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A Study of the Hydrolysis of Iron(III) Ion by Sodium Bicarbonate Using an Inert NMR Probe Technique

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The hydrolysis of ferric perchlorate by sodium bicarbonate at ionic strengths of 0.5–0.8 was studied by the proton peak broadenings and bulk susceptibility shifts of added methylene chloride in D_2O and by pH measurements of the solutions in H_2O. Hydrolysis was carried out by the addition of solid sodium bicarbonate. The proton peak broadenings decreased monotonically as the molar ratio of $NaHCO_3/Fe(ClO_4)_3$ was increased from 0.0 to 2.0 while the pH values and bulk susceptibility shifts changed from 0.0 to 1.0 but remained nearly constant from 1.0 to 2.0. Above a ratio of 2.0 the pH increased again and precipitation occurred. From the present work it is concluded that in the molar ratio range of 0.0–1.0 a paramagnetic monohydroxo monomer and a diamagnetic μ-oxo dimer are formed in approximate agreement with equilibrium expressions developed by earlier workers. In the 1.0–2.0 molar ratio range the ratio of monomers to dimers remains constant but new species of each type are formed. Postulated for the monomer is the FeO^+ species and for the dimer the $(OH)Fe–O–Fe(OH)^{2+}$ species. The latter is diamagnetic while the former still has five unpaired electrons but a short electron spin relaxation time, thus accounting for the constancy of the susceptibility but also the monotonic decrease of the proton peak broadenings in this range.

Introduction

The nature of the aquated Fe(III) ionic species in solutions of varying pH is a venerable problem. There seems to be general agreement on the behavior at low pH values. At pH values below 1, the sole species present is $Fe(H_2O)_6{}^{3+}$ while above this value hydrolysis occurs in steps. The first step is the formation of the hydroxopentaaquo complex (eq 1). A

$$Fe(H_2O)_6{}^{3+} = Fe(H_2O)_5(OH)^{2+} + H^+ \quad K_{11} \qquad (1)$$

small amount of the dihydroxotetraaquo complex is also formed (eq 2). The next step in the hydrolysis is in more

$$Fe(H_2O)_6{}^{3+} = Fe(H_2O)_4(OH)_2{}^+ + 2H^+ \quad K_{12} \qquad (2)$$

dispute. Until recently most workers in the field believed that the product was the dihydroxo dimer:[1-3]

$$2Fe(H_2O)_6{}^{3+} = (H_2O)_4Fe(OH)_2Fe(H_2O)_4{}^{4+} + 2H^+ \quad K_{22} \qquad (3)$$

But a recent Mössbauer study[4] has given fairly convincing evidence that the dimer is a μ-oxo complex (eq 4). However,

$$2Fe(H_2O)_6{}^{3+} = (H_2O)Fe–O–Fe(H_2O)_5{}^{4+} + 2H^+ \quad K_{22}' \qquad (4)$$

the Mössbauer study shows that at higher $NaHCO_3/Fe^{3+}$ ratios the μ-oxo species is converted into another species. The values of the equilibrium constants above have been determined by many workers and variations were found due to differences in ionic strength, but agreement is generally good. A typical set of values is $K_{11} = 1.84 \times 10^{-3}$, $K_{12} = 5 \times 10^{-7}$, and $K_{22} = 1.69 \times 10^{-3}$. The value for K_{22}' is presumably the same as for K_{22} since it is only the nature of the species that is in dispute. In all measurements ferric perchlorate was used as the source of iron in order to minimize the formation of complexes containing the anion in the inner sphere, as has been well-known to occur with chlorides and sulfates.[5] The pH values of the solutions were adjusted by the addition of sodium bicarbonate rather than sodium hydroxide because adding the latter, unless very carefully done, results in the formation of precipitates of hydrated iron oxides at pH values lower than would be expected from stoichiometry.

At pH values above 2.0 all measurements are in agreement with more associated species being dominant. Evidence for the trimer has been given by Arnek and Schylter[6] and by Judkins.[7] In a more recent study of the Fe(III) ion at higher pH values in 3 M sodium perchlorate, Ciavatta and Grimaldi[8] postulated the existence of $Fe_{12}(OH)_{34}{}^{2+}$ at pH values above 3.0. They did not find it necessary to include the trimer in order to explain their results.

The magnetic properties of the complexes are also in dispute. Mulay and Selwood[9] measured the magnetic susceptibilities of the solutions during hydrolysis and concluded that the dimer is diamagnetic. Schugar et al.[10] on the basis of their measurements concluded that the dimer has three unpaired electrons. From their Mössbauer measurements, Knudsen et al.[4] have argued for the diamagnetic complex.

In a new approach to the problem a study has been carried out at 30 °C with NMR by using an "inert second-coordination-sphere proton" probe. It was shown earlier[11] that while methylene chloride never enters the first coordination sphere of a complex ion, proton peak broadening occurs by an electronic–nuclear dipolar interaction with the unpaired electrons in paramagnetic ions. Although the broadenings are not very large, first-coordination-sphere interactions that occur in all complexes are avoided. This permits direct observation of the small but significant differences that take place as the pH values vary.

In conjunction with the NMR studies, a series of pH measurements were carried out. The pH values were measured at the same molar ratio of $NaHCO_3/Fe(ClO_4)_3$ as were used in the peak-broadening measurements except that H_2O was used instead of D_2O in the magnetic resonance study. Recent measurements have shown that the equilibrium constants measured in H_2O can vary by as much as a factor of 2 from those in D_2O but this difference was not considered to be important for the purposes of the present study. Because of the procedure for making the solutions the ionic strength varied but was in the range of 0.5–0.8.

Experimental Section

Anhydrous ferric perchlorate from Alfa Inorganics and sodium perchlorate monohydrate from G. Frederick Smith were used as received. The deuterium oxide was nominally 99.8% pure and was obtained from Merck Sharp & Dohme of Canada. All other chemicals and solvents were reagent grade.

All pH measurements were carried out at 25 °C with a Beckman Research pH meter with a Beckman glass electrode and a calomel electrode filled with NaCl to avoid precipitation of $KClO_4$. NMR peak-broadening measurements were made with a Varian A-60 spectrometer at 30 °C. Each complete set of measurements was made within the shortest possible time to avoid drift problems. All of the peak-broadening measurements at different iron concentrations extrapolated back to a zero-concentration broadening of $\Delta\nu_{1/2}$ of 1.5 ± 0.2 Hz.

Solutions were prepared by weighing ferric perchlorate, sodium perchlorate, and H_2O or D_2O in that order into volumetric flasks. For the pH measurements about 10 mL of solution was prepared for each measurement. Weighed amounts of solid sodium bicarbonate were added successively and pH measurements taken after the ev-

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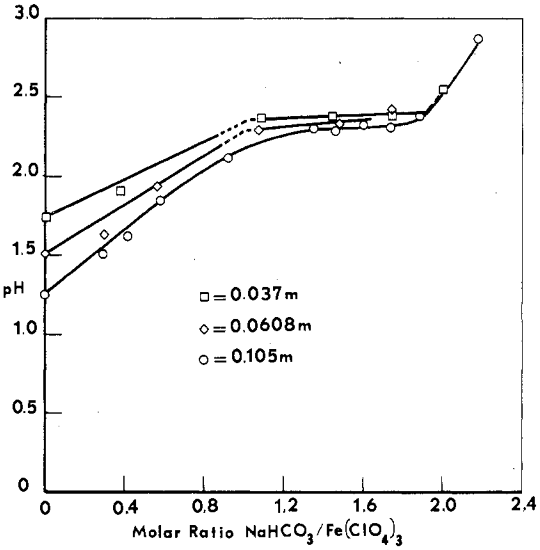

Figure 1. Plot of pH as a function of the molar ratio of $NaHCO_3/Fe(ClO_4)_3$.

olution of carbon dioxide had ceased. It was ascertained that little if any excess carbon dioxide was left in the solutions by passing gaseous nitrogen through some runs for a period of about 15 min. No change in the pH was observed. For the NMR measurements, approximately 6 mL of solution was prepared at each iron concentration. Weighed amounts of sodium bicarbonate were added to weighed amounts of about 1 mL of solution and peak broadenings observed. Each of the pH and peak-broadening measurements were made at as nearly the same molalities of ferric perchlorate, sodium perchlorate, and sodium bicarbonate as possible in order to minimize activity problems in the comparisons. For each set of sodium bicarbonate concentrations, the peak broadenings were proportional to the amount of ferric perchlorate as was shown earlier[11] for other transition metals.

Results

The pH measurements as a function of the $NaHCO_3/Fe(ClO_4)_3$ molar ratio are shown in Figure 1. All measurements were made within 1 h after the addition of solid sodium bicarbonate since there are slow changes that occur in the solution over a period of days that were not studied in the present work. The striking feature of the results is the plateau of constant pH values between 2.15 and 2.3 depending on the iron concentration over a molar ratio of 1.0–2.0. Surprisingly, this does not seem to have been reported previously. Any earlier plot or calculation of iron species as a function of pH is suspect since there is a region in which the iron species can change in an unrecognized manner.

The proton peak broadenings as a function of $NaHCO_3/Fe(ClO_4)_3$ molar ratio for the same iron concentrations are shown in Figure 2. The broadenings are greatest at low pH values where there is little else present but the hexaaquo and hydroxopentaaquo monomers and where Fe(III) is in a $^6A_{1g_{5/2}}$ state. The state is isoelectronic with that of Mn(II) which is known to have a long electron spin relaxation time, causing the correlation time for proton relaxation to be controlled by the rotational correlation time for methylene chloride. With the addition of sodium bicarbonate the concentration of dimer and higher polymers increases and the peak broadenings decrease as would be expected from a lower μ_{eff} as well as from a shorter electron spin relaxation time. The constancy of the measured magnetic susceptibility values in the 1.0–2.0 molar ratio range shown in Figure 2 contrasts with the montonic peak broadening decrease but is in agreement with the plateau of pH values in Figure 1.

Since the methylene chloride does not enter into the first coordination sphere of the complexes it can be used to measure the bulk susceptibility of the solution and from this the susceptibility of the complexes on the basis of the Evans method.[12] In the present situation it was assumed that the suceptibility values of the Fe(III) complexes at low pH values are due to five unpaired electrons. As the pH increases there will be a bulk susceptibility shift of the methylene chloride proton resonance as the magnetic susceptibility of the mixture decreases. In Figure 3 are shown the relative frequency shifts for the various iron concentrations as a function of pH, taking Fe^{3+} as zero. The change in susceptibility is then a decrease from that due to the five unpaired electrons of Fe^{3+}. In Figure 4 are shown the calculated magnetic susceptibility values in terms of Bohr magnetons as a function of molar ratio. In the molar ratio range 1.0–2.0 the number of unpaired electrons is nearly constant, suggesting that the degree of polymerization does not change.

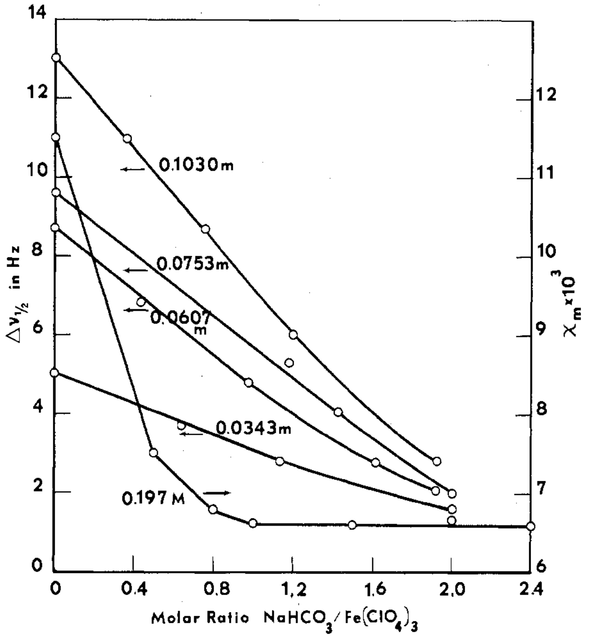

Figure 2. Plot of methylene chloride proton peak broadening and solution susceptibility as a function of the molar ratio of $NaHCO_3/Fe(ClO_4)_3$.

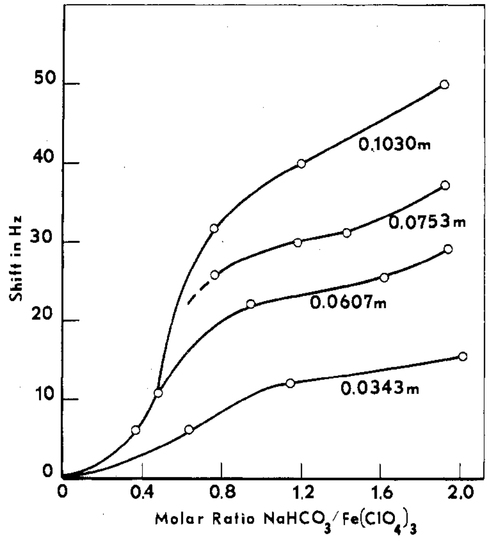

Figure 3. Plot of proton shifts of methylene chloride as a function of the molar ratio of $NaHCO_3/Fe(ClO_4)_3$.

Discussion

Any explanation of the present results must account for the observations that the pH and magnetic susceptibility values of the solutions vary in the $NaHCO_3/Fe(ClO_4)_3$ molar ratio

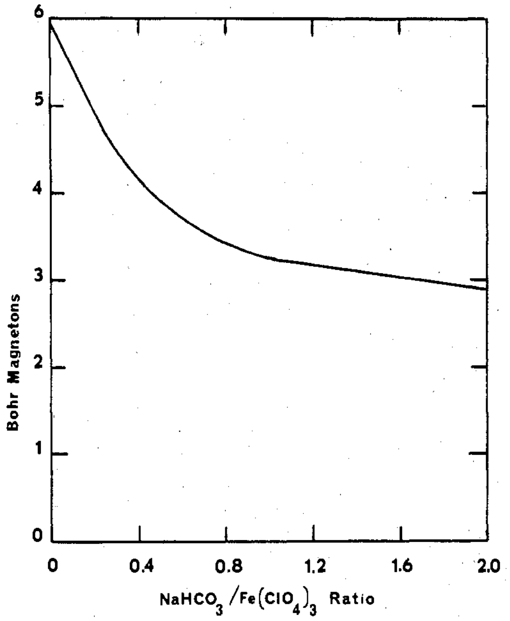

Figure 4. Plot of susceptibility of Fe(III) in Bohr magnetons as a function of the molar ratio of $NaHCO_3/Fe(ClO_4)_3$.

range of 0.0–1.0 but remain nearly constant in the 1.0–2.0 molar ratio range while the proton peak broadenings vary monotonically across the entire molar ratio range. In addition the results must be rationalized in the face of preceding work that in many cases is in disagreement. In the 0.0–1.0 molar ratio range the situation is reasonably described by the successive hydrolysis of Fe^{3+} to give first $FeOH^{2+}$ and then a dimer. The nature of the dimer or dimers is in dispute. Knudsen et al.[4] have interpreted their Mössbauer results as showing the presence of the decaaquo–μ-oxo dimer at mole ratios up to 0.5, in disagreement with most earlier workers. They further concluded that the dimer is diamagnetic at room temperature. This is in agreement with the present work. We find that the peak broadenings for each measured iron concentration at mole ratio 1.0 have decreased to approximately half of the corresponding value at mole ratio 0.0. If we make the assumption that both Fe^{3+} and $FeOH^{2+}$ have the same magnetic moment of 5.91 μ_B and their electron spin relaxation times are nearly the same, we would conclude that the magnetic susceptibilities of the solutions have decreased by a factor of 4 since $\chi \propto \mu^2$. On the basis of the bulk susceptibility shifts shown in Figure 3 and calculated magnetic moments in Figure 4, the relative measured magnetic moment at mole ratio 1.0 is about 0.55 of that at 0.0, giving a relative susceptibility of 0.30 compared with that at mole ratio 0.0.

The present susceptibility values in the molar range of 1.0–2.0 are less than those of Schugar and co-workers[10] which correspond to a magnetic moment of 3.96 μ_B. The Evans method used in the present work should be capable of higher accuracy than the Guoy-balance technique used earlier since it depends only on the frequency-shift difference between the starting solution containing monomer and the dimer solutions. This eliminates all bulk corrections that are necessary in the Guoy method. It should be noted that the plot in Figure 4 is the result of all of the frequency shifts shown in Figure 3 and that all measured points fell on the curve.

On the basis of the measured pH values shown in Figure 1 estimates were made of the concentrations of Fe^{3+}, $FeOH^{2+}$, and the dimer by using the K values and formula given by Knight and Sylva[14]

$$C = [Fe^{3+}](1.00 + K_{11}/[H^+] + 2K_{22}[Fe^{3+}]/[H^+]^2) \quad (5)$$

where C is the total iron concentration and the K values are those given in eq 1 and 3. Values of the two monomers and the dimer were calculated and used to calculate the expected peak broadenings of the proton on the assumption that the diamagnetic dimer does not contribute. The calculated peak broadenings were consistently less than those observed by about 25%. The reason for the deviation is not clear but it may be that eq 5 is not valid at the relatively high pH values. In the original work mole ratios up to 0.8 were calculated.

The behavior of Fe(III) in the 1.0–2.0 molar ratio range has not been considered previously since the constant pH value in this region has been shown only in this work. In this region the relatively constant magnetic susceptibility despite the decrease in proton peak broadenings must be explained. In an earlier work[15] Knudsen and co-workers suggested that in this range the oxo dimer reacts with the bicarbonate ion to form the dihydroxo species shown in eq 3. The dihydroxo species was supported by Deszi et al.[16] on the basis of Mössbauer studies at 4 K. However, in the more recent work,[4] Knudsen argues against the dihydroxo dimer since the Mössbauer spectrum of Deszi at 4 K does not match that of Spiro and co-workers[17] of an analogue of ferritin, a polymeric hydroxide, also taken at 4 K. The present work indicates that the susceptibility of the solution is nearly constant in this range, suggesting that no further polymerization occurs, assuming that all species except the monomer are diamagnetic. Since at a molar ratio of 1.0 there are appreciable amounts of monomer and dimer present, it is postulated that the effect of the bicarbonate is to produce new types of monomer and dimer in which the former has the same susceptibility but a shorter electron spin relaxation time while the latter is still diamagnetic. Three possible reactions are

$$Fe(H_2O)^{3+} + 2HCO_3^- = FeO^+ + 2H_2O + 2CO_2 \quad (6)$$

$$FeOH^+ + HCO_3^- = FeO^+ + H_2O + CO_2 \quad (7)$$

$$(H_2O)Fe{-}O{-}Fe(H_2O)^{4+} + 2HCO_3^- = (OH)Fe{-}O{-}Fe(OH)^{2+} + 2H_2O + 2CO_2 \quad (8)$$

None of the species on the right-hand sides of (6)–(8) have been suggested previously. However, the following arguments can be advanced in their favor. Most important, if eq 6–8 and 9 are added together, they give an overall stoichiometry of the

$$2Fe(H_2O)_2^{3+} + 2HCO_3^- = (H_2O)Fe{-}O{-}Fe(H_2O)^{4+} + 2H_2O + 2CO_2 \quad (9)$$

reaction of two bicarbonate ions for each Fe^{3+}. Second, they are in agreement with the conclusion that there is no further polymerization in the 1.0–2.0 molar ratio range, the latter based on the constancy of the pH and susceptibility. The magnetic susceptibility of the dihydroxo–μ-oxo dimer would be expected to be similar to that of the μ-oxo species in agreement with the observed constant susceptibility in this range. Likewise the susceptibility of the FeO^+ species should be similar to the other monomers but the electron spin relaxation time is expected to be shorter, accounting for the decreased peak broadening in the 1.0–2.0 molar ratio range. The dimer is a reasonable intermediate in the formation of the ferritin polymer suggested by Spiro et al.[17] since each iron atom in the latter is surrounded by two oxo and two hydroxo bridges to adjacent iron atoms. The monomer could condense between two dimer molecules to give the resultant structure. Finally, the reaction results in a reduction of charge densities on both dimer and monomer. Such behavior is to be expected since the presence of highly positively charged species with increasing pH leads to hydrolysis.

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Registry No. Fe^{3+}, 20074-52-6; HCO_3^-, 71-52-3; FeO^+, 70644-17-6; $(OH)Fe\text{-}O\text{-}Fe(OH)^{2+}$, 70644-18-7.

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Carbon-13 Nuclear Magnetic Resonance Study of Coordinated Thiocyanate, Selenocyanate, and Cyanate[1]

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Carbon-13 chemical shifts have been measured for thiocyanate, cyanate, and selenocyanate in a variety of transition-metal complexes. The effects of cation and solvent changes upon the chemical shifts of the ionic pseudohalides have been determined. Changes in hybridization are more important than electron excitation energy changes and substituent changes in determining chemical shifts, for both ionic and complexed species. The ordering of the ions in terms of increasing shielding is $SCN^- < OCN^- < SeCN^-$. The ordering for thiocyanate and selenocyanate in terms of increasing shielding as a function of bonding mode is M–NCS(Se) < NCS(Se)$^-$ < M–S(Se)CN. The technique is therefore of considerable utility in the determination of the bonding mode adopted by these groups in solutions of the complexes.

Introduction

The problem of determining the bonding modes adopted by coordinated ambidentate pseudohalide ions such as NCO^-, NCS^-, and $NCSe^-$ has been addressed by the implementation of a wide variety of physical techniques,[2,3] e.g., X-ray diffraction, ESCA, mass spectrometry, and infrared, Raman, electronic, nuclear quadrupole resonance, and nuclear magnetic resonance spectroscopy. These studies of pseudohalide complexes in the solid and gaseous phases, as well as in liquid solution, have met with widely varying degrees of success, and the pros and cons of each technique have been discussed in the reviews cited and in the references contained therein.[2,3]

The NMR techniques employed have ranged from indirect methods, wherein nuclei external to the pseudohalides are probed, to direct utilization of NMR-active nuclei in the pseudohalides themselves. An excellent example of the former is found in the study, by Marzilli et al.,[4] of the Co–SCN/Co–NCS ratios in a series of *trans*-[Co(dimethylglyoximate)$_2$L(thiocyanate)] complexes as a function of the chemical shifts and relative peak areas of the methyl protons of the dimethylglyoximate groups. Most of the work in the latter class has involved ^{14}N NMR studies of thiocyanate complexes,[5] although the technique has been successfully applied to cyanate[6,7] and selenocyanate[8] complexes to a much more limited extent. Prior to our preliminary report[9] of this work, the only published studies involving ^{13}C NMR data for pseudohalides were restricted to organic and ionic species[10] and four chromium– and tungsten–alkyl thiocyanate complexes of the type $M(CO)_5(NCS\text{–}R)$.[11] We now wish to report the details of our complete study, which has demonstrated the efficacy of using the ^{13}C chemical shifts of coordinated thiocyanate and selenocyanate as an excellent diagnostic tool for bonding-mode determinations of these groups. The use of the ^{13}C data as a solution probe for pseudohalide complexes promises to be a powerful complement to the recently developed[12] ^{14}N NQR solid-state probe.

Experimental Section

Preparation of Compounds. All chemicals and solvents used were of reagent grade or better. Ethyl thiocyanate, ethyl isothiocyanate, potassium cyanate, $K_2[Hg(SCN)_4]$, and all simple thiocyanate salts were used as obtained commercially. Samples of $K_2[Pt(SCN)_4]$, $K_2[Pd(SCN)_4]$, and $K_2[Zn(NCS)_4]$ were provided by Mr. W. C. Fultz of the University of Delaware. The $K_2[Pd(SCN)_4]$ was converted to the tetra-*n*-butylammonium salt by metathesis in methanol using [*n*-Bu_4N]Cl. The following compounds were prepared according to methods given in the literature (modifications in parentheses): $K[Au(SCN)_2]$,[13] [Au(ethylenethiourea)SCN],[14] $[Co(CN)_5X]^{3-}$,[15,16] $[Co(NH_3)_5X]^{2+}$ ($[Co(NH_3)_5NCS]SO_4$ was converted to the more soluble acetate salt by suspending it in aqueous solution and treating it with an aqueous solution of barium acetate; the latter was added until the former completely dissolved, whereupon the precipitated barium sulfate was removed by filtration, and the product was isolated by evaporating the solution to dryness),[15,16] [M(pyridine or 4-*tert*-butylpyridine)$_2$(NCO)$_2$] (M = Cd, Zn),[17] $K_2[Hg(SeCN)_4]$,[18] [*n*-Bu_4N]NCSe,[18] KSeCN,[19] *trans*-[Co(dimethylglyoximate)$_2$(4-*tert*-butylpyridine)CNS] (allowed to isomerize in solution, giving both linkage isomers, prior to the ^{13}C NMR measurement),[20] [*n*-Bu_4N]$_2$[Pd(SeCN)$_4$],[18] $[Ni(PR_3)_2(NCS)_2]$ (R = Et, *n*-butyl; solutions of $Ni(NCS)_2$ in ethanol prepared by metathesis from $Ni(NO_3)_2 \cdot 6H_2O$ and KSCN, with KNO_3 removed by filtration; addition of phosphines carried out under N_2),[21] [M(4-*tert*-butylpyridine)$_2X_2$] (M = Cd, Zn; X = NCS^-, $NCSe^-$; order of addition of reagents altered for $NCSe^-$ complexes: 4-*tert*-butylpyridine added to the aqueous solution of $M(NO_3)_2 \cdot 6H_2O$ prior to the addition of an acetonitrile (rather than aqueous) solution of KSeCN, thereby minimizing the decomposition of $SeCN^-$),[22] $[Et_4N]_2[M(NCS)_4]$ (M = Zn, Cd),[23] [Cu(P-*n*-Bu$_3$)SCN]$_4$.[24]

^{13}C NMR Measurements. The ^{13}C chemical shifts were obtained by using a pulsed Bruker HFX-90 spectrometer. The chemical shifts were measured at natural abundance; compounds were therefore chosen with reasonably good solubility in the deuterated solvents used for locking purposes. In the case of ethyl thiocyanate, a few drops of C_6D_6 were added for this reason. A concentration of ca. 0.5 M

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