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^{15}N NMR Spectra of Cobalt(III) Complexes Containing $^{15}NO_2^-$

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Synopsis. The nitrogen-15 nuclear magnetic resonance spectra of the cobalt(III) complexes containing $^{15}NO_2^-$ were first measured; the coordination chemical shifts, $\Delta\delta$ ($=\delta_{complex}-\delta_{free}$), were found to be from 135.0 to 161.5 ppm. The relationship between $\Delta\delta$ and the geometrical configuration was discussed in terms of the paramagnetic anisotropy of the cobalt(III) ion.

The nuclear magnetic resonance spectroscopy of nitrogen in coordination compounds is an area of considerable potential interest. Only a few ^{15}N chemical shift data of the cobalt(III) complexes have, however, been reported.[1–4] In our previous paper,[5] we reported the ^{15}N-NMR data for the bis (L-aspartato)cobaltate(III) and discussed the main factor which affects the ^{15}N chemical shift by using the magnetic anisotropy[6,7] of the central cobalt ion. This method could explain the trend of the ^{15}N chemical shifts of $[Co(L\text{-}asp)_2]^-$ to a certain extent. However, it is necessary to collect a great many ^{15}N chemical-shift information concerning metal complexes. Herein we report on the ^{15}N NMR spectroscopy of the cobalt(III) complexes containing the $^{15}NO_2^-$ ion.

Experimental

Cis-$[Co(^{15}NO_2)_2(en)_2]Cl$[8] is prepared from $[Co(CO_3)(en)_2]Cl$, and *trans*-$[Co(^{15}NO_2)_2(en)_2]Cl$,[9] from $Co(NO_3)_2\cdot 6H_2O$. These cis and trans complexes are too insoluble in water for the ^{15}N NMR spectra to be measured. In order to change the counter anion, a solution of these complexes was placed in a Sephadex C-25 cation-exchange column (Cl^- form). After the column had then been swept with water, the adsorbed material was eluted with 1 mol dm^{-3} sodium aspartate. The eluate was concentrated with a rotary evaporator at about 5 °C. The resulting complexes, $[Co(NO_2)_2(en)_2]$ aspNa, were very soluble in water. *Cis*-$[CoCl(^{15}NO_2)(en)_2]Cl$[10] and *trans*-$[CoCl(^{15}NO_2)(en)_2]NO_3$[11] were prepared from *trans*-$[Co(^{15}NO_2)_2(en)_2]NO_3$. These two complexes are soluble enough in water for the ^{15}N NMR spectra to be measured. The ^{15}N NMR spectra were measured in the Fourier transform mode with a Varian FT-80A spectrometer. The chemical shifts at 8.104 MHz were determined by the use of a 2-kHz range and a 16-K memory and were measured with respect to external ^{15}N ammonium chloride or ^{15}N sodium nitrite in D_2O. About 200 mg of material was dissolved in 1.5 cm^3 of H_2O in a 10-mm tube, and the spectra were accumulated 50000-70000 times at 37 °C.

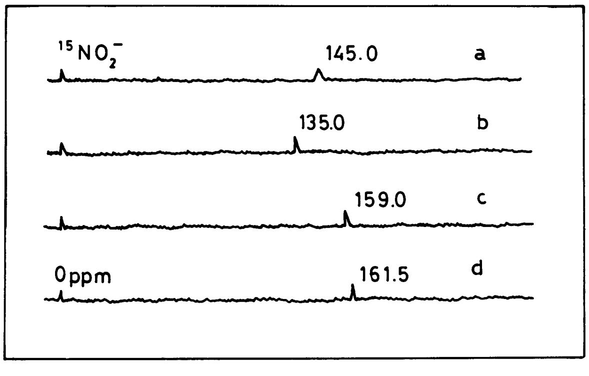

Fig. 1. ^{15}N NMR spectra in H_2O; a; *cis*-$[Co(NO_2)_2(en)_2]^+$, b; *trans*-$[Co(NO_2)_2(en)_2]^+$, c; *cis*-$[CoClNO_2(en)_2]^+$, d; *trans*-$[CoClNO_2(en)_2]^+$.

Results and Discussion

Figure 1 shows the ^{15}N NMR spectra of *trans*- and *cis*-$[Co(^{15}NO_2)_2(en)_2]$aspNa (asp=aspartate), *trans*-$[CoCl(^{15}NO_2)(en)_2]Cl$, and *cis*-$[CoCl(^{15}NO_2)(en)_2]NO_3$. The chemical shifts of the nitrogen-15 of the NO_2^- type coordinating to the cobalt(III) ion, were first obtained. The sharp singlet peaks on the left side of all the spectra are the peaks of the ^{15}N-enriched sodium nitrite. The chemical shifts are interpreted by means of Ramsey equations[12] as

$$\delta = \delta_p + \delta_d + \delta_i, \tag{1}$$

where the δ_p term is the paramagnetic component, the δ_d term is the diamagnetic term, and the δ_i term is the anisotropy term, which arises from the effects of neighboring atoms. Since the metal ion was the same in all cases, the paramagnetic and the diamagnetic contribution should be fairly constant, as was suggested by Bose and Abott[3]. Nakashima *et al.*[4] stated that the chemical shift, δ_i, induced by the paramagnetic anisotropy of cobalt(III) ion is of minor importance to the ^{15}N chemical shifts; this is in contrast with the finding that they are of dominant importance to the ^{1}H chemical shift. However, we reported in our previous paper that the

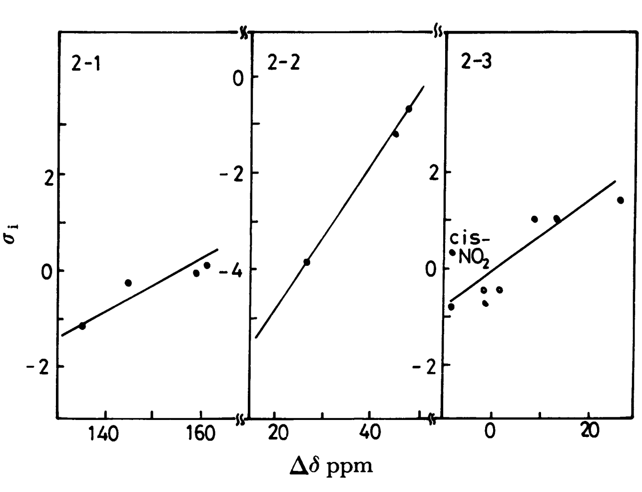

Fig. 2. The correlation between $\Delta\delta$obsd and σ_i, NO_2^- complex (from NO_2^-)(Fig. 2-1), ^{15}N-aspartate complex (from ^{15}N-asp)(Fig. 2-2), and the $^{15}NH_3$ complex (from $[Co(^{15}NH_3)_6]^{3+}$(Fig. 2-3), In Fig. 2-3, ○: Denotes the cis complex, ●: The trans complex.

calculated anisotropy shift could be correlated with the observed ^{15}N chemical shift if the former values are multiplied about 10 or 20 times. We tried again to calculate the δ_i term by using the method demonstrated by Yoneda.7) For the complexes dealt with here, we postulate the following values $\delta(^1H) \propto \delta(^{15}N)$; $\langle r^{-3} \rangle = 5.77$ a.u, which is the value for $[Co(NH_3)_6]^{3+}$; the distance between nitrogen-15 and metal is 1.95 Å (=3.68 a.u.); $\delta(NO_2) = -4073$ ppm; $\delta(Cl) = -5910$ ppm, and $\delta(en/2) = -4603$ ppm. If the coordinated NO_2^- is placed in the Z axis, then $\theta = 0$, $\varphi = 0$, and the chemical shifts ($[Co(NH_3)_6]^{3+}$ is taken as a standard) can easily be evaluated to be as follows; −1.13 for *trans*- $[Co(NO_2)_2(en)_2]^+$, −0.28 for *cis*-$[Co(NO_2)_2(en)_2]^+$, 0.08 for *trans*-$[CoClNO_2(en)_2]^+$, and −0.21 for *cis*-$[CoClNO_2(en)_2]^+$. The correlation between the calculated and the experimental values is shown in Fig. 2-1. The slope is 0.040, and the standard deviation, *R*, is 0.925. This value is smaller than those for $[Co(L\text{-}asp)_2]^-$ (0.154) and *R*(0.996)(Fig. 2-2). In Fig. 2-3, the correlation between the calculated chemical shift and the ^{15}N chemical shift of $[CoX(NH_3)_5]^{n+}$ is shown. The slope for the trans complex is 0.068, and *R*, 0.929. These good standard deviations of the three series confirm that paramagnetic anisotropy is one of the factors influencing the ^{15}N chemical shift of the cobalt(III) complexes. The ^{15}N chemical shift of the cis NH_3 of $[CoNO_2(NH_3)_5]^{2+}$ is not in line with those of the other $[CoX(NH_3)_5]^{n+}$-type complexes. We considered that hydrogen bonding exists in *cis*-$[CoNO_2(NH_3)_5]^{2+}$ between the NH_3 hydrogen and NO_2^- and that this hydrogen-bonding ^1H atom may influence the magnetic field around the ^{15}N atom. Fung *et al.*13) reported that the chemical shifts of ^{15}N directly bound to cobalt are hardly affected at all by the solvents. This implies intramolecular hydrogen bonding. The difference in the slopes among the three series is natural because the atoms around the cobalt are different. Though, in every series, the experimental values are ten times those calculated, the calculated chemical shifts are useful in predicting which complex among similar complexes shows the chemical shift at a higher magnetic field.

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