the following arguments. Spin–spin coupling (J_{PH} and J_{PP}) results in "filled-in" doublet methyl resonances[12] in the ^1H NMR of these two complexes, and not the singlet or doublet which are characteristic of phosphorus ligand exchange in systems of this type.[13] Platinum sattelites are observed in the $^{13}C\{^1H\}$ spectrum of *cis*-$[(CH_3O)_3P]_2PtCl_2$ (Table II). Moreover, carbon–phosphorus coupling is seen in the *cis*-$LL'PdCl_2$ complexes (Table II) though the coupling constants differ from those of the free ligands (Table I). It has been shown[14] that J_{POCH} is positive for both the free ligand[15] and Ni(II) complexes of phosphites, phosphonites, and phosphinites. For the free ligands[15] J_{POC} is positive, but it may change sign upon coordination since J_{POC} is negative in pentavalent phosphorus compounds.[15] The analogous complexes *cis*-$[(CH_3O)_nP(C_6H_5)_{3-n}]_2PdCl_2$ ($n = 1, 2$) each exhibit "filled-in" doublets for their ^1H methyl resonances[16] and non 1:2:1 triplets[6] for their $^{13}C\{^1H\}$ methyl resonances.[17] For the complexes *trans*-$[P(o\text{-neopentyl})_3]_2MCl_2$ (M = Pd, Pt) the C_1 carbon resonance is a singlet, yet the C_2 carbon resonance is a triplet (Table II). Thus, it can be concluded that rapid exchange is not occurring and neither $^2J_{PC}$ nor $^4J_{PC}$ are zero for the $[(RO)_3P]_2MCl_2$ complexes.

The separation[6,7] of the most intense lines in the X part of the $[A]_2X$ multiplet is given by $|^nJ_{PC} + {}^{n+2}J_{PC}|$. Using the above arguments, this implies that when singlets are observed for the C_1 carbon resonances, $^nJ_{PC} = -{}^{n+2}J_{PC}$; that is, the two phosphorus–carbon coupling constants are equal in magnitude and opposite in sign and algebraically cancel! A complete analysis was possible for the complex $[P(o\text{-}i\text{-Pr})_3]_2PtCl_2$, where a five-line spectrum was observed for the C_1 resonance and $^2J_{PC}$ and $^4J_{PC}$ had opposite signs (Table II). Thus, a singlet can arise for these resonances depending upon the magnitude of $^2J_{PP}$ and the relative magnitudes of $^2J_{PC}$ and $^4J_{PC}$. As can be seen in Figure 2, it is not necessary that $^2J_{PC}$ exactly equal $^4J_{PC}$ in order to observe a singlet.

From the data in Table II it can be concluded that for phosphite complexes of palladium(II) and platinum(II), except those of $(C_6H_5O)_3P$, $^2J_{PC} \simeq -{}^4J_{PC}$ in general. Also, $|^3J_{PC} + {}^5J_{PC}|$ may be zero for the same reason. Similarly, it may be concluded from the spectral data[7] on alkylphosphine complexes of these metals that $^2J_{PC} = -{}^4J_{PC} \neq 0$ and $|^1J_{PC} + {}^3J_{PC}| \neq 0$ in line with the above arguments. For organodiphosphines of the type $R_2PCH_2CH_2PR_2$ it appears[18] that $^1J_{PC} = -{}^2J_{PC}$. Consequently, algebraic cancelation of coupling in $[A]_2X$ spin systems of compounds containing two phosphorus nuclei may be fairly common in ^{13}C NMR.

Conclusion

Although it was hoped at the outset of this investigation that the geometry of phosphite complexes of the type ML_2X_2 could be determined from their ^{13}C NMR spectra, it appears that this will be the exception rather than the rule. This is so, since $^2J_{PP}$ is generally larger than 25 Hz for the palladium(II)–phosphorus ester complexes regardless of geometry.[19] Generally, however, the geometry may be ascertained by utilizing a combination of ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra.[8,19,20]

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Registry No. $(MeO)_3P$, 121-45-9; $(EtO)_3P$, 122-52-1; $(o\text{-allyl})_3P$, 102-84-1; $(i\text{-PrO})_3P$, 116-17-6; $(o\text{-neopentyl})_3P$, 14540-52-4; *cis*-$[(MeO)_3P]_2PdCl_2$, 17787-26-7; *cis*-$[(MeO)_3P]_2PtCl_2$, 28374-51-8; *cis*-$[(EtO)_3P]_2PdCl_2$, 15649-89-5; *cis*-$[(o\text{-allyl})_3P]_2PdCl_2$, 57738-91-7; *trans*-$[(i\text{-PrO})_3P]_2PdCl_2$, 57738-92-8; *cis*-$[(i\text{-PrO})_3P]_2PtCl_2$, 21869-63-6; *trans*-$[(o\text{-neopentyl})_3P]_2PdCl_2$, 57738-93-9; *trans*-$[(o\text{-neopentyl})_3P]_2PtCl_2$, 57738-94-0; *cis*-$[(PhO)_3P]_2PdCl_2$, 38897-83-5; *cis*-$[(PhO)_3P]_2PtCl_2$, 30053-58-8; *cis*-$[(EtO)_3P][Ph_3P]PdCl_2$, 57738-95-1; *cis*-$[(MeO)_3P][Et_3As]PdCl_2$, 57739-00-1; *cis*-$[(PhO)_3P][Ph_3P]PdCl_2$, 57738-96-2; ^{13}C, 14762-74-4.

References and Notes

(1) (a) University of Nevada. (b) Stanford Research Institute.

(2) R. B. King, *Inorg. Chem.*, **2**, 936 (1963).

(3) J. M. Jenkins and B. L. Shaw, *Proc. Chem. Soc., London*, 279 (1963).

(4) C. A. McAuliffe, Ed., "Transition Metal Complexes of Phosphorus, Arsenic and Antimony Ligands", Halsted Press, New York, N.Y., 1973.

(5) R. L. Keiter, Ph.D. Thesis, The University of Maryland, College Park, Md., 1967; J. H. Nelson, A. W. Verstuyft, J. D. Kelly, and H. B. Jonassen, *Inorg. Chem.*, **13**, 27 (1974).

(6) D. A. Redfield, J. H. Nelson, and L. W. Cary, *Inorg. Nucl. Chem. Lett.*, **10** 727 (1974), and references contained therein.

(7) (a) B. E. Mann, B. L. Shaw, and R. E. Stainbank, *J. Chem. Soc., Chem. Commun.* 51 (1972); (b) P. S. Pregosin and R. Kunz, *Helv. Chim. Acta*, **58**, 423 (1975).

(8) A. W. Verstuyft, L. W. Cary, and J. H. Nelson, *Inorg. Chem.*, **14**, 1495 (1975).

(9) A. W. Verstuyft and J. H. Nelson, *Synth. React. Inorg. Met.-Org. Chem.*, **5**, 69 (1975).

(10) J. G. Verkade and K. J. Coskran in "Organic Phosphorus Compounds", Vol. 2, G. M. Kosolapoff and L. Maier, Ed., Wiley, New York, N.Y., 1972.

(11) D. A. Redfield, L. W. Cary, and J. H. Nelson, *Inorg. Chem.*, **14**, 50 (1975); L. W. Cary, *Rev. Sci. Instrum.*, **46**, 1422 (1975).

(12) F. B. Ogilvie, J. M. Jenkins, and J. G. Verkade, *J. Am. Chem. Soc.*, **92**, 1916 (1970).

(13) J. B. Fackler, Jr., J. A. Fetchin, J. A. Mayhew, W. C. Seidel, T. J. Swift, and M. Weeks, *J. Am. Chem. Soc.*, **91**, 1941 (1969).

(14) E. J. Lukosius and K. J. Coskran, *Inorg. Chem.*, **14**, 1926 (1975).

(15) W. McFarlane, *Proc. R. Soc. London, Ser. A*, **306**, 185 (1968).

(16) D. A. Couch, S. D. Robinson, and J. N. Wingfield, *J. Chem. Soc., Dalton Trans.*, 1309 (1974).

(17) A. W. Verstuyft, Ph.D. Thesis, University of Nevada, Reno, Nev., 1976.

(18) R. B. King, private communication for R = phenyl; M. Akhtar, P. D. Ellis, A. G. MacDiarmid, and J. D. Odom, *Inorg. Chem.*, **11**, 2917 (1972), for R = methyl; K. W. Morse and J. G. Morse, *J. Am. Chem. Soc.*, **95**, 8469 (1973), for R = F. Singlets were observed for the CH_2 carbon resonance in each case.

(19) A. W. Verstuyft, D. A. Redfield, L. W. Cary, and J. H. Nelson, *Inorg. Chem.*, in press.

(20) A. W. Verstuyft, J. H. Nelson, and L. W. Cary, *Inorg. Nucl. Chem. Lett.*, **12**, 53 (1976).

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Synthesis and Spectroscopic Studies of β,β',β''-Triaminotriethylamine Chelates of the Trivalent Lanthanide Perchlorates

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Few NMR isotropic shift studies of lanthanide complexes with strictly nitrogen donors have been attempted[1] although the volume of literature concerning the paramagnetic lanthanide shift reagents involving oxygen-donor ligands has been substantial. The mechanism of interaction between the paramagnetic lanthanide ion and ligand protons has been shown to be a combination of contact and dipolar effects for the nitrogen-donor ligands, while the isotropic shifts of substrate protons in the presence of lanthanide shift reagents are thought to be primarily dipolar in nature.[2]

High-coordinate lanthanide complexes derived from the strongly basic nitrogen donors, ethylenediamine,[3] 1,2-propanediamine,[4] and diethylenetriamine[5] with a variety of anions utilizing a nonaqueous solvent as the reaction medium have been isolated. In addition, both the mono- and bis(β,-β',β''-triaminotriethylamine (tren)) chelates of the lanthan-

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ide(III) nitrates have been prepared and characterized.[6]

We report here the syntheses and some spectroscopic studies of the lanthanide(III) perchlorate complexes of the tetradentate nitrogen donor β,β',β''-triaminotriethylamine.

Experimental Section

Materials. The anhydrous lanthanide perchlorates were prepared according to methods previously described.[3] Reagent grade acetonitrile and deuterated acetonitrile (Diaprep Corp.) were dried and purified by distillation from phosphorus(V) oxide. Thiophene-free benzene was dried by refluxing over calcium hydride and distilled. β,β',β''-Triaminotriethylamine was extracted as the hydrochloride salt from technical grade triethylenetetramine as previously described.[6]

Spectroscopic Studies. Variable-temperature ^1H NMR spectra were obtained using a Varian HA-100 spectrometer equipped with the standard Varian variable-temperature accessory. Infrared spectra in the region 4000–600 cm^{-1} were obtained with a Perkin-Elmer Model 457 grating instrument as Nujol and hexachlorobutadiene mulls. Electronic spectra from 600 to 550 nm were obtained on a Cary 14 spectrophotometer operating in the absorption mode. Solid samples were mulled with Kel-F and placed between quartz plates. A reference mull of magnesium carbonate between quartz plates was used. Solution samples and solvent blanks were placed in matched 0.5-cm silica cells.

Preparation of Ln(tren)(ClO_4)$_3$, Ln = Pr, Gd, Er. The ligand (2 mmol) was added to 10 ml of acetonitrile containing 2 mmol of lanthanide perchlorate. The solution was desolvated in vacuo (0.1 Torr) at 25 °C, followed by in vacuo heating at 80 °C.

Preparation of Ln(tren)$_2$(ClO_4)$_3$, Ln = La, Pr, Nd, Gd, Er, Y. The ligand (4 mmol) was added neat to an acetonitrile solution (5 ml) containing 2 mmol of a lanthanide perchlorate. An equal volume of dry benzene was added, and the mixture was allowed to stand overnight. The crystalline product was collected by filtration and washed three times with a 50:50 acetonitrile–benzene mixture. A stoichiometric product was obtained after heating the product in vacuo (80 °C, 0.1 Torr).

Analyses. Elemental carbon and hydrogen analyses were performed by Galbraith Laboratories, Inc. Lanthanide analyses were performed in this laboratory by titration with ethylenediaminetetraacetic acid, using xylenol orange as the indicator. All compounds gave satisfactory analyses.

Results and Discussion

Conductivity, NMR, and calorimetric studies of lanthanide(III) perchlorates and tren in acetonitrile have established the existence of Ln(tren)$_2^{3+}$ ion in solution and that tren is a tetradentate ligand.[6] In order to determine possible perchlorate ion coordination in the solid state, electronic and infrared spectra of the solid complexes were obtained.

Several studies have been reported on the line shapes and intensities of the hypersensitive transitions of lanthanide complexes as solid mulls and in solution as a qualitative indication of coordination number and symmetry about the metal ion.[7] One of the usual transitions observed in such studies is the hypersensitive transition of the neodymium(III) ion, $^4I_{9/12} \rightarrow {}^4G_{5/2}, {}^2G_{7/2}$, occurring at ca. 580 nm. This transition for both the Nd(tren)$_2^{3+}$ ion in acetonitrile solution and the solid Nd(tren)$_2$(ClO_4)$_3$ chelate are shown in Figure 1. The similarity in the splitting patterns indicates the probable lack of coordination by the perchlorate ion in the solid bis complexes. It is not expected that the perchlorate ion would be coordinated in the heavier lanthanides due to the decrease in the radii of the lanthanide(III) ions in moving across the series.

Lack of coordination of perchlorate ion is corroborated by the infrared spectra of the bis complexes in the regions of perchlorate ion absorption (Figure 2). The undistorted perchlorate ion has regular T_d symmetry and has a very strong and broad infrared-active band, ν_3, centered at ca. 1100 cm^{-1}.[8] The nondegenerate frequency, ν_1, forbidden in the infrared region, occurs as a very weak absorption at 930 cm^{-1} when the ion is slightly distorted in a crystal field of symmetry lower than T_d. The triply degenerate asymmetric bending frequency, ν_4, is infrared active and usually occurs at 626 cm^{-1}. All bis complexes gave identical infrared spectra in these regions and seem to indicate only a small amount of distortion from T_d symmetry, as shown by the appearance of the relatively weak band at 930 cm^{-1}. The distortion of the perchlorate ion could be due to packing in the crystal lattice.

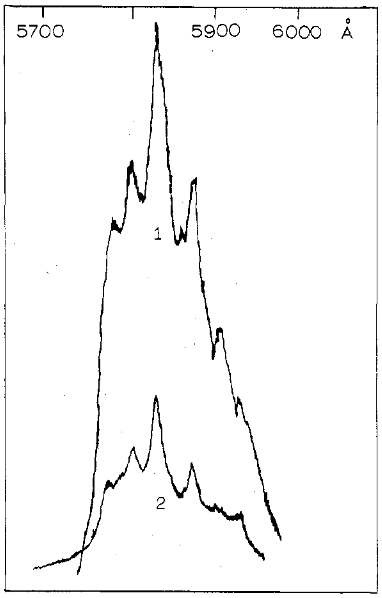

Figure 1. Hypersensitive transition of Nd(III), $^4I_{9/2} \rightarrow {}^4G_{5/2}$, $^2G_{7/2}$: 1, Nd(tren)$_2$(ClO_4)$_3$ in CH_3CN; 2, Nd(tren)$_2$(ClO_4)$_3$ mull.

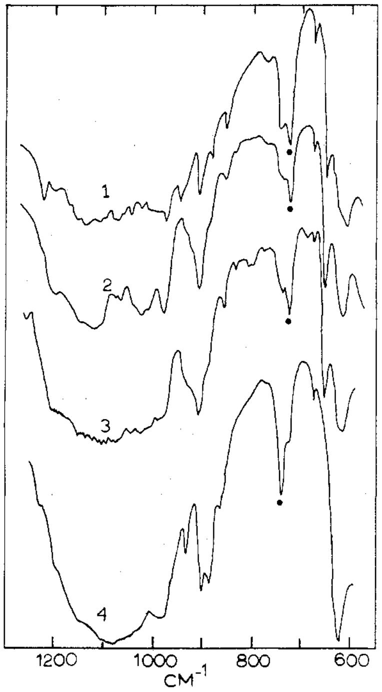

Figure 2. Infrared spectra in regions of perchlorate ion absorptions: 1, Pr(tren)(ClO_4)$_3$; 2, Gd(tren)(ClO_4)$_3$; Er(tren)(ClO_4)$_3$; 4, Ln(tren)$_2$(ClO_4)$_3$; ●, Nujol.

Spectra of the mono complexes in the perchlorate regions (Figure 2) change as the lanthanide ion is varied. Strong absorptions of the ligand in the vicinity of the 1100-cm^{-1} band prevent unambiguous conclusions about the number and symmetries of perchlorate ions distorted from T_d symmetry. It is expected, however, that some of the perchlorate ions will be in the first coordination sphere in the mono complexes, since the lanthanide ions commonly display large coordination numbers (ca. 8–12). The mono chelates all have a strong band

Table I. Ratio of $-CH_2-$ Shifts ("B":"A")

Temp, °C	Pr	Nd	Eu
80	2.45	3.00	1.14
70	2.51	3.40	1.22
60	2.58	3.65	1.27
50	2.64	4.03	1.31
40	2.71	4.56	1.36
30	2.75	5.26	1.41
20	2.82	6.34	1.44
10	2.88	7.90	1.48
0	2.91	11.80	1.51
−10	2.90	18.40	1.55
−20	3.20	105.00	1.59
−30	3.44		

at 653 cm^{-1}, which is assigned to the nondegenerate ClO_3 symmetrical bending frequency, ν_3, indicative of a monodentate perchlorate ion of C_{3v} symmetry. The changing appearance of the band at 910–940 cm^{-1} could indicate the presence of perchlorate ions of C_{2v} and/or C_{3v} symmetry, since both have nondegenerate infrared-active stretching modes in that region.[8]

Infrared spectra of the NH stretching region in all of the mono chelates are identical showing two peaks centered at 3310 cm^{-1}, shifted 10 cm^{-1} to lower frequency from the center of the free tren absorption. That the stretching frequencies of the coordinated NH groups is less than the free ligand value may be attributed to the combined effects of coordination to a positive metal ion[9] and hydrogen bonding between the perchlorate ion present and the NH proton.[10] The magnitude of this shift has been found to be greater when the anions are nitrate or halide.[3,4,6] The NH stretching region for the bis chelates differs from that of the mono chelates, being shifted an additional 10–20 cm^{-1} to lower frequency. The higher frequency observed for the mono chelates might result from entry of the perchlorate ions into the coordination sphere, similar to the shift observed in the NH stretching frequency upon entry of nitrate ions into the coordination sphere of tris- and tetrakis(ethylenediamine) chelates of the La(III) ions.[3]

Isotropic Shifts. The 100-MHz proton magnetic resonance spectra for the paramagnetic species $Ln(tren)_2^{3+}$ (Ln = Pr, Nd, Eu) in deuterated acetonitrile between +80 and −30 °C each displayed two peaks which are assigned to two magnetically nonequivalent methylene groups.[11] In addition, a third resonance attributed to the amine protons was observed. However, the amine groups were deuterated by the solvent in the course of recording the spectra so temperature studies could not be obtained.

The methylene peaks in the various systems were related to one another by double-resonance experiments[12] carried out in equimolar mixtures of the complexes at 70 °C. The designations "A" and "B" in Table I refer to the methylene shifts which are related by exchange in the mixed systems. The "A" protons, then, should be geometrically similar for each of the complexes; the same holds for the "B" protons.

Isotropic shifts for the paramagnetic complexes were calculated by referencing the shifts to the center of the observed methylene resonances in diamagnetic $La(tren)_2^{3+}$ to account for any inductive effects caused by coordination to the metal ion. A spectrum identical with that of $La(tren)_2^{3+}$ was obtained with Y(III) ion, indicating that the inductive effect is insensitive to the ionic radius of the metal. Temperature variation of the average methylene shift for $La(tren)_2^{3+}$ ranged from −283 Hz at 80 °C to −260 Hz at −30 °C. It should be noted that the center of this shift at 25 °C is approximately 20 Hz downfield from free tren.

Isotropic shifts of paramagnetic complexes may be interpreted in terms of either a contact interaction or a dipolar interaction.[13] A typical plot of isotropic shift vs. T^{-1} (Figure 3) shown for the paramagnetic $Nd(tren)_2^{3+}$ system indicates deviation of both methylene resonances from Curie law behavior. Although protons A demonstrate linear behavior, the isotropic shift *decreases*, rather than increases, with decreasing temperature, contrary to the behavior expected. Regardless of the origin of the isotropic shift, i.e., contact or dipolar, the ratio of the methylene proton resonances for a particular lanthanide ion should remain constant in the temperature range studied if only one geometry for the complex exists in solution. That this is not the case is demonstrated in Table I. Alternatively, the ratio of isotropic shifts would also remain constant if several geometric isomers were rapidly exchanging with respect to the NMR time scale, provided that the populations of the various geometrical isomers were independent of temperature.

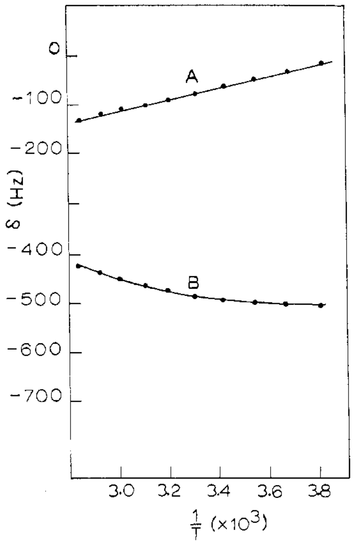

Figure 3. Plot of isotropic shift vs. T^{-1} for $Nd(tren)_2(ClO_4)_3$ in CH_3CN.

Birnbaum and Moeller[14] have observed Curie law behavior for a series of alkyl-substituted pyridine complexes and have demonstrated the presence of both contact and dipolar interactions to account for the observed isotropic shifts. The anomalous behavior of the shifts in the tren systems may be due to an equilibrium among two or more structures in solution, the equilibrium shifting with temperature variation and causing changes in the average observed shift for each methylene group.

That an intramolecular rearrangement of ligands in the coordination sphere may be occurring is corroborated by the observed line width at half-height for the methylene proton resonances in $Nd(tren)_2^{3+}$.[11] The broadening which occurs at low temperature, e.g., 75 Hz at −30 °C, is too severe to be attributed to paramagnetic relaxation by the Ln(III) ion, since the line width of the corresponding methylene resonance in $Nd(tren)^{3+}$ is only 26 Hz at −30 °C. Thus the broadening observed in the bis complex is attributed to a decreasing rate of intramolecular exchange between geometric isomers at low temperatures.

King[15] has calculated the relative coulombic repulsions, T (repulsivity), for possible polyhedra of coordination numbers 4–9, assuming equal charges and bond distances for all metal–ligand bonds. The repulsivity should indicate directly the relative favorability of various coordination polyhedra, with minimum-repulsivity polyhedra being most favored. For coordination number 8, the three lowest repulsivity polyhedra are the D_{4d} square antiprism (T = 14.337), the D_{2d} dodecahedron (T = 14.354), and the D_{3d} bicapped octahedron (T = 14.501). Because of the similarity in these repulsivities, it seems reasonable that two or more geometries might be in equilibrium in these solutions, with intramolecular exchange so rapid that only average resonances are observed. Stereochemical 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. $\mathrm{Pr(tren)(ClO_4)_3}$, 57674-50-7; $\mathrm{Gd(tren)(ClO_4)_3}$, 57674-51-8; $\mathrm{Er(tren)(ClO_4)_3}$, 57674-52-9; $\mathrm{La(tren)_2(ClO_4)_3}$, 57674-54-1; $\mathrm{Pr(tren)_2(ClO_4)_3}$, 57674-56-3; $\mathrm{Sm(tren)_2(ClO_4)_3}$, 57674-57-4; $\mathrm{Eu(tren)_2(ClO_4)_3}$, 57674-58-5; $\mathrm{Nd(tren)_2(ClO_4)_3}$, 57674-59-6; $\mathrm{Gd(tren)_2(ClO_4)_3}$, 57674-60-9; $\mathrm{Er(tren)_2(ClO_4)_3}$, 57674-61-0; $\mathrm{Y(tren)_2(ClO_4)_3}$, 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.

References and Notes

(1) (a) E. R. Birnbaum and T. Moeller, *J. Am. Chem. Soc.*, **91**, 7274 (1969); (b) E. R. Birnbaum and S. Stratton, *Inorg. Chem.*, **12**, 379 (1973); (c) F. A. Hart, J. E. Newbery, and D. Shaw, *J. Inorg. Nucl. Chem.*, **32**, 3585 (1970).
(2) W. D. Horrocks, Jr., and J. P. Sipe, III, *J. Am. Chem. Soc.*, **93**, 6800 (1971), and references within.
(3) J. H. Forsberg and T. Moeller, *Inorg. Chem.*, **8**, 883 (1969).
(4) L. J. Charpentier and T. Moeller, *J. Inorg. Nucl. Chem.*, **32**, 3575 (1970).
(5) J. H. Forsberg and C. A. Wathen, *Inorg. Chem.*, **10**, 1379 (1971).
(6) J. H. Forsberg, T. M. Kubik, T. Moeller, and K. Gucwa, *Inorg. Chem.*, **10**, 2656 (1971).
(7) (a) G. R. Choppin, D. E. Henrie, and K. Buijs, *Inorg. Chem.*, **5**, 1743 (1966); (b) J. H. Forsberg, Doctoral Dissertation, University of Illinois, 1968; (c) D. G. Karraker, *Inorg. Chem.*, **6**, 1863 (1967); (d) D. G. Karraker, *J. Inorg. Nucl. Chem.*, **33**, 3713 (1971); (e) O. A. Serra, M. L. R. Gibran, and A. M. B. Galindo, *Inorg. Nucl. Chem. Lett.*, 673 (1972).
(8) B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.*, 3091 (1961).
(9) G. F. Svatos, C. Curran, and J. V. Quagliano, *J. Am. Chem. Soc.*, **77**, 6159 (1955).
(10) J. Fjita, K. Nakamoto, and M. Kobayashi, *J. Am. Chem. Soc.*, **78**, 3095 (1956).
(11) M. F. Johnson and J. H. Forsberg, *Inorg. Chem.*, **11**, 2683 (1972).
(12) S. Forsén and R. A. Hoffman, *J. Chem. Phys.*, **39**, 2892 (1963).
(13) J. H. Forsberg, *Coord. Chem. Rev.*, **10**, 195 (1973).
(14) E. R. Birnbaum and T. Moeller, *J. Am. Chem. Soc.*, **91**, 7274 (1969).
(15) R. B. King, *J. Am. Chem. Soc.*, **92**, 6455 (1970).
(16) E. L. Muetterties, *Inorg. Chem.*, **12**, 1963 (1973).
(17) W. D. Horrocks, *J. Am. Chem. Soc.*, **96**, 3022 (1974).

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Synthesis of Monocyanocobaloximes

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The air oxidation method of Tschugaeff[1] has been applied to the synthesis of numerous monoacidocobaloximes[2,3] of the type $\mathrm{Co(dmgH)_2(X)(B)}$, 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 $\mathrm{[Co(dmgH)_2(B)_2][Co(dmgH)_2(X)_2]}$.

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 $\mathrm{Co(dmgH)_2(CN)(B)}$, 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 $\mathrm{Co(dmgH)_2(Cl)(py}$-*t*-$\mathrm{Bu)}$ to $\mathrm{Co(dmgH)_2(CN)(py}$-*t*-$\mathrm{Bu)}$ in 44% yield but have not extended the method to ligands other than *tert*-butylpyridine. Egen and Krause[9] reported the synthesis of $\mathrm{Co(dmgH)_2(CN)(B)}$ (B = py, aniline, or 3,5-lutidine) from $\mathrm{[(C_6H_5)_2I][Co(dmgH)_2(CN)_2]}$. 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 $\mathrm{Co(dmgH)_2(CN)(B)}$ in high yields without the formation of the mixed-salt coordination isomer.

Experimental Section

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

$\mathrm{Co(dmgH)_2(SCN)(NH_3)}$ was synthesized by treating a water suspension of $\mathrm{Co(dmgH)(dmgH_2)(NCS)(SCN)}$[10] with concentrated $\mathrm{NH_4OH}$. 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 $\mathrm{Co(dmgH)_2(SCN)(OH_2)}$, the infrared spectrum and elemental analyses conclusively demonstrate the presence of coordinated $\mathrm{NH_3}$.

$\mathrm{K[Co(dmgH)_2(SCN)(CN)]}$ was synthesized by treating a suspension of $\mathrm{Co(dmgH)_2(SCN)(py)}$, 2.50 g (5.86 mmol), or $\mathrm{Co(dmgH)_2(SCN)(NH_3)}$, 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 $\mathrm{K[Co(dmgH)_2(SCN)(CN)]}$, 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 $\mathrm{cm^{-1}}$.[10,12] Isomeric purity was demonstrated on the basis of ^{1}H NMR data in $\mathrm{CH_2Cl_2}$ for $\mathrm{Co(dmgH)_2(SCN)(py)}$ and $\mathrm{Co(dmgH)_2(SCN)(NH_3)}$ and in $\mathrm{C_6H_5NO_2}$ for $\mathrm{K[Co(dmgH)_2(SCN)(CN)]}$.

$\mathbf{Co(dmgH)_2(CN)(py)}$. 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 $\mathrm{CH_3OH}$ solution of the product was loaded onto the column (1 g of product/100 g of Florisil), which was in $\mathrm{CHCl_3}$, and then eluted with a solvent containing increasing amounts of $\mathrm{CH_3OH}$ in $\mathrm{CHCl_3}$, beginning with 10% (v/v) $\mathrm{CH_3OH}$. A yellow band which represented <10% of the product mixture was eluted first and identified as the desired product $\mathrm{Co(dmgH)_2(CN)(py)}$ by ^{1}H 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% $\mathrm{CH_3OH}$. 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 $\mathrm{cm^{-1}}$, consistent with $\mathrm{[Co(dmgH)_2(CN)_2]^-}$ [10] and cyano-bridged species,[13] such as $\mathrm{[NCCo(dmgH)_2–CN–Co(dmgH)_2CN]^-}$ and $\mathrm{NCCo(dmgH)_2–CN–Co(dmgH)_2py}$, and/or higher molecular weight cyano-bridged species being present.

Alternatively, $\mathrm{K[Co(dmgH)_2(SCN)(CN)]}$, 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%.

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

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