and the consecutive values for the rhodium(III) and rhodium(II) species $Rh(bpy)_2(H_2O)_2^{3+}$ and $Rh(bpy)_2(H_2O)_2^{2+}$ are 4.8, 6.87 and 8.6, 11.1, respectively;[13] these results are consistent with our data.

The MLCT band positions of the hydroxy species span the halide data, suggesting that hydroxide ion acts as a soft ligand toward ruthenium(II), transferring appreciable charge density to the metal.

Further photochemical studies of these species are in hand. We note that the hydroxy species may be useful starting materials toward the generation of Ru(IV) oxo species, which would parallel those formed with bipyridine[12,14] but would be much stronger oxidizing agents. Indeed, the procedures outlined here provide new synthetic routes into bis(bipyrazine)ruthenium(II) chemistry and later may allow the generation of bis(bipyrazine)osmium(II) complexes whose bipyridine analogues are of especial photocatalytic interest.[15]

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Registry No. $Ru(bpz)_3^{2+}$, 75523-96-5; $Ru(bpz)_2(NO_2)_2$, 86497-09-8; $Ru(bpz)_2(NCS)_2$, 86497-10-1; $Ru(bpz)_2Cl_2$, 80907-59-1; $Ru(bpz)_2Br_2$, 86497-11-2; $Ru(bpz)_2I_2$, 86497-12-3; $Ru(bpz)_2(Ox)$, 86497-13-4; $Ru(bpz)_2CO_3$, 86497-14-5; $Ru(bpz)_2(H_2O)_2^{2+}$, 86497-15-6; $Ru(bpz)_2(H_2O)(OH)^+$, 86497-16-7; $Ru(bpz)_2(OH)_2$, 86497-17-8; bpz, 10199-00-5.

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Contribution from the General Education Department,
Kogakuin University, Hachioji Campus,
2665-1 Nakano-cho Hachioji-shi, Tokyo 192, Japan

Nitrogen-15 NMR Spectroscopy of Bis(aspartato)cobaltate(III)

Masatoshi Watabe,* Machiko Takahashi, and Akira Yamasaki

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The nuclear magnetic resonance spectroscopy of nitrogen in coordination compounds is an area of considerable potential interest. Nitogen is a constituent of many ligands that are important in coordination chemistry and biochemistry. Several researchers have tried to elucidate the main factor that governs the nitrogen-15 chemical shift of coordination complexes, but this main factor has not yet been discovered.[1-4] It is necessary to collect a great deal of ^{15}N chemical shift information concerning metal complexes. We have given a method for assigning proton magnetic resonance spectra of diamagnetic cobalt complexes and found a general trend for the chemical shifts of a proton in a H-C-N-Co-X fragment, where X is a nitrogen or an oxygen atom and occupies the trans (to N) position.[5] The proton resonates at higher or lower field according to whether X is oxygen or nitrogen. Freeman et al.[6-8] at first elucidated qualitatively and Yoneda et al.[9,10] studied quantitatively that these shifts were primarily determined by the magnetic anisotropy of the central cobalt ion. It would

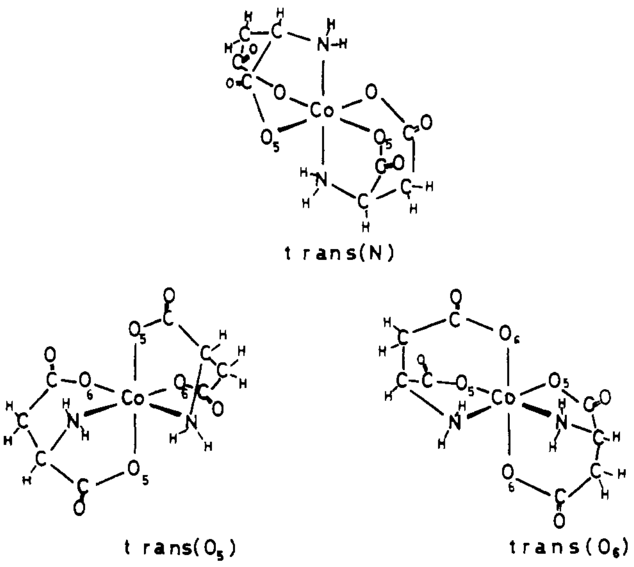

Figure 1. The three isomers of $[Co(L\text{-}asp)_2]^-$.

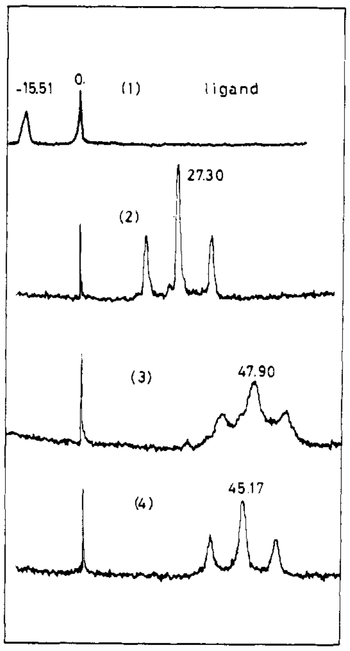

Figure 2. ^{15}N NMR spectra in H_2O: (1) free ligand at pH 9.0; (2) trans(N) isomer; (3) trans(O_5) isomer; (4) trans(O_6) isomer.

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be interesting to know whether or not the order of the nitrogen-15 chemical shifts can be correlated by using the anisotropic effect in the paramagnetism of the chemical cobalt(III) ion. Herein we report on the enriched ^{15}N NMR spectroscopy of the three isomers of the bis(aspartato)cobaltate complex.

Experimental Section

The three somers of the bis(aspartato)cobaltate(III) complex were prepared according to Yamada's method.[11] The ^{15}N NMR spectra were obtained in the Fourier transform mode with a Varian FT-80A spectrometer. Chemical shifts at 8.059 Hz were determined with use of a 2-kHz range and 16K memory and were measured with respect to an external ammonium chloride solution. The pulse width was 10 ms, and pulse delay, 2 s. About 200 mg of materials was dissolved in 1.5 mL of H_2O in a 10-mm tube, and the spectra were accumulated 50 000–70 000 times at 37 °C. The spectrum of the free ligand was obtaiend in a solution of pH 9.

Results and Discussion

The three possible isomers of $[Co(L\text{-}asp)_2]^-$ are shown in Figure 1. They are designated as trans with respect to the nitrogen atoms, the oxygen atoms of five-membered chelate rings, and the oxygen atoms of six-membered chelate rings, that is, trans(N), trans(O_5), and trans(O_6). Figure 2 shows the ^{15}N NMR spectra of all the isomers of $[Co(L\text{-}asp)_2]^-$ in H_2O along with that of the free ligand. Sharp singlet peaks at the left side of all the spectra are the peaks of ^{15}N-enriched ammonium chloride. In part 1 of Figure 2 the relatively broad peak that lies at 15.51 ppm lower field than that for NH_4Cl is that for the free aspartate ligand at pH 9. Part 2 of Figure 2 shows the spectrum of the trans(N) isomer of $[Co(L\text{-}asp_2)]^-$ in H_2O, in which one triplet peak appeared at 27.30 ppm higher field with respect to the NH_4Cl peak. The triplet pattern is attributed to the coupling of ^{15}N and protons in the NH_2 moiety because the ^{15}N signal collapsed in a D_2O solution. The coupling constant J_{N-H} is 75 Hz, which is comparable to that for CH_3NH_3Cl (75.4 Hz).[12] Part 3 of Figure 2 shows the ^{15}N spectrum of the trans(O_5) isomer, in which a collapsed triplet peak appeared at 47.90 ppm higher field compared to the NH_4Cl peak. Part 4 of Figure 2 shows the ^{15}N spectrum of the trans(O_6) isomer in which a relatively sharp triplet lies at 45.17 ppm higher field with respect to that for the peak of NH_4Cl.

Chemical shifts are interpreted by means of the Ramsey equation,[13] which treats the observed shielding as a combination of three terms as in eq 1. The σ_p term is the paramagnetic component, the σ_d term is the diamagnetic term, and the σ_i term is one arising from the effects of neighboring atoms.

$$\sigma = \sigma_p + \sigma_d + \sigma_i \qquad (1)$$

Roberts and co-workers[2] have studied the ^{15}N magnetic resonances of a large group of closed-shell metal complexes of EDTA. Shifts of less than 20 ppm were observed for all complexes. To rationalize the relatively small shifts observed, they postulated that a large paramagnetic term must arise from coordination and that its magnitude must nearly equal the diamagnetic term. Bose and Abbott[3] studied the ^{15}N resonances of a series of Rh(III) complexes of both aliphatic and aromatic diamine chelate ligands. Since the metal ion was the same in all the cases, its contribution to the diamagnetic term should be fairly constant from complex to complex. They considered that, if the σ_d term must be constant and the σ_p term is large, the observed shielding should be correlated with the spectrochemical series. No such correlation could be made from their data of Rh(III) complexes. They considered that the σ_p term for the effect of the metal ion on the ligand nitrogen atom was not large in their complexes because the metal ion was the same. Since the metal ion was also the same in all our complexes, its contribution to the diamagnetic term should be constant from complex to complex. Moreover we postulated the σ_p term to be nearly constant as was suggested by Bose and Abbott.[3] We tried to calculate the σ_i term by using the method demonstrated by Yoneda et al.[9]

They devised the theoretical method for assigning proton magnetic spectra of diamagnetic cobalt complexes, in which shifts are primarily determined by the anisotropy in the second-order paramagnetism of the central cobalt ion. The same method is expected to be useful in evaluating the order of ^{15}N chemical shifts if ^{15}N chemical shifts should depend mainly on the paramagnetic anisotropy of the central cobalt ion. As seen from eq 28–30 of ref 10, the nitrogen-15 chemical shifts of the amine group of amino acidate coordinated in solution are expected to appear respectively as

$$\sigma(\text{trans(N)}) = [\sigma(O_5) + \sigma(O_6) - 2\sigma(N)]/3R^3\langle r^{-3}\rangle$$

$$\sigma(\text{trans}(O_5)) = [2\sigma(O_5) - \sigma(O_6) - \sigma(N)]/6R^3\langle r^{-3}\rangle$$

$$\sigma(\text{trans}(O_6)) = [2\sigma(O_6) - \sigma(O_5) - \sigma(N)]/6R^3\langle r^{-3}\rangle$$

where $\sigma(\text{trans(X)})$ stands for the chemical shift of nitrogen-15, which probably does not give a real magnitude because the difference between the nitrogen and the proton is not considered, and $\sigma(X)$ is the component of the ^{59}Co chemical shift that is assigned to each ligand (where X = N, O_5, O_6). We assumed them to be –4600, –6000, and –6500 for $\sigma(N)$, $\sigma(O_5)$, and $\sigma(O_6)$, respectively, by taking into consideration that $\sigma(X)$ is proportional to the ligand field strength[6] R, which is the distance between cobalt and nitrogen atoms, is 1.95 Å, 3.68 au, and $\langle r^{-3}\rangle$, which is an average of r^{-3} over a metal 3d orbital, is 5.77 au.[10] Then we obtained the calculated chemical shifts –3.81, –0.52, and –1.21 ppm for trans(N), trans(O_5), and trans(O_6) isomers, respectively. Though the differences between calculated chemical shifts are smaller by more than an order of magnitude than those measured, it suggests that the ^{15}N chemical shift of the trans(N) isomer should be lower than those of trans(O_5) and trans(O_6). In the case of the ^{15}N chemical shifts of pentaamminecobalt complexes, $[CoX(NH_3)_5]^{n+}$, ammine nitrogens trans to X resonated in the order of H_2O, Cl^-, Br^-, and NO_2^- to lower magnetic field. The calculated values obtained by the same method for the four complexes were 1.48, 1.10, 1.07, and –0.08, respectively. The order of the proton chemical shifts of $[CoX(NH_3)_5]^{n+}$ also agreed with this trend, but that of $[RhX(NH_3)_5]^{n+}$ did not agree with it. Moreover rhodium pentaammines show only one peak, whereas most of the cobalt pentaammines show two peaks with an intensity ratio 4:1. Hendrickson and Jolly[7] considered that the greater electron distance would result in a marked reduction in the shielding influence. We understand that there is a certain difference between cobalt(III) complexes and rhodium(III) complexes when one wants to discuss the order of proton chemical shifts and that of nitrogen chemical shifts. There are two opposite valuations on this approximation, that is (1) these calculated values are irrelevant because the difference at even more than an order of magnitude between experimental and calculated values is too large and (2) even though this large difference exists, the calculated data are useful to predict which isomer peak should appear at higher magnetic field within limited complexes. At present we can not say which way is better than the other.

Registry No. *trans(N)*-$[Co(L\text{-}asp)_2]^-$, 33848-80-5; *trans(O_5)*-$[Co(L\text{-}asp)_2]^-$, 70982-04-6; *trans(O_6)*-$[Co(L\text{-}asp)_2]^-$, 70982-05-7; ^{15}N, 14390-96-6.

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