reochemical lability of eight-coordinate species in solution is well established.[16] The existence of many interconverting geometrical isomers has been proposed previously as an explanation to account for the apparent axial symmetry of lanthanide shift reagent adducts in solution.[17]

Registry No. $Pr(tren)(ClO_4)_3$, 57674-50-7; $Gd(tren)(ClO_4)_3$, 57674-51-8; $Er(tren)(ClO_4)_3$, 57674-52-9; $La(tren)_2(ClO_4)_3$, 57674-54-1; $Pr(tren)_2(ClO_4)_3$, 57674-56-3; $Sm(tren)_2(ClO_4)_3$, 57674-57-4; $Eu(tren)_2(ClO_4)_3$, 57674-58-5; $Nd(tren)_2(ClO_4)_3$, 57674-59-6; $Gd(tren)_2(ClO_4)_3$, 57674-60-9; $Er(tren)_2(ClO_4)_3$, 57674-61-0; $Y(tren)_2(ClO_4)_3$, 57674-63-2.

Supplementary Material Available: Tables II and III listing elemental analyses and chemical shift data (2 pages). Ordering information is given on any current masthead page.

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Contribution from the P. M. Gross Chemical Laboratory, Department of Chemistry, Duke University, Durham, North Carolina 27706

Synthesis of Monocyanocobaloximes

Alvin L. Crumbliss* and Paul L. Gaus

Received July 28, 1975 AIC505491

The air oxidation method of Tschugaeff[1] has been applied to the synthesis of numerous monoacidocobaloximes[2,3] of the type $Co(dmgH)_2(X)(B)$, where X represents an acido anion and B an uncharged ligand. However, there have been reports[4-6] concerning the inadequacy of this general synthetic method for certain cobaloxime complexes. In these cases, the primary product isolated was the undesirable coordination isomer $[Co(dmgH)_2(B)_2][Co(dmgH)_2(X)_2]$.

Two explanations have been presented to account for the appearance of these mixed salts. One argument is based on the relative lability of the ligands X and B,[5] and the other[4] proposes a catalytic path involving trace amounts of cobalt(II).[7,8]

Although numerous approaches to the synthesis of monocyanocobaloximes can be taken, they are not all equally reliable or efficient. For example, whereas the direct air oxidation method[1] does produce $Co(dmgH)_2(CN)(B)$, the yields are low and separation of this material from the product mixture can be difficult (see below and ref 6). Marzilli and co-workers reported[4] the direct conversion of $Co(dmgH)_2(Cl)(py\text{-}t\text{-}Bu)$ to $Co(dmgH)_2(CN)(py\text{-}t\text{-}Bu)$ in 44% yield but have not extended the method to ligands other than *tert*-butylpyridine. Egen and Krause[9] reported the synthesis of $Co(dmgH)_2(CN)(B)$ (B = py, aniline, or 3,5-lutidine) from $[(C_6H_5)_2I][Co(dmgH)_2(CN)_2]$. However, this appears not to be a general synthetic route, and in the case of pyridine the reaction is very slow (1 week at reflux).

In this report we wish to describe a general synthetic method for the synthesis of monocyanocobaloximes $Co(dmgH)_2(CN)(B)$ in high yields without the formation of the mixed-salt coordination isomer.

Experimental Section

Preparation of Complexes. $Co(dmgH)_2(Cl)(py)$[3,4] and $Co(dmgH)_2(SCN)(py)$[3] were synthesized according to published procedures.

$Co(dmgH)_2(SCN)(NH_3)$ was synthesized by treating a water suspension of $Co(dmgH)(dmgH_2)(NCS)(SCN)$[10] with concentrated NH_4OH. The resulting dirty yellow suspension was filtered, washed with ethanol and ether, and dried in vacuo. Although the compound was previously reported[11] as the aquo complex $Co(dmgH)_2(SCN)(OH_2)$, the infrared spectrum and elemental analyses conclusively demonstrate the presence of coordinated NH_3.

$K[Co(dmgH)_2(SCN)(CN)]$ was synthesized by treating a suspension of $Co(dmgH)_2(SCN)(py)$, 2.50 g (5.86 mmol), or $Co(dmgH)_2(SCN)(NH_3)$, 2.13 g (5.86 mmol), in 100 ml of ethanol with 0.382 g (5.86 mmol) of KCN dissolved in a minimum of water. (Product yields are maximized when pure S-bonded starting materials are used.) This suspension was heated to 40–50 °C for 20 min, during which time the brown suspension changed to a red solution. The solution was concentrated and cooled to give red crystals of $K[Co(dmgH)_2(SCN)(CN)]$, which were filtered, washed with methanol and ether, and dried in vacuo; yield 90%.

The bonding mode of all thiocyanato complexes was established in solution or solid state on the basis of the intensity of the SCN group ν_{CN} absorption band at ca. 2120 cm^{-1},[10,12] Isomeric purity was demonstrated on the basis of ^1H NMR data in CH_2Cl_2 for $Co(dmgH)_2(SCN)(py)$ and $Co(dmgH)_2(SCN)(NH_3)$ and in $C_6H_5NO_2$ for $K[Co(dmgH)_2(SCN)(CN)]$.

$Co(dmgH)_2(CN)(py)$. The direct air oxidation method[1,3] resulted in the isolation of a light brown product mixture which was separated using a chromatographic column of 60–100 mesh Florisil (Fisher Scientific Co., F-100). A CH_3OH solution of the product was loaded onto the column (1 g of product/100 g of Florisil), which was in $CHCl_3$, and then eluted with a solvent containing increasing amounts of CH_3OH in $CHCl_3$, beginning with 10% (v/v) CH_3OH. A yellow band which represented <10% of the product mixture was eluted first and identified as the desired product $Co(dmgH)_2(CN)(py)$ by ^1H NMR, ir, and elemental analysis. A second band was partially separated into two more bands (dark brown and orange). Resolution was lost, however, upon elution with 100% CH_3OH. The product from the second band was isolated and found to be only sparingly soluble in polar solvents. Ir spectra (KBr disk) of this fraction show two broad ν_{CN} absorptions centered at 2150 and 2190 cm^{-1}, consistent with $[Co(dmgH)_2(CN)_2]^-$ [10] and cyano-bridged species,[13] such as $[NCCo(dmgH)_2\text{–}CN\text{–}Co(dmgH)_2CN]^-$ and $NCCo(dmgH)_2\text{–}CN\text{–}Co(dmgH)_2py$, and/or higher molecular weight cyano-bridged species being present.

Alternatively, $K[Co(dmgH)_2(SCN)(CN)]$, 0.965 g (2.34 mmol), was suspended in 100 ml of methanol and treated with 10 ml of pyridine. The resulting red solution was stirred at 50–60 °C for 24 h. The methanol was removed under reduced pressure, and water was added to induce precipitation as a yellow powder. The product was recrystallized from methanol–water, washed with water, ethanol, and ether, and dried in vacuo; recrystallized product yield 60%.

$Co(dmgH)_2(CN)(B)$ (B = py-3-Cl, py-4-NH_2, NH_3). These compounds were prepared from $K[Co(dmgH)_2(SCN)(CN)]$ in a manner analogous to the above synthesis of $Co(dmgH)_2(CN)(py)$, using 10 ml of py-3-Cl, 5 ml of concentrated NH_4OH, or 0.958 g of py-4-NH_2 in 10 ml of H_2O; recrystallized product yield 60–80%.

$Co(dmgH)_2(CN)(pip)$. The piperidine complex was prepared from $K[Co(dmgH)_2(SCN)(CN)]$ as described above for the pyridine and 3-chloropyridine complexes; recrystallized product yield 50%. The

Table I. ^{1}H NMR and Ir Data for the Monocyanocobaloximes $Co(dmgH)_2(CN)(B)$

Complex	δ_{dmgH},[a] ppm	ν_{CN},[b] cm^{-1}
$Co(dmgH)_2(CN)(py\text{-}3\text{-}Cl)$	2.27	2149
$Co(dmgH)_2(CN)(py)$	2.23	2147
$Co(dmgH)_2(CN)(py\text{-}4\text{-}NH_2)$	2.19	2144
$Co(dmgH)_2(CN)(pip)$	2.35	2142
$Co(dmgH)_2(CN)(NH_3)$	[c]	2140

[a] $CDCl_3$ solvent with TMS internal reference. [b] $CHCl_3$ at ca. 10^{-5} M. [c] Low solubility.

piperidine complex was also prepared via a substitution reaction whereby piperidine substitutes for pyridine in $Co(dmgH)_2(CN)(py)$. $Co(dmgH)_2(CN)(py)$, 1.0 g, was suspended in 20 ml of water, and treated with 1.0 ml of piperidine. The piperidine served to dissolve the $Co(dmgH)_2(CN)(py)$, presumably by reason of an acid–base reaction with an oxime proton. When heated to 50 °C, the yellow solution slowly (10 h) deposited the desired product as a yellow powder, which was recrystallized from methanol–water; recrystallized product yield 80%.

Physical Measurements. Infrared spectra were obtained using a Perkin-Elmer 621 spectrophotometer. ^{1}H NMR spectra were obtained using a JEOL JNM-MH-100 spectrometer. Satisfactory elemental analyses were obtained for all compounds by MHW Laboratories, Garden City, Mich.

Results and Discussion

Application of the air oxidation method[1] to the synthesis of $Co(dmgH)_2(CN)(py)$ resulted in the formation of a mixture containing less than 10% of the desired product, cyano-bridged cobaloximes, and $[Co(dmgH)_2(py)_2][Co(dmgH)_2(CN)_2]$. An improved general synthesis of $Co(dmgH)_2(CN)(B)$ in high yield is afforded by a method which was adapted from the work of Ablov et al.[14] and is depicted in reactions 1–3 where

$$Co(dmgH)_2(X)(B') + CN^- \rightarrow Co(dmgH)_2(X)(CN)^- + B' \quad (1)$$

$$Co(dmgH)_2(X)(CN)^- + CN^- \rightarrow Co(dmgH)_2(CN)_2^- + X^- \quad (2)$$

$$Co(dmgH)_2(X)(CN)^- + B \rightarrow Co(dmgH)_2(CN)(B) + X^- \quad (3)$$

X = SCN^-, B' = py or NH_3, and B is an uncharged ligand. When S-bonded $Co(dmgH)_2(SCN)(B')$ (B' = NH_3, py) is treated with 1 equiv of CN^-, reaction 1 proceeds to completion, requiring ca. 20 min for the consumption of 1 mmol of $Co(dmgH)_2(SCN)(B')$ in 100 ml of solvent at 50 °C. The full equivalent of CN^- can be isolated as $K[Co(dmgH)_2(SCN)(CN)]$. When the reaction is performed with more than 1 equiv of CN^-, reaction 1 again proceeds to completion within the same time interval. Further reaction with the excess CN^- according to reaction 2 does occur, but on the time scale of hours, not minutes. Thus, even in the presence of excess ionic CN^-, the complex exclusively isolated is $K[Co(dmgH)_2(SCN)(CN)]$. This allows the intermediate $[Co(dmgH)_2(SCN)(CN)]^-$ to be purified prior to reaction with an excess of ligand B according to reaction 3.

Care must be taken to ensure the isomeric purity of the starting material, since when a sample containing an appreciable amount of N-bonded $Co(dmgH)_2(NCS)(py)$[15] was treated with CN^-, reaction 1 produced a mixture of products containing $K[Co(dmgH)_2(SCN)(CN)]$ as only a minor fraction. The major product in this case was a yellow powder with infrared ν_{CN} absorption bands at 2115, 2150, and 2190 cm^{-1}, indicating the presence of terminally bound thiocyanate, cyanide, and bridging cyanide, respectively. This suggests a dimeric or higher molecular weight material containing the unit $[NCS\text{–}Co(dmgH)_2\text{–}CN\text{–}Co(dmgH)_2\text{–}CN]^-$, which may be formed when the $[Co(dmgH)_2(NCS)(CN)]^-$ initially produced in reaction 1 isomerizes to the more stable S-bonded isomer $[Co(dmgH)_2(SCN)(CN)]^-$,[10] the N of –CN effectively competing with SCN^- for the coordination site vacated by the isomerizing (–NCS).

The reaction scheme (1)–(3) was utilized in the synthesis of the monocyanocobaloximes listed in Table I. These data demonstrate that this synthetic route does not produce the coordination isomer $[Co(dmgH)_2(B)_2][Co(dmgH)_2(CN)_2]$. Table I lists a single, distinct dimethylglyoxime ^{1}H NMR methyl resonance for each compound. The ^{1}H NMR spectra for the mixed-salt coordination isomers would be characterized by two dimethylglyoxime methyl resonances, one characteristic for the cation $[Co(dmgH)_2(B)_2]^+$ and one for the dicyano anion $[Co(dmgH)_2(CN)_2]^-$. Furthermore, the compounds listed in Table I exhibit variable absorptions in the region of the ir spectrum corresponding to coordinated cyanide, ν_{CN}. If the mixed salt were present, then the ir spectrum should exhibit a ν_{CN} band at 2130 cm^{-1}, characteristic of $[Co(dmgH)_2(CN)_2]^-$.[10] No such ir peak was observed.

When the method of direct air oxidation[1] is applied to the synthesis of the compounds $Co(dmgH)_2(CN)(B)$, the cyano ligand initially coordinated can promote substitution at the trans position to give the inert anion of the coordination isomer, $[Co(dmgH)_2(CN)_2]^-$, which can subsequently react to produce the cyano-bridged species noted above. The suitability of reaction scheme (1)–(3) in the synthesis of $Co(dmgH)_2(CN)(B)$ depends on the ability of the SCN^- ligand to prevent the formation of the mixed-salt coordination isomers by acting as a good trans director in reaction 1, as a poor leaving group in reaction 2 thus enabling reaction 1 to proceed to completion prior to any appreciable amount of reaction 2 occurring, and as a better leaving group than CN^- in reaction 3 producing the desired product. The importance of this relative reactivity of the SCN^- ligand can be illustrated by substituting Cl^- for SCN^- in the above reaction scheme. The reaction of CN^- with $Co(dmgH)_2(Cl)(py)$ results in the rapid formation of $[Co(dmgH)_2(py)_2][Co(dmgH)_2(CN)_2]$ regardless of the reactant proportions employed. Evidence to support the occurrence of reaction sequence (1)–(2) in this case comes from our inability to isolate $[Co(dmgH)_2(CN)(Cl)]^-$ from the reaction of CN^- with $[Co(dmgH)_2(Cl)_2]^-$ due to the rapid formation of $[Co(dmgH)_2(CN)_2]^-$ and the inertness of $Co(dmgH)_2(CN)(py)$ to substitution by CN^-. Thus reaction 2 is much faster when X^- = Cl^- than when X^- = SCN^-, allowing the first formed intermediate $[Co(dmgH)_2(Cl)(CN)]^-$ to react substantially with available CN^- which has not yet been consumed in reaction 1.

Acknowledgment. We wish to thank J. M. Ciskowski for a sample of $Co(dmgH)_2(NCS)(py)$ and for helpful discussions. Financial support through a Frederick Gardner Cottrell Grant from the Research Corp. is gratefully acknowledged.

Registry No. $K[Co(dmgH)_2(SCN)(CN)]$, 15186-64-8; $Co(dmgH)_2(CN)(py)$, 23318-65-2; $Co(dmgH)_2(CN)(py\text{-}3\text{-}Cl)$, 57808-58-9; $Co(dmgH)_2(CN)(py\text{-}4\text{-}NH_2)$, 57808-59-0; $Co(dmgH)_2(CN)(NH_3)$, 19570-05-9; $Co(dmgH)_2(CN)(pip)$, 53632-13-6.

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Contribution from the Department of Chemistry, P. M. Gross Chemical Laboratory, Duke University, Durham, North Carolina 27706

Carbon-13 Nuclear Magnetic Resonance Spectra of Cyanocobaloximes Containing Carbon-13-Labeled Cyanide

Paul L. Gaus and Alvin L. Crumbliss*

Received September 9, 1975 AIC50668G

We wish to report on the ^{13}C NMR spectra of the ^{13}C-labeled cyanide ligand in selected cyanocobaloxime and cyano-bridged dicobaloxime complexes listed in Tables I and II.[1] These results bear a close relationship to those reported by Doddrell et al.[2] and Needham[3] et al. for the cyano- and dicyanocobalamins and -cobinamides. They are also of immediate interst due to the techniques employed in obtaining the data of Tables I and II.

Methods and Results

The compounds listed in Tables I and II were prepared according to published procedures[4-6] using 90% ^{13}C-enriched $K^{13}CN$ (Merk Sharp and Dohme, Ltd.). Samples used in this study were characterized by elemental analysis and infrared and ^1H NMR spectra.

The data of Tables I and II were obtained at 298 K on a Bruker HFX-10 spectrometer (22.6 MHz) equipped with a Nicolet NIC-80 data processor, by using a pulse-wait Fourier transform method. Magnetic field stabilization was provided by locking on the ^{19}F signal from a 3-mm coaxial insert of hexafluorobenzene in 10-mm sample tubes. Chemical shifts were measured by reference to the center resonance of DMSO and then converted to values relative to TMS. Positive numbers indicate a chemical shift downfield from TMS.

The ^{13}C NMR spectra were obtained according to the methods described below on saturated solutions (ca. 10^{-2}–10^{-4} M) of the monomeric cyanocobaloximes in DMSO-d_6. The spectra of the cyano-bridged dicobaloximes $RCo(dmgH)_2$–NC–$Co(dmgH)_2B$ (R = CH_3, CF_3; B = py, pip) and $RCo(dmgH)_2$–CN–$Co(dmgH)_2R'$ (R, R' = CH_3, C_2H_5) were obtained by adding an excess of the complex $Co(dmgH)_2(R)(H_2O)$[7] to solutions containing the appropriate monomeric cyanocobaloximes $Co(dmgH)_2(CN)(B)$ (10^{-3} M) (see Table I) and $[AsPh_4][Co(dmgH)_2(R)(CN)]$ (10^{-2} M) (see Table II).

The generally low solubility of the cyanocobaloximes in DMSO necessitated the accumulation of up to 60000 spectra per sample, prior to Fourier transformation. It was the buildup of the DMSO signal which often placed an upper limit on the number of spectral scans obtained for a particular sample. This problem was overcome by obtaining spectra without proton decoupling. This prevented a nuclear Overhauser enhancement of the signals due to carbons bound to protons and resulted in a decrease in the intensity of the DMSO carbon resonance relative to that of the cyanide carbon, as compared with the same spectrum obtained with broad-band proton decoupling. Assignment of the coordinated cyanide resonance, in addition to observing an increase in intensity upon using compounds synthesized from 90%-enriched ^{13}C cyanide, was made by identifying that resonance which did not suffer a diminution in intensity or a change in multiplicity in the absence of proton decoupling. When proton decoupling was used, resonances for ligands other than cyanide (such as those due to the dimethylglyoximato ligands) were observed. These data are comparable to those reported previously for dimethylglyoxime bound to cobalt(III).[8]

A second factor which facilitated the observation of the cyanide carbon resonances in these dilute solutions was the observation that the carbon nuclei (especially that of the cyanide ligand) were efficiently relaxed as a result of the interaction with the quadrupole moment on cobalt. This allowed the use of a full 90° pulse width, with a high repetition rate which was limited only by the acquisition time necessary for obtaining a 5000-Hz spectrum width. This resulted in an effective enhancement of the cyanide carbon resonance relative to the resonance due to DMSO (which was less efficiently relaxed), and it allowed the accumulation of more spectra prior to computer memory overflow due to the DMSO signal than would have been possible using, for example, a 30° pulse width.

The dipole–quadrupole interaction also accounts for the fact that all cyanide carbon resonances listed in Tables I and II were observed as single lines; i.e., no spin–spin coupling was observed between $^{59}Co(I = 7/2)$ and $^{13}C(I = 1/2)$. The rapid nuclear relaxation caused by this dipole–quadrupole interaction is responsible (through $1/T_2$, the spin–spin relaxation rate[9]) for the broadness of the signals listed in Tables I and II.

This latter line width effect is further modulated by chemical exchange of the cyanide between the tightly coordinated environment and the cyanide ion, free in solution. The compounds of Table I are known to be kinetically inert[4] toward substitution, and as such, these complexes represent the limit of slow chemical exchange with respect to the cyanide ligand. In contrast, the alkylcobaloximes of Table II are known to be

Table I. ^{13}C NMR Spectra of the Cyanide Ligand in Inert Cyanocobaloximes[a]

Compd	Line width,[b] Hz	δ-(*CN,)[c] ppm
$[Co(dmgH)_2(SCN)(*CN)]^-$ [d]	95	118.2
$Co(dmgH)_2(*CN)(py\text{-}3\text{-}Cl)$	65	114.7
$Co(dmgH)_2(*CN)(py)$	65	115.3
$Co(dmgH)_2(*CN)(pip)$	65	118.3
$CH_3Co(dmgH)_2$–NC*–$Co(dmgH)_2py$[e]	35	122.4
$CH_3Co(dmgH)_2$–NC*–$Co(dmgH)_2pip$[e]	25	125.4
$CF_3Co(dmgH)_2$–NC*–$Co(dmgH)_2pip$[e]	30	128.6
Na*CN	10	166.6

[a] Solvent DMSO-d_6. [b] Peak width at half-peak-height. [c] Relative to TMS. [d] Tetraphenylarsonium salt. [e] Ref 16.

Table II. ^{13}C NMR Spectra of the Cyanide Ligand in Labile Cyanocobaloximes[a]

Compd	Line width,[b] Hz	δ(*CN),[c] ppm
$[Co(dmgH)_2(CH_3)(*CN)]^-$	10	146.9
$[Co(dmgH)_2(C_2H_5)(*CN)]^-$	10	147.9
$[CH_3Co(dmgH)_2$–NC*–$Co(dmgH)_2$–$CH_3]^-$	10	156.0
$[CH_3Co(dmgH)_2$–NC*–$Co(dmgH)_2$–$C_2H_5]^-$	10	156.2[d]
$[C_2H_5Co(dmgH)_2$–NC*–$Co(dmgH)_2$–$CH_3]^-$	10	157.0[d]
Na*CN	10	166.6

[a] As the tetraphenylarsonium salt in DMSO-d_6. [b] Peak width at half-peak-height. [c] Relative to TMS. [d] The facile isomerization noted in ref 5 implies that this resonance may be due to an equilibrium mixture of cyano-bridged isomers.