in their IR spectra, after CO_2 is bubbled. In addition, the complexes with CO_2 form in the presence of a 3:1 excess of triflic acid, when the most basic surface oxygens become protonated. Figure 6 shows three possible structures of real CO_2 complexes, as well as carbonato and bicarbonato complexes.

All investigated complexes of the heteropolyanions with carbon dioxide show two new absorptions in IR spectra, one around 1673 cm^{-1} (1672−1675 cm^{-1}) and the second one a round 1349 cm^{-1} (1348−1350 cm^{-1}). Comparison of these absorptions with literature data reveals that they could be assigned most likely as originating from either real metal−CO_2 or metal-bicarbonato complexes.[20a,21]

Recently, Masceti et al.[20] developed vibrational spectroscopic criteria for the assignment of structure in CO_2 complexes. According to this work, there are two vibrations in CO_2 complexes with metals that should be considered. They are referred to as ν_1 and ν_3, symmetric and asymmetric stretching modes, and $\sum\Delta\nu$ represents the sum of the frequency shifts observed in the ν_1 and ν_3 modes in the labeled complexes ($^{13}CO_2$ and $C^{18}O_2$). The following relationships were developed.

(a) The C-coordination mode is characterized by small splittings of the ν_1 and ν_3 modes ($\nu_3 - \nu_1 \leq 400\ cm^{-1}$); $\sum\Delta\nu(^{13}C) \geq \sum\Delta\nu(^{18}O)$ with $60 < \sum\Delta\nu(^{18}O) < 70\ cm^{-1}$.

(b) For the end-on coordination mode $\nu_3 - \nu_1$ is very large ($>400\ cm^{-1}$) and isotropic shifts by ^{18}O are very large as well; $\sum\Delta\nu(^{13}C) < \sum\Delta\nu(^{18}O)$ and $\sum\Delta\nu(^{18}O) > 70\ cm^{-1}$.

(c) For the complexes with the side-on coordination mode $\nu_3 - \nu_1$ is of the same order of magnitude as the end-on mode, but the relationship between isotropic frequency shifts is reversed; $\sum\Delta\nu(^{13}C) \geq \sum\Delta\nu(^{18}O)$ and $\sum\Delta\nu(^{18}O) \leq 60\ cm^{-1}$.

Unfortunately, no similar research was performed for carbonato or bicarbonato complexes. Data reported in the literature concerning isotopic labeling for bicarbonato complexes include ^{13}C but not ^{18}O labeling.[22]

Infrared data for complexes formed by CO_2 and $SiW_{11}Co^{6-}$ show a relatively small splitting between ν_3 and ν_1 (324 cm^{-1}) and $\sum\Delta\nu(^{13}C) \geq \sum\Delta\nu(^{18}O)$ ($47 \geq 32$). These two observations support the η^1(C) coordination mode in the real CO_2 complex. According to Mascetti et al. that bonding mode should also be characterized by $60 < \sum\Delta\nu(^{18}O) < 70\ cm^{-1}$. However, the observed value is only 32 cm^{-1}. It is possible that the presence of hydrogen bonding involving oxygen atoms from CO_2 (vide infra) could affect the latter value significantly. However, no supporting data are present in the literature. The IR data including isotopic ^{13}C labeling for H-bonded CO_2 complexes[23] do not include any $C^{18}O_2$ studies.

Formation of CO_2 complexes with TMS HPA's requires some presence of water (or alcohols). We considered the following three hypotheses to explain this observation: (1) the complexes formed are really carbonato or bicarbonato compounds (alkyl carbonato in the presence of alcohols); (2) water (or alcohol) serves as a bridging ligand, and (3) water (or alcohol) is used for hydrogen bonding.

To investigate the first possibility (formation of carbonato or bicarbonato complexes), we attempted the preparation of real bicarbonato complexes by two different procedures. First, $SiW_{11}Co^{6-}$ was reacted with $TBAHCO_3$ in toluene. The solution remained green, indicating no reaction, even when a 20-fold excess of bicarbonate was added and the temperature was lowered to −80 °C. Similarly, no reaction was observed with $SiW_{11}Co^{6-}$ and the neat dry acid anhydride of monoethyl ester of carbonic acid, the reagent used successfully in the past to prepare alkyl carbonato complexes.[24] When water was added to these solutions, the HPA was decomposed, indicating acid hydrolysis of HPA by ethylcarbonic acid. In addition, there was no reaction between $SiW_{11}Co^{6-}$ and dimethyl and dialkyl carbonates. Another important observation is that vibrational frequencies of CO_2 complex with $SiW_{11}Co^{6-}$ do not change when alcohol replaces water. If the complexes formed in the presence of water and alcohol were bicarbonato and alkyl carbonato complexes, respectively, the vibrational frequencies would not be identical. Signals for bicarbonato and alkyl carbonato complexes of the same metal in an identical coordination environment reported in the literature differ by 15 cm^{-1}.[24]

On the basis of all of these observations, it seems very unlikely that the compounds prepared by reactions of carbon dioxide with TMS HPA's are either carbonato or bicarbonato complexes.

The possibility that water is a bridging ligand is rejected on the basis of the magnetic susceptibility measurements in solution. The magnetic moments of hydrated $SiW_{11}Co^{6-}$, dry $SiW_{11}Co^{6-}$, and $SiW_{11}Co^{6-}$ complexed with CO_2 have almost identical values: 4.7, 4.6, and 4.6, respectively. If two cobalt centers were bridged by a water molecule, then significant antiferromagnetic electron pairing would be expected, leading to lowering of the magnetic moment either when the complex is dried or when it is reacted with CO_2.

Therefore, we propose the hypothesis that water (or alcohol) is used to stabilize the CO_2 complex by hydrogen bonding. In fact, hydrogen bonding was also proposed by Katsoulis and Pope[2d] to explain a similar water requirement for complex formation between $SiW_{11}Mn^{6-}$ and dioxygen in toluene.

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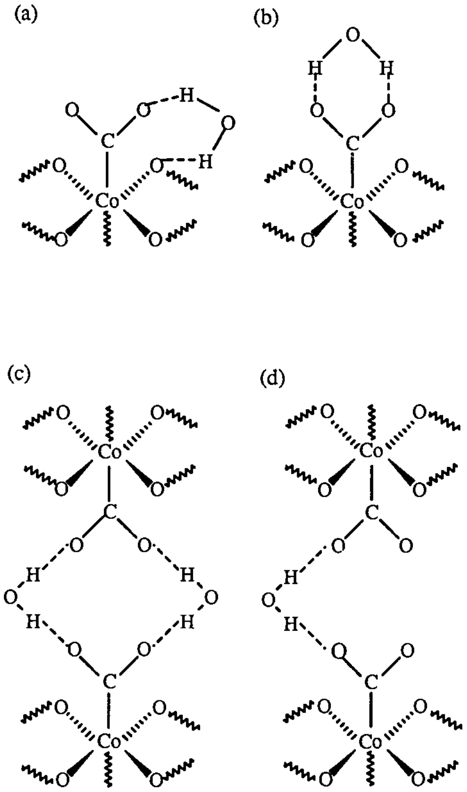

Figure 7. Proposed hypothetical bonding modes for CO_2 with cobalt in α-$[SiW_{11}O_{39}Co(CO_2)]^{6-}$, stabilized by hydrogen bonding utilizing both hydrogen atoms from water.

Oxygen atoms from coordinated CO_2 should be even more suitable for H-bonding than coordinated dioxygen.

Additional information concerning the bonding between CO_2 and cobalt is obtained from ^{13}C NMR spectra. Three new signals are observed in the ^{13}C NMR spectrum after CO_2 gas is reacted with $SiW_{11}Co^{6-}$. One of these peaks, located at 125 ppm, is easily assigned to CO_2 gas dissolved in the solvent.[16] Interestingly, there is no other new peak in the diamagnetic region, indicating that there is no free bicarbonate or carbonate present in solution. Carbon dioxide is the only diamagnetic carbon-containing species (except tetraheptylammonium groups and the solvent) present in solution. In addition to the signal at 125 ppm, there are two different ^{13}C NMR signals in the paramagnetic region of the spectrum when water is present, but only one in the presence of alcohol. Since the IR spectrum indicates only one kind of bonded CO_2, we postulate that both of these NMR signals represent CO_2 bound to cobalt and H-bonded to water at the same time. The only difference between the bondings is in the type of hydrogen bonding. One of the signals represents CO_2 bound to water using two hydrogen atoms for H-bonding, while the other one requires only one H atom from water or alcohol. Figure 7 shows four hypothetical ways in which a water molecule could H-bond with a complexed CO_2 molecule, using both of its hydrogens. Structures c and d contain water as a part of an extended bridge between two cobalt centers. This is not inconsistent with our previous statement concerning exclusion of water as a bridging ligand, on the basis of magnetic moments measurements. In Figure 7c,d the cobalt atoms are separated by six covalent and two hydrogen bonds, a highly unlikely situation for any significant antiferromagnetic coupling. Figure 8 shows two hypothetical structures in which only one atom of hydrogen from water molecule (or from an alcohol) is utilized for hydrogen bonding.

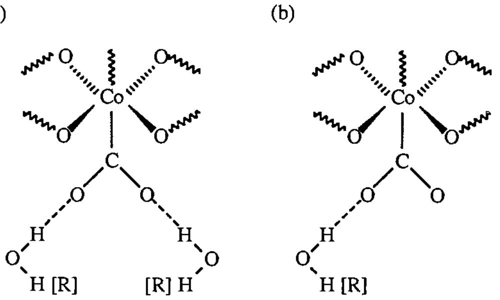

Figure 8. Proposed hypothetical bonding modes for CO_2 with cobalt in α-$[SiW_{11}O_{39}Co(CO_2)]^{6-}$, stabilized by hydrogen bonding utilizing one hydrogen atom from water or alcohol.

It is important to consider the reasons for stabilization of these CO_2 complexes by hydrogen bonding. They could be related to "anchoring" CO_2 to the heteropolyanion (Figure 7a), similarly to the structures reported for cobalt tetraaza macrocyclic complexes,[23] to stable ring formation (Figure 7b), or simply to the stabilization of a "bent" polar CO_2 molecule in the environment of the ion pair formed by HPA and tetraheptylammonium cations (the rest of the structures in Figures 7 and 8). The last possibility would explain why the water requirement is concentration-dependent. It is possible that as the concentration of the heteropoly complex increases, the structures of ion pairs change, affecting the environment within the ion pairs and subsequently the number of water molecules required to stabilize the CO_2 complex by H-bonding. In fact, it is highly likely that, depending on water concentration, the ion pairs between THA cations and HPA anions involve aggregates of various sizes, i.e., more than one HPA anion surrounded by THA cations.

The fact that the line widths for the two paramagnetic signals in the presence of water decrease with increasing temperature at lower temperatures, but that the trend is reversed at higher temperatures, clearly indicates that the two species are exchanging with each other.[25] Since the diamagnetic CO_2 signal remains narrow, the dissolved CO_2 does not participate in this exchange. There is considerably slower, if any, chemical exchange in the presence of alcohol. The line width of this signal is comparable to the line widths of two signals in the presence of water at lower temperatures, but it is much smaller at higher temperatures. The chemical shifts of both broad signals change with temperature, as expected for the paramagnetic species.

Conclusions

Multiple spectroscopic evidence indicates that certain transition-metal-substituted heteropolyanions react with carbon dioxide, forming reversible complexes. Our data support the hypothesis that these complexes are "real" CO_2 complexes with a direct η^1 metal−carbon bond. However, since we were unsuccessful in obtaining crystalline samples in the solid state of any of these complexes, our hypothesis cannot be confirmed by X-ray crystallography. In fact, it may be impossible ever to obtain crystals for these very bulky tetraheptylammonium cations.

Comparison of our data with the data reported by Pope et al. for reactions of TMS HPA's in nonpolar solvents with dioxygen and sulfur dioxide reveals a striking similarity between CO_2 data and the data for dioxygen.[2] In both cases the reactions are fully reversible and they both require the presence of water,

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(25) La Mar, G. N., Horrocks, W. D., Jr., Holm, R. H., Eds. *NMR of Paramagnetic Molecules*; Academic Press: New York, 1973; Chapters 2 and 8.

supposedly for hydrogen bonding. The reactions with SO_2 gas are irreversible for almost all HPA's, and they do not require the presence of water.

The reactivity pattern is not very well understood at this time. Clearly there must be a very delicate balance between the facility with which the terminal water ligand on the substituted transition metal is lost, the redox potential of the substituted metal, and the detailed geometry around the metal. The fact that the water ligand cannot be complexed too tightly to the metal for the reaction to take place is clearly seen in the nonreactivity of Mn(III) complexes, in which it is impossible to create the pentacoordinate environment around that metal. The importance of the detailed geometry is demonstrated by the nonreactivity of any of the Cu(II) derivatives, where a large Jahn–Teller distortion is expected. Most likely, the combination of all three effects determines the stability of a possible CO_2 complex. A very interesting observation concerns the reactivity of two different isomers of the cobalt-substituted Wells–Dawson complex. Of the two isomers, only one (α_2) reacts with CO_2. This observation could be explained by assuming that there is a real cobalt–carbon bond in the complex (supported also by IR data), which would require a certain amount of back-bonding. It was reported by Contant and Ciabrini[12a] that metals substituted in the belt of the Wells–Dawson structure (α_1 isomer) are easier to reduce than metals substituted in the cap (α_2 isomer). Therefore, cobalt in the α_1 isomer is more difficult to oxidize than cobalt in the α_2 isomer, which would make the back-bonding more favorable for Co in the α_2 isomer, leading to a stronger cobalt–carbon bond.

Final Comments Concerning the NMR Data. The NMR data presented in this paper deserve special comment. They represent the first ^{13}C NMR signals ever reported for octahedral paramagnetic Co(II) complexes, regardless of which structure of the two considered in this paper is proposed. To the best of our knowledge no ^{13}C NMR data exist in the literature for carbonato, bicarbonato, or real CO_2 complexes with Co(II). The lack of data for the last group is not surprising, owing to the small number of known CO_2 complexes. In fact, only one paramagnetic CO_2 complex (with Ni(II)) has been reported to date, although its ^{13}C NMR spectrum was not measured.[26] There were attempts to record ^{13}C spectra for paramagnetic cobalt–bicarbonato complexes in cobalt(II) human carbonic anhydrase, but no direct signal for carbon in a paramagnetic environment was ever detected.[16b] The conclusions in that work were based on the effect that the paramagnetic cobalt has on the line width of the *diamagnetic* bicarbonate ion present in solution, which is in exchange with the paramagnetic signal. Therefore, the ^{13}C NMR data presented in this paper are highly unique.

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(26) Fujita, E.; Brunschwig, B. S.; Cabelli, D.; Renner, M. W.; Furenlid, L. R.; Ogata, T.; Wada, Y.; Yanagida, S. In *Proceedings of the Fourth International Conference on Carbon Dioxide Utilization*; Elsevier Science: Amsterdam, in press.