38731-30-5; Co(en)$_2$(OOCCH(CH$_3$)OH)$^{2+}$, 38641-66-6; Co(en)$_2$(HOCH$_2$CH$_2$OH)$^{3+}$, 38673-81-3.

Acknowledgments. Support for this research from the National Science Foundation (Grants GP-12223 and GP-30612) and the donors of the Petroleum Research Fund, administered by the American Chemical Society (Grant 5189), is gratefully acknowledged. We are indebted to Professors Henry Taube, Teddy Traylor, Ed Grubbs, Hal Walba, and Bill Richardson for helpful comments.

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Hydrogen-1, Nitrogen-15, and Cobalt-59 Chemical Shifts in Several Cobalt(III) Complexes

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Received September 14, 1972

Nuclear magnetic resonance (nmr) is a useful method in studying the structure of transition metal complexes and gives valuable information on the second coordination sphere. Here we report the ^{1}H, ^{15}N, and ^{59}Co chemical shift data for several cobalt(III) complexes in D$_2$O-D$_2$SO$_4$ solutions. The results are interpreted in terms of changes in the properties of the complexes with the change in the second coordination sphere.

Experimental Section

cis- and *trans-*Co(gly)$_3$ were prepared according to the method of Mori, *et al.*[2] However, since the cis form of Co(gly)$_3$ was more difficult to synthesize, we have made only the trans isomer of ^{15}N-enriched Co(gly)$_3$. Co(en)$_3$Cl$_3$ was prepared by a standard method[3] and recrystallized from aqueous ethanol. The preparation of [Co(^{15}NH$_3$)$_5$Cl](ClO$_4$)$_2$ was described previously.[4]

Proton nmr spectra were recorded at 100 MHz with a Varian HA-100 spectrometer. ^{59}Co nmr spectra were recorded on a Varian VF-16 spectrometer at 12.0 MHz using concentrated Co(NH$_3$)$_6$Cl$_3$ as an external standard in a coaxial tube. Measurements of ^{15}N chemical shifts using the proton resonance with H$_2$SO$_4$ as an internal lock signal were made by the "spin-tickling" technique which is described elsewhere.[4]

The cryroscopic measurement on *cis*-Co(gly)$_3$·H$_2$O was carried out by using the procedure described by Hammett and Deyrup[5] using an apparatus described by Newman, *et al.*[6]

Results and Discussion

The proton nmr spectrum of [Co(en)$_3$]$^{3+}$ (en = ethylenediamine) is probably the most widely studied among those of all cobalt(III) complexes.[7,8] In acidified D$_2$O solutions, the proton exchange is slow and the NH protons show two distinct signals at both low and high acid concentrations (Figure 1), which are not resolved at 60 MHz.[9] The origin of the two NH peaks was attributed to either different conformers[10] or different (axial and equatorial) configurations in the same conformer.[9] In a recent review,[7] Beattie presented a detailed analysis of the proton nmr spectrum of the methylene group in a number of transition metal complexes with ethylenediamine, including [Co(en)$_3$]$^{3+}$. He concluded that the ligands undergo rapid inversion between δ and λ conformations, and the observed (time-averaged) chemical shift difference between the two diastereotopic methylene protons arises from a preference for the δ conformation, which has a lower free energy than the λ conformation for the Λ conformation. A similar argument is applicable to the NH$_2$ group. However, another factor that is not important for the methylene protons now may be operative. Because of the proximity of the NH protons to three of the Co-N bonds in the two other ligands, the interaction with the neighboring rings may be important in determining their chemical shifts. In both the δ and the λ conformations, one of the NH bonds is more or less parallel to the C_3 axis of the complex, and the other NH bond is more or less perpendicular to the C_3 axis. Their interactions with the two other rings are different and they do not convert to each other during the inversion of the ring. Therefore, the nonequivalence due to the total chirality of the complex is probably a major factor in determining the proton chemical shift difference for the NH$_2$ group, although it is less important for the methylene protons.

The two protons in the NH$_2$ group in [Co(en)$_3$]$^{3+}$ are in a complicated spin system. Appreciable spin-spin interactions with nitrogen, cobalt, the adjacent methylene protons, and each other are expected. However, because of the effect of quadrupolar relaxation, no spin-spin splittings were observed in the nmr spectrum of the NH$_2$ protons. In D$_2$O-D$_2$SO$_4$ solutions, the NH proton signal of [Co(en)$_3$]$^{3+}$ moves downfield with the increase in D$_2$O content because of an increase in hydrogen bonding.[9] A more careful examination of the spectra at 100 MHz (Figure 1) suggests that the two NH signals shift differently with the change in the solvent composition. The peak that has a larger change (labeled e in Figure 1) can be assigned to the proton with the NH bond roughly parallel to the C_3 axis of the complex, because it is sterically less hindered and therefore more susceptible to hydrogen-bond formation with D$_2$O. The proton with the NH bond roughly perpendicular to the C_3 axis (labeled a in Figure 1) is more crowded because of two other a protons in the neighboring NH$_2$ groups and is less affected by the change in the solvent composition, because the formation of the second coordination sphere with D$_2$O *via* hydrogen bond is less favorable. Therefore, the overlapping of the two NH signals at intermediate acid concentration is due to a coincidence in the chemical shifts. Variable-temperature studies show that the coalescence of the two signals is not due to chemical exchange. For example, in a solution with a ratio of D$_2$O:D$_2$SO$_4$ = 4, the two NH proton signals coalesce at room temperature; at 100°, the width of the peak increases by about 30%. This can be explained either by the increase of the chemical shift difference between the two NH protons or by the decrease in the ^{59}Co quadrupole relaxation rate but is inconsistent with an exchange mechanism. A previous calculation[9] on the activation energy of ring inversion based upon the proton nmr spectra of the NH$_2$ group for [Co(en)$_3$]^{3}

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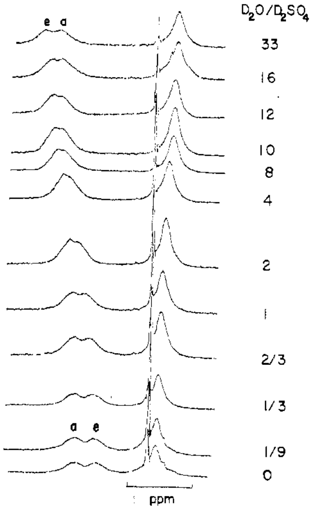

Figure 1. Proton nmr of $[Co(en)_3](ClO_4)_3$ in $D_2O-D_2SO_4$ solutions at 100 MHz and 30°. The sharp peak is due to added tetramethylammonium chloride. The assignment of the NH_2 signals (the peaks at lower field) is discussed in the text.

in dimethyl sulfoxide at different temperatures is therefore probably erroneous.

Co(III) complexes show large ^{59}Co chemical shifts because of the paramagnetic contribution from low-lying paramagnetic states.[11-13] ^{59}Co chemical shifts are very sensitive to small changes, such as substitution of hydrogen by deuterium in $[Co(en)_3]^{3+}$,[8] the composition of organic solvents for tris(acetylacetonato)cobalt(III) ($Co(acac)_3$),[14] and the formation of an outer-sphere complex between $[Co(en)_3]^{3+}$ and PO_4^{3-}.[15] The data in Figure 2 show that the ^{59}Co shift for $[Co(en)_3]^{3+}$ is substantially affected by the H_2SO_4 concentration. The magnitude of change is almost twice that for $Co(acac)_3$ (80 ppm) in a $CHCl_3-CCl_4$ mixture,[14] showing that the effect of the second coordination sphere is more pronounced in $[Co(en)_3]^{3+}$, which is reasonable because it involves definitive hydrogen bonding.

^{14}N chemical shifts for the ligands in cobalt(III) complexes are also appreciable.[16-18] However, the signals are usually severely broadened by quadrupole interaction, and small changes cannot be detected. On the other hand, ^{15}N is a spin $^1/_2$ nucleus and shows sharp absorptions. Its chemical shift can be obtained either from direct ^{15}N nmr or $\{^{15}N\}-{}^1H$ double resonance. Because of economic reasons, we have not endeavored the synthesis of ^{15}N-enriched $[Co(en)_3]^{3+}$ complexes. Instead, we have studied the solvent dependence in the ^{15}N chemical shifts of a related complex, $[Co(^{15}NH_3)_5Cl]^{2+}$, by $\{^{15}N\}-{}^1H$ double resonance. The ^{15}N chemical shifts for the trans and the cis ammonia ligands differ by about 15 ppm.[4] However, both signals had *no* change in their ^{15}N chemical shifts when the solvent was changed gradually from concentrated to very dilute D_2SO_4, whereas the resonance of the trans protons moves downfield about 0.50 ppm, and that of the cis protons moves downfield about 0.40 ppm. (The slightly smaller change for the cis protons is most likely due to a small steric hindrance by the chlorine to the hydrogen bond formation.[9])

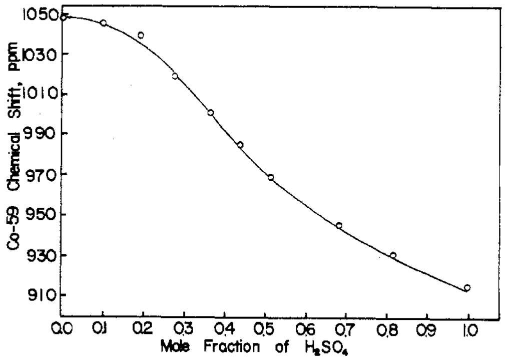

Figure 2. ^{59}Co chemical shifts of $[Co(en)_3](ClO_4)_3$ with respect to an external concentrated aqueous solution of $[Co(NH_3)_6]Cl_3$. The resonance was performed at 12.0 MHz at 25° on a Varian VF-16 spectrometer.

Complexes with amino acids as ligands are of interest in the study of the second coordination sphere, because in each chelate there are two different sites (NH_2 and C=O) that can form hydrogen bonds with proton acceptors and proton donors, respectively. There are two geometric isomers for $Co(gly)_3$ (gly = glycinato) and other amino acid complexes; in the cis form all three NH_2 groups are cis to each other and all three chelate rings are equivalent, whereas in the trans form only two NH_2 groups are adjacent to each other and all three chelate rings are different. *cis*-$Co(gly)_3$ is soluble in water and crystallizes in the form of monohydrate. *Anal.* Calcd for $Co(NH_2CH_2COO)_3 \cdot H_2O$: Co, 19.70; C, 24.09; H, 4.72; N, 14.05. Found: Co, 18.98; C, 24.08; H, 4.47; N, 14.02. We have performed a cryoscopic measurement of *cis*-$Co(gly)_3 \cdot H_2O$ in concentrated sulfuric acid and found that the van't Hoff *i* factor was 5.7 ± 0.2, which implies that the complexes are practically completely protonated

$$Co(gly)_3 \cdot H_2O + 4H_2SO_4 \rightarrow Co(glyH)_3{}^{3+} + H_3O^+ + 4HSO_4^-$$

When the concentration of water in the solvent increases, the NH_2 group would gradually increase its hydrogen bonding with water, and deprotonation of the carbonyl group would also occur. The two processes have opposite effects on the NH_2 proton chemical shift, but the CH_2 resonance is mainly affected by the latter and little affected by the formation of a second coordination sphere with water. This effect has been discussed in detail for $Co(ala)_3$,[19] and the result for *cis*-$Co(gly)_3$ is shown in Figure 3. The two different protons in each NH_2 group do not show clearly resolvable signals at 100 MHz, but the overlapping is less severe at intermediate acid concentrations. For *trans*-$Co(gly)_3$, the three different amino groups show two signals with an intensity ratio of 1:2. The changes of their chemical shifts with the acid concentration are similar to those of the cis isomer.

The symmetries of the amino acid complexes are low and the ^{59}Co quadrupole interactions are probably very large. The ^{59}Co resonances were too broad to be detected at low concentrations of the complexes and the solvent dependence could not be studied.

The ^{15}N chemical shifts were found from $\{^{15}N\}-{}^1H$ double resonance by "spin tickling." In concentrated D_2SO_4 the

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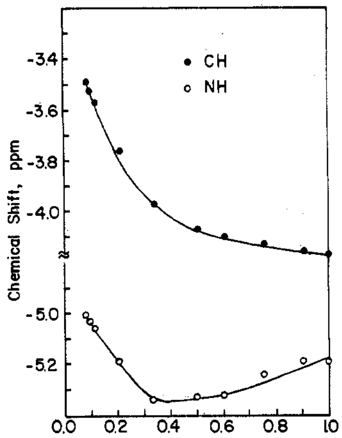

Figure 3. Proton chemical shifts of *cis*-Co(gly)$_3$ at 100 MHz and 30°. Tetramethylammonium chloride was used as the internal standard, and the chemical shift was measured at a scale on which the methyl group of 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) was taken as zero.

values for the three different NH_2 groups in *trans*-Co(gly)$_3$ are 39.4 ± 0.5, 37.8 ± 0.5, and 42.5 ± 0.2 ppm, respectively, from $^{15}NH_4^+$ in the same solution. It was determined from the double-resonance experiment that the three nitrogens correspond to the three -NH_2 groups that have proton chemical shifts at −6.66, −5.28, and −5.28 ppm, respectively (in contrast, the three ^{14}N peaks in *trans*-Co(gly)$_3$ were found to be unresolvable and appeared at 36 ± 7 ppm from $^{14}NH_4^+$ [18]). The ^{15}N-^1H coupling constants are all 72 ± 2 Hz for the NH_2 group and not resolvable for N-C-H. Again the ^{15}N chemical shifts did not change with the acid concentration from $D_2O:D_2SO_4 = 0$ to 8, indicating that the shielding of the nitrogen nucleus is not affected by the change in the second coordination sphere, in contrast to proton and the cobalt nucleus. This indicates that there is no appreciable change in the two factors that determine the nitrogen chemical shift in cobalt(III) complexes,[18] namely, the mixing of excited states and the difference in charge distribution (or the changes are in opposite directions and exactly cancel each other, which is unlikely). Those two kinds of changes are larger at the cobalt and the hydrogen nuclei, respectively, so that appreciable variations in their chemical shifts were observed.

Registry No. *cis*-Co(gly)$_3$, 21520-57-0; *trans*-Co(gly)$_3$, 19963-68-9; ^{15}N-enriched *trans*-Co(gly)$_3$, 38656-89-2; Co(en)$_3$Cl$_3$, 13408-73-6; [Co($^{15}NH_3$)Cl](ClO$_4$)$_2$, 38656-88-1; cobalt, 7440-48-4; ^{15}N, 14390-96-6.

Acknowledgment. This work was supported by the National Science Foundation.

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Complexes of Silver(I) Thiocyanate with Some Tertiary Phosphines, Triphenylarsine, and Triphenylstibine[1]

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Received September 26, 1972

In the growing literature on thiocyanate complexes of transition metal ions and the ambidentate nature of the thiocyanate ion, very little has appeared to date on complexes with silver(I) ion. Turco and coworkers[2-5] have prepared silver thiocyanate complexes with a few trialkylphosphines and Capacchi and coworkers[6] have reported a silver thiocyanate complex with thiosemicarbazide. This paper reports on the synthesis and some properties of a number of new silver(I) thiocyanate complexes.

Experimental Section

Analyses. The carbon and hydrogen microanalyses were performed by Crobaugh Laboratories. Silver analyses were performed in our laboratory by an electrogravimetric procedure. This procedure entailed the digestion of the sample by the method described by Norwitz.[7] The digestion was followed by electrodeposition of the metal on a platinum gauze electrode from a basic cyanide solution. The melting points were determined with a Fisher-Johns melting point apparatus. Molecular weight determinations were carried out with a Model 301A Mechrolab Inc. vapor pressure osmometer at 37°. The latter was calibrated with solutions of benzil in acetone and chloroform.

Infrared Spectra. The infrared spectra were measured over the 4000–400-cm^{-1} region on a Perkin-Elmer Model 621 spectrophotometer. All samples were prepared as Nujol or Halocarbon mulls and recorded using potassium bromide windows. The accuracy and reproducibility of the reported band maxima, which were taken from the frequency counter, were estimated to be well within ±2 cm^{-1}.

Reagents. Most of the reagents used in this investigation were commercially available and used as such without further purification. The few exceptions included the benzil, acetone, and chloroform used in the molecular weight studies. Benzil was purified by vacuum sublimation at 90° (oil bath temperature). Reagent grade acetone was dried 48 hr over anhydrous calcium sulfate and distilled at 48° while the chloroform was dried over calcium hydride for 24 hr and distilled at 54°.

Diethylphenylphosphine, PEt$_2$Ph. The preparation of this ligand was carried out under a nitrogen atmosphere in diethyl ether by the method of Adams and Raynor.[8] The product was distilled at 75–85° and 6 mm (reported value: 96–97° (10 mm)[9]).

Diphenylethylphosphine, PPh$_2$Et. This ligand was likewise prepared by the method of Adams and Raynor.[8] The crude product was purified by distillation at 105–107° (0.2 mm) (reported value: 129–132° (0.7 mm)[10]).

Preparation of Complexes. With the exceptions of the trimethylphosphine, tri-*n*-butylphosphine, diethylphenylphosphine, and diphenylethylphosphine adducts, in which the preparations were carried out under a nitrogen atmosphere, no special techniques or procedures were employed. The analytical data for the complexes have been included in Table I.

Thiocyanatotrimethylphosphinesilver(I), AgCNS·PMe$_3$. About 3 ml (~31.5 mmol) of PMe$_3$ was vapor transferred into a frozen, degassed aqueous solution containing 4.47 g (26.3 mmol) of AgNO$_3$ and excess KSCN. After warming to room temperature, followed by 5 min of vigorous shaking, the white product obtained was separated by filtration, washed with 0.25 *M* KSCN and then with water, and finally dried in a desiccator over anhydrous CaSO$_4$. The compound was recrystallized from acetone, in which it was only very slightly soluble, to yield colorless, needlelike crystals.

Thiocyanatotri-*n*-butylphosphinesilver(I), AgCNS·P(*n*-Bu)$_3$. Ten milliliters (38.5 mmol) of P(*n*-Bu)$_3$ was added to 20.0 g (118.0 mmol) of AgNO$_3$ dissolved in 300 ml of a nitrogen-purged water-ethanol (3:1) solution containing excess KSCN. This mixture was vigorously stirred for 2 hr after which time the white product was separated by filtration and washed with 0.25 *M* KSCN, then with water, and finally

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[1] Taken in part from Ph.D. Thesis of J. L. C. (April 1971) submitted to the Chemistry Department of the University of Wyoming.

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