

The difference in the Cu^{2+} site location between hydrated CuNa-X and hydrated CuK-X can be attributed to the difference in the hydration energies of Na^+ and K^+ . The hydration energy for Na^+ is greater than that of K^+ because of the difference in their ionic radii which are 0.097 and 0.133 nm, respectively. Let us assume that the Cu^{2+} is initially located in SII*. The migration of Cu^{2+} from the SII* to SI requires the displacement of an alkali cation from SI.^{21,22} Since the hexagonal prism offers the same electrostatic field to both Na^+ and K^+ , the energy for removing an unhydrated alkali cation is the same for Na^+ and K^+ . However, the net energy gain for transferring an unhydrated alkali cation from SI to a more exposed site, where it will be hydrated, is greater for Na^+ because it has a larger hydration energy. So it is energetically more favorable for Cu^{2+} to displace Na^+ from SI than to displace K^+ . This argument seems consistent with our findings that a small concentration of Cu^{2+} in hydrated CuNa-X migrates into the SI sites whereas Cu^{2+} stays in SII* in hydrated CuK-X . After dehydration the hydration energy argument is moot and the Cu^{2+} location is the same in CuK-X and CuNa-X .

It is relevant to compare our structural results with previous literature based only on ESR and optical spectra.²³ In most cases

a critical comparison of CuNa-X and CuK-X was not carried out. However, this was the focus of a recent optical study.²³ In hydrated CuNa-X the optical spectra have been assigned to $\text{Cu}^{2+}(\text{H}_2\text{O})_6$ species in the super cages. We have found that the $\text{Cu}^{2+}(\text{H}_2\text{O})_6$ species can be removed by repeated washing of an A zeolite with water and the same may apply to X and Y zeolites. So the $\text{Cu}^{2+}(\text{H}_2\text{O})_6$ species may be simply entrapped solution and may not be a cation state or site of catalytic relevance.

The optical spectrum for Cu^{2+} in CuK-X has been found to be different from that for $\text{Cu}^{2+}(\text{H}_2\text{O})_6$ in CuNa-X and has been assigned to hydrated Cu^{2+} in the sodalite cages.²³ This assignment is admittedly speculative and we suggest that it should be reassigned to SII* in the super cage. Distinct changes in the optical spectra occur on dehydration and a band grows in at higher wavenumber; we suggest that this new band should be assigned to the site in or near the hexagonal prism that we deduce from ESE studies.

It is interesting that this optical study points out the differences between Cu^{2+} locations in hydrated CuK-X and CuNa-X . However, we believe that the specific site locations suggested from that study need to be modified based on the ESE studies which are able to count numbers of coordinated waters.

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Registry No. Cu, 7440-50-8; methanol, 67-56-1.

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Coordination Shifts in ^{15}N Nuclear Magnetic Resonance Spectra of Glycinato and Ethylenediamine Ligands in Cobalt(III) Complexes

N. Juranić*† and R. L. Lichter*

Contribution from the City University of New York, Department of Chemistry, Hunter College, New York, New York 10021. Received February 1, 1982

Abstract: Nitrogen-15 nuclear magnetic resonance spectra of the 12 complexes of the type $[\text{Co}(\text{ox})_x(\text{gly})_y(\text{en})_z]$ have been determined ($\text{oxH}_2 = \text{oxalic acid}$, $\text{glyH} = \text{glycine}$, $\text{en} = \text{ethylenediamine}$). ^{15}N resonances of glycinato and ethylenediamine ligands exhibit shielding coordination shifts ranging from -19 to -62 ppm. Coordination shifts are very sensitive to the trans influence; a nitrogen nucleus in an amino group trans to oxygen is shielded by about 18 ppm more than one in a group trans to nitrogen. The cis influence is about 4 times less pronounced and in the opposite direction. An estimation of the Cornwell-Santry effect in low-spin d^6 complexes suggests that this may be the major cause of the observed coordination shifts as well as of coordination shift variations arising from trans and cis influences.

Introduction

Shielding of nuclei directly bonded to transition-metal ions with spin-paired d^6 electronic configurations has been observed in a number of complexes.¹⁻⁴ These shifts are sensitive both to the nature of the ligands and to the geometrical configuration of the complexes.^{3,5-7} Hence, nuclear magnetic resonance (NMR) spectroscopy of nuclei directly bonded to metal ions could show promise as a sensitive probe for bonding and for coordination geometry. However, few experimental data are available, so that systematic investigation is still required in order to establish areas and limits of applicability of this technique. ^{15}N NMR spectroscopy is of particular interest because nitrogen is the ligating atom of many ligands that are important in coordination chemistry and biochemistry.

The only published systematic study of cobalt(III) complexes by ^{15}N NMR spectroscopy is on the effect of ligand replacement in pentaamminecobalt(III) complexes.⁶ ^{15}N chemical shifts vary widely with the nature of X in $[\text{CoX}(\text{NH}_3)_5]^{n+}$. Furthermore, chemical shifts of the NH_3 group depend on the trans or cis geometry with respect to X. These changes have been shown to be much larger than could be accounted for by paramagnetic

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* Visiting Fulbright scholar (1980-1981), University of Belgrade, Department of Chemistry and Physical Chemistry, 11001 Beograd, Yugoslavia.

Table I. ^{15}N Chemical Shifts and Coordination Shifts of $\text{CoN}_x\text{O}_{6-x}$ -Type Complexes

compd	complex	$\delta(\text{NH}_3)$, ppm ^a	Δ_c , ppm ^b
1	$[\text{Co}(\text{en})_3]\text{Cl}_3$	-15	-35
2	$[\text{Co}(\text{gly})(\text{en})_2]\text{Cl}_2$	-11.3 -27.0 -33.4	-31.3 -47.0 -53.4
3	<i>trans</i> -(O)- $[\text{Co}(\text{gly})_2(\text{en})]\text{Cl}$	-5.7 -28.6	-25.7 -48.6
4	<i>cis</i> -(O)- C_1 - $[\text{Co}(\text{gly})_2(\text{en})]\text{Cl}$	-5.1 -19.0 -23.6 -41.1	-25.1 -39.0 -43.6 -61.1
5	$[\text{Co}(\text{ox})(\text{en})_2]\text{Cl}$	0.7 -21.3	-19.3 -41.3
6	<i>mer</i> - $[\text{Co}(\text{gly})_3]$	-22.7 -23.5 -39.2	-42.7 -43.5 -59.2
7	<i>mer</i> - $[\text{Co}(\text{ox})(\text{gly})(\text{en})]$	1.1 -16.6 -20.5	-18.9 -36.6 -40.5
8	<i>fac</i> - $[\text{Co}(\text{gly})_3]$	-42.4	-62.4
9	$\text{Na}[\text{Co}(\text{ox})_2(\text{en})]$	-17.4	-37.4
10	<i>cis</i> -(N)- C_1 - $\text{K}[\text{Co}(\text{ox})(\text{gly})_2]$	-36.5	-56.5
11	<i>trans</i> -(N)- $\text{K}[\text{Co}(\text{ox})(\text{gly})_2]$	-16.0	-36.0
12	$\text{K}_2[\text{Co}(\text{ox})_2(\text{gly})]$	-39.4	-59.4

^a Experimental error is ± 0.2 ppm. ^b $\Delta_c = \delta(\text{coordinated ligand}) - \delta(\text{free ligand})$.

anisotropy of the metal ion, and it was suggested that the shifts are related to Co-N bond strength. Recently, we have reported a natural-abundance ^{15}N NMR study of amino acids coordinated to cobalt(III) in λ -*cis*-(NO_2)-*trans*-(NH_2)- $[\text{Co}(\text{NO}_2)_2(\text{Am})_2]^{(-/+)}$ complexes (AmH = amino acid).⁸ This study established that an additional shielding of 24–42 ppm is experienced by the amino nitrogen when an amino nitrogen proton is replaced by cobalt(III). To continue the study and to further understand the shielding of nuclei directly bonded to cobalt(III), we report here the influence of both ligand replacement and geometrical isomerism on ^{15}N chemical shifts of amine nitrogens in a series of $[\text{Co}(\text{ox})_x(\text{gly})_y(\text{en})_z]$ complexes. This series is appropriate for the following reasons: it is of the type $\text{CoN}_x\text{O}_{6-x}$, so that ligand field symmetry is well-defined for each member of the series.⁹ Moreover, nitrogen and oxygen as ligands exhibit very different ligand fields, which may facilitate observation of *trans* and *cis* effects. Finally, the second-order paramagnetism of the cobalt(III) ion changes markedly through the series.¹⁰ Thus, these compounds may allow understanding of the shielding of the ^{15}N nucleus when nitrogen is bonded to cobalt(III).

Experimental Section

Preparation of the complexes has been reported previously.⁹ For the investigation, concentrated solutions (~ 1 M) were prepared by dissolving the complexes in a 5 M aqueous solution of LiBr, which dramatically increases the solubility of the complexes. All solutions contained 5% D_2O for field locking. Natural-abundance proton-noise-decoupled Fourier transform ^{15}N spectra were recorded in 10-mm tubes at 10.09 MHz on a JEOL PS/PFT 100 NMR spectrometer equipped with the JEOL EC-100 data system. With a pulse angle of about 60° and a repetition time of 3 s, 15–20 h were required to achieve a signal-to-noise ratio of $\sim 4:1$. ^{15}N chemical shifts are reported relative to anhydrous liquid ammonia at 25 $^\circ\text{C}$, using a capillary of nitromethane as the external standard and a conversion constant of 380.2 ppm.¹¹

Results

The chemical shifts of amine nitrogens and both glycinato and ethylenediamine ligands in the complexes studied are given in

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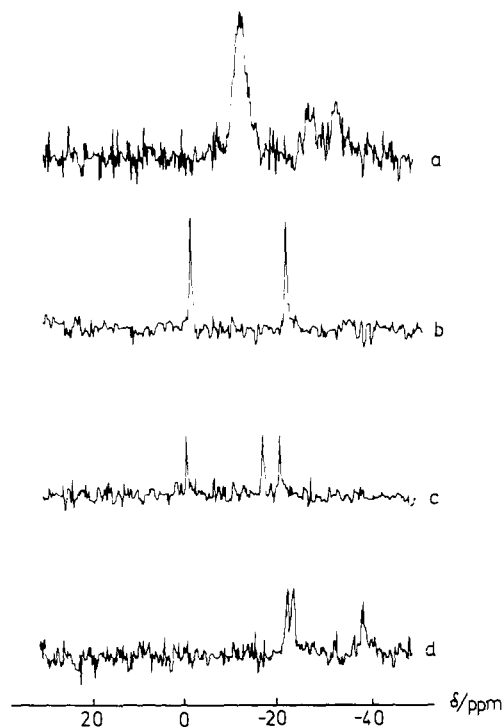


Figure 1. ^{15}N NMR spectra of selected complexes: (a) $[\text{Co}(\text{gly})(\text{en})_2]\text{Cl}_2$; (b) $[\text{Co}(\text{ox})(\text{en})_2]\text{Cl}_2$; (c) *mer*- $[\text{Co}(\text{ox})(\text{gly})(\text{en})]$; (d) *mer*- $[\text{Co}(\text{gly})_3]$.

Table I. The geometric isomers of the series are generally stable, and there was no isomerization during spectrum acquisition. This was confirmed by subsequent recording of the ^{13}C spectrum for each sample and by comparison with the spectra of freshly dissolved compounds. The importance of a possible solvent effect was checked by recording the ^{15}N spectrum of the *fac*- $[\text{Co}(\text{gly})_3]$ complex both in concentrated H_2SO_4 and in concentrated LiBr solution; the chemical shift difference is about 2 ppm. This is a rather small difference compared to the observed variations in ^{15}N chemical shifts and is ignored in the discussion. Because of the fast quadrupolar relaxation of the cobalt nucleus, the ^{15}N - ^{59}Co coupling is not observable in the spectra. However, resonances are broadened to some extent, especially in more symmetric complexes, so that line widths are in the range 3–20 Hz (Figure 1). An exception is the highly symmetric tris(ethylenediamine)cobalt(III) complex, for which the signal is very broad. Indeed, the resonance line is nearly split into an octet with an estimated coupling constant of about 50 Hz; the shift value given in Table I corresponds to the midpoint of the observed band. For some of the complexes in Table I, Fung and Wei³ have reported ^{14}N NMR chemical shifts. A few discrepancies in what otherwise should be identical values have been noted. For $[\text{Co}(\text{en})_3]\text{Cl}_3$ their result is close to ours, but for *fac*- $[\text{Co}(\text{gly})_3]$ the values do not correspond. Their investigations afforded a shift of +46 ppm relative to $\text{NH}_3(\text{liq.})$ for the *fac* isomer while we find -42.4 ppm. Fung et al.¹² also reported INDOR ^{15}N chemical shifts for *mer*- $[\text{Co}(\text{gly})_3]$. These values are referenced to $^{15}\text{NH}_4^+$ as an internal standard, prepared under ill-defined conditions, which makes comparison with our results uncertain. In accordance with our result, three lines were observed in the INDOR spectrum, but the spacing between the lines differs from ours.

Our primary interest lies in the coordination shifts, i.e., the difference between chemical shifts of the free and coordinated ligands. Because both glycinato- and ethylenediamine-free ligands have practically the same shift (20 ppm^{4,11}), coordination shifts could be determined without prior assignment of the signals. Table I shows that coordination shifts Δ_c are in the direction of substantially higher shielding and range from -19 to -62 ppm. From

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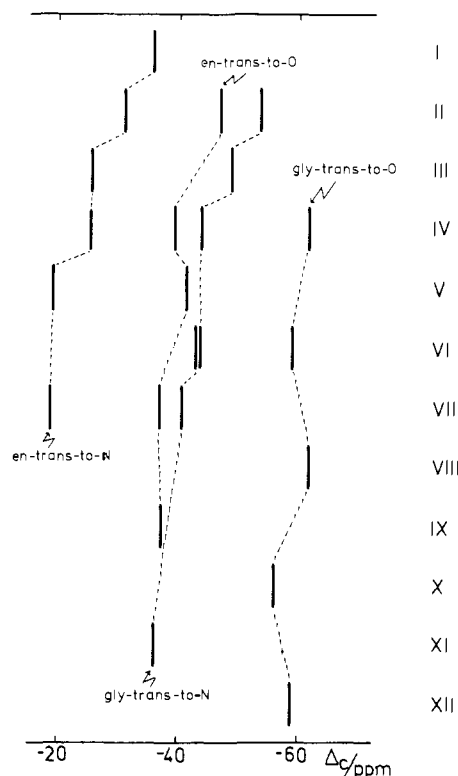


Figure 2. Assignment of the observed coordination shifts in the ^{15}N spectra of the complexes investigated (ordinal numbers correspond to those in Table I).

assignments in spectra with only one signal (complex 1 and 8–12), more complex spectra could be assigned. For instance, two signals are expected for *cis*-(N)- C_1 - $\text{K}[\text{Co}(\text{ox})(\text{gly})_2]$ because of its C_1 symmetry; however, these evidently coincide. Both signals belong to the amino group of the glycinato ligand, which is trans to the oxygen ligator. In the geometrical isomer of the same complex, *trans*-(N)- $\text{K}[\text{Co}(\text{ox})(\text{gly})_2]$, both nitrogens are trans to the nitrogen ligator and exhibit smaller coordination shifts. Thus, a ligator trans to oxygen appears to induce a more pronounced coordination shift, as is evidenced by complexes 8, 10, and 12, all of which have the glycinato amino group trans to the oxygen ligator.

Next, it is instructive to consider the *mer*- $[\text{Co}(\text{gly})_3]$ complex. Of the three signals in the spectrum (Figure 1), the one with the large coordination shift can be assigned to the amino group trans to oxygen. The two closely spaced signals with smaller coordination shifts correspond to the amine groups trans to each other, i.e., to groups trans to nitrogen. The difference between the glycinato amino group ^{15}N chemical shifts when the group is trans to oxygen and trans to nitrogen averages about 18 ppm. Similar differences exist for ethylenediamine amino group ^{15}N shifts when that group occupies analogous positions, as is seen in the spectrum of the $[\text{Co}(\text{ox})(\text{en})_2]\text{Cl}$ complex (Figure 1). However, the ethylenediamine coordination shifts are smaller. For instance, if we compare complexes 9 and 10, which are both of the type *cis*-(N)- CoO_4N_2 , then the glycinato and ethylenediamine amino groups, which are all trans to oxygen, differ in their coordination shifts by about 20 ppm.

The $[\text{Co}(\text{gly})(\text{en})_2]\text{Cl}_2$ spectrum is especially instructive. In this example three ethylenediamine amino groups trans to nitrogen yield one signal (intensity 3, Figure 1), while one ethylenediamine amino group trans to oxygen gives rise to a signal at ~ 16 ppm to higher shielding. Close to this resonance is a signal from the glycinato amino group trans to nitrogen. Again, and in general, an amino group ^{15}N nucleus trans to oxygen is shielded by ~ 18 ppm compared to the same group trans to nitrogen. Nearly the same difference (20 ppm) exists between glycinato and ethylenediamine amino group coordination shifts when they are in corresponding positions. On the basis of these regularities we have assigned all the signals of the complexes; these are summarized

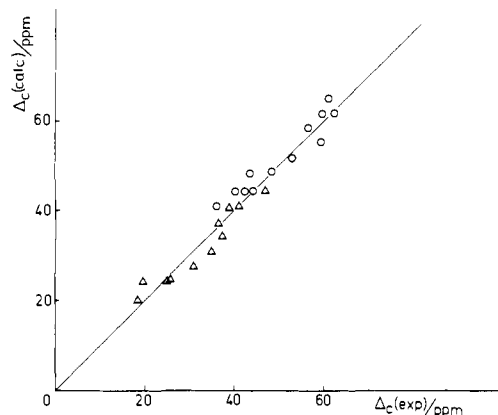


Figure 3. Correlation between observed and calculated coordination shifts using eq 1: (Δ) ethylenediamine, (O) glycinato ligand.

in Figure 2. Figure 2 also shows that, besides the strong influence of the trans ligator, which allows distinction of amino nitrogens trans to oxygen and trans to nitrogen, the influence of the cis ligator is also important. Replacement of a cis nitrogen with an oxygen ligator generally diminishes the coordination shift. That is, the influence of cis ligators on the coordination shift is smaller and opposite that of trans ligators.

From these data, an empirical expression that accounts for most of the observed cis and trans influences on the ^{15}N coordination shifts may be derived, that has the form

$$\Delta_c = C - 4\chi^{\text{trans}} + \sum_i \chi_i^{\text{cis}} \quad (1)$$

Here, χ is a parameter characteristic of a given ligator (N or O) independent of its position cis or trans to the observed nitrogen. Parameter C is the coordination shift when all ligators are the same, with values different for glycinato and ethylenediamine ligands. The best fit between observed coordination shifts and those calculated from eq 1 is obtained with the following parameters: $C(\text{gly}) = -55$ ppm, $C(\text{en}) = -31$ ppm, and $\chi(\text{O}) - \chi(\text{N}) = 3.5$ ppm (correlation coefficient = 0.975, standard deviation 1.6 ppm). The corresponding correlation is presented in Figure 3.

Discussion

As discussed in the Introduction, coordination shifts of nuclei directly bonded to spin-paired d^6 metal ions move markedly to higher shielding. For instance, ^{19}F resonance positions in diamagnetic metal hexafluorides² lie about 200–300 ppm to higher shielding for metal ions with d^6 spin-paired configurations than for other metal ions, including those with d^0 electronic configurations. The peculiar feature of the spin-paired d^6 electronic configuration of metal ions is that these ions have available easily excitable d electrons which produce strong paramagnetic currents. This second-order paramagnetism completely dominates the magnetic shielding of metal nuclei in the complexes.¹³ As a result, several authors have attempted to explain the shielding of metal-bonded nuclei in the same terms. Thus, Buckingham and Stephens¹⁴ have explained the shielding of protons coordinated to d^6 metal ions on the basis of the second-order paramagnetism caused by d - d electronic transitions. However, the theory they presented predicts large effects only on nuclei very close to the ion. For metal–ligand bond lengths that are >0.2 nm, this effect is reduced to a point-dipole magnetic anisotropy influence of the metal ion, which accounts for an additional shielding of only a few ppm. Nakashima et al.⁶ have calculated the influence of the magnetic anisotropy of cobalt(III) complexes and obtained a maximum shielding of 1.5 ppm. This result contrasts with the experimental coordination shifts of ~ 50 ppm. In the series of complexes presented here, although the magnetic anisotropy of cobalt(III) may be quite large,¹⁰ we have calculated that in the

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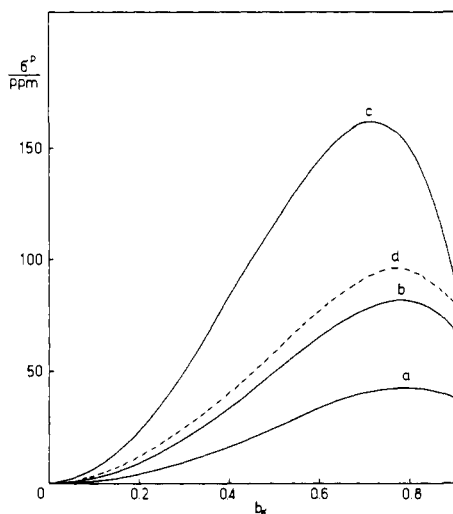


Figure 4. Additional shielding of the nitrogen nucleus from the Cornwell-Santry effect, according to eq A5: (a) $b_\sigma/b_\pi = 10$, $\Delta E = 20000 \text{ cm}^{-1}$; (b) $b_\sigma/b_\pi = 5$, $\Delta E = 20000 \text{ cm}^{-1}$; (c) $b_\sigma/b_\pi = 3$, $\Delta E = 20000 \text{ cm}^{-1}$; (d) $b_\sigma/b_\pi = 5$, $\Delta E = 17000 \text{ cm}^{-1}$. In all cases $(r^{-3})_{2PN} = 20 \times 10^{24} \text{ cm}^{-3}$ and $a_i = (1 - b_i^2)^{1/2}$.

most favorable case, the anisotropy contributes only an additional 5 ppm to the nitrogen shielding. Hence, the cobalt(III) magnetic shielding anisotropy is of minor importance.

Another mechanism suggested² as a possible explanation of the d⁶ metal ion influence is the so called "Cornwell-Santry effect". This effect, first introduced by Cornwell¹⁵ and Santry¹⁶ to explain the "anomalous" high-field ¹⁹F shifts of ClF, is based on the idea that electronic excitation involving only antibonding molecular orbitals causes opposing shielding on the two atoms involved in the bond. In this way, strong paramagnetic circulation on a spin-paired d⁶ metal ion may produce considerable diamagnetic circulation on a directly bonded nucleus.

The evaluation of the Cornwell-Santry effect in the spin-paired d⁶ complexes with octahedral ligand field symmetry is given in the Appendix. It is assumed that the relevant ¹A_{1g} → ¹T_{1g} electronic transition occurs between antibonding molecular orbitals. When the final expression (A5) is applied to the nitrogen nucleus directly bonded to cobalt(III), an additional shielding is predicted that may amount to 200 ppm, depending upon the mixing coefficients of the atomic orbitals in the antibonding molecular orbital (Figure 4). As is seen from Figure 4, this additional shielding is very sensitive to the mixing coefficients, b_σ and b_π , of the nitrogen orbitals. The associated excitation energy change has a smaller impact on the shielding. Bonding of the amino nitrogen to cobalt(III) involves mainly σ bonds. For instance, the ab initio calculation reported for the [Co(NH₃)₆]³⁺ complex ion¹⁷ shows that 1.1 units of electronic charge are transferred from the ligands to cobalt(III) by σ bonding, which would correspond to $b_\sigma \sim 0.7$. Bonding through π bonds is far less important. However, t_{2g} molecular orbitals are slightly antibonding owing to participation of occupied π orbitals of the ligands,¹⁷ but the coefficient b_π should be rather small. From Figure 4 one may see that for $b_\sigma = 0.7$ and $b_\sigma/b_\pi = 10$ there is still enough additional shielding to account for the observed coordination shifts.

Although the Cornwell-Santry effect predicts opposing changes in the shielding of the two atoms involved, there is in fact no clear correlation between reported ⁵⁹Co chemical shifts¹⁰ and the ¹⁵N values presented here. This observation may be rationalized by noting that the paramagnetic circulation is heavily centered on the cobalt ion and hence is only slightly influenced by minor changes in electron circulation on the ligands. The nitrogen

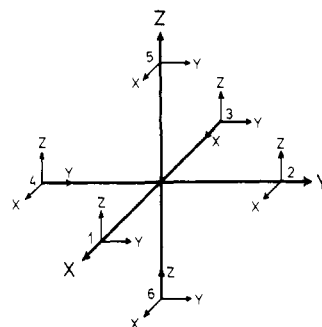


Figure 5. Coordinate systems of the octahedral complex used in the calculation of the Cornwell-Santry effect (coordinate systems on ligands are all right handed, i.e., collinear with the central ion coordinate system).

ligators derive their electron circulation predominantly through mixing of the nitrogen orbitals with the cobalt d orbitals. Consequently, while a very good correlation exists between the ⁵⁹Co chemical shifts and electron excitation energies,¹⁰ a corresponding correlation of the ¹⁵N shifts with either the ⁵⁹Co values or electron excitation energies is obscured by the far more important changes in the mixing coefficients.

An attractive feature of the Cornwell-Santry effect is that the additional shielding is proportional to the mixing coefficient of the nitrogen orbital in the σ antibonding molecular orbital. This coefficient is larger for stronger Co-N bonds. Such a correspondence between Co-N bond strength and coordination shifts had already been proposed,⁶ and our results provide a theoretical basis for this suggestion.

Let us now consider the cis and trans influence on the coordination shifts in the CoN_xO_{6-x}-type series of complexes examined here. Although the basic nature of the trans effect is not fully understood, ligands giving rise to a large trans effect usually seem to weaken the bond of a second, trans-oriented, ligand.¹⁸ Since nitrogen ligators generally have larger trans effects than oxygen ligators,¹⁶ an amino group forms a weaker bond with cobalt(III) when it is trans to nitrogen than when it is trans to oxygen. The observed coordination shift changes are then in agreement with predictions based on the Cornwell-Santry effect. The cis effect is generally less observable, and even less is known about it. The observed changes in coordination shifts suggest that this effect is about 4 times less important than, and opposite in sign to, the trans effect. This means that a ligator with a strong trans effect strengthens the Co-N bond in the cis position. Thus, the empirical correlation given by eq 1 is a consequence of the competitive influence of trans and cis ligators on the Co-N bond strength. In addition, one must also consider that changes in π bonding may have a large impact on the Cornwell-Santry effect even though the overall metal-ligand bond strength is little affected, because the contribution of π bonding to the total bond strength is low. This may also be the reason for the large difference between the coordination shifts of the glycinate and ethylenediamine ligands.

Conclusion

The study presented here has demonstrated the large sensitivity of ¹⁵N chemical shifts of amino group nitrogens coordinated to cobalt(III) to mutual influences of the ligators. The trans influence is so pronounced that it may be used for determination of geometrical isomerism in CoN_xO_{6-x}-type complexes. This is of special interest for bioinorganic chemistry, where metal ions are coordinated nearly exclusively to nitrogen and oxygen ligators.

Shielding coordination-induced displacement of amino group ¹⁵N resonance lines, and its variation with the nature of the trans and cis ligators, may be understood in terms of the Cornwell-Santry effect in spin-paired d⁶ complexes. While this effect is not likely to be solely responsible for the shielding coordination shifts, it is estimated to be large enough to be the major influence. Investigation of coordination shifts of ligators with different σ and

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π bonding abilities is in progress and will provide definite answers regarding the importance of the Cornwell-Santry effect in the spin-paired d^6 transition-metal complexes.

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Appendix

The paramagnetic shielding term in a molecular orbital description has the following form:¹⁹

$$\sigma_{\alpha\alpha}^p = -2\beta^2 \sum_n (E_n - E_0)^{-1} \left[\left\langle \psi_0 \left| \sum_k \frac{l_{\alpha,k}}{r_k^3} \right| \psi_n \right\rangle \langle \psi_n | \sum_j l_{\alpha,j} | \psi_0 \rangle + CC \right] \quad (A1)$$

For cobalt(III) complexes with octahedral ligand field symmetry, paramagnetic shielding arises from the ${}^1A_{1g} \rightarrow {}^1T_{2g}$ transition,¹³ and expression A1 can be reduced to

$$\sigma_{\alpha\alpha}^p = \frac{8\beta^2}{\Delta E({}^1A_{1g} \rightarrow {}^1T_{1g})} \left\langle \psi_{t_{2g}} \left| \frac{l_{\alpha}}{r^3} \right| \psi_{e_g} \right\rangle \langle \psi_{e_g} | l_{\alpha} | \psi_{t_{2g}} \rangle \quad (A2)$$

$\alpha \in x, y, z$

Expression A2 is the basis for calculating the shielding of a nucleus directly bonded to cobalt(III). Molecular orbitals ψ_{e_g} and $\psi_{t_{2g}}$ are expressed as linear combinations of metal and ligand atomic orbitals. The paramagnetic term is calculated following the procedure of Cornwell.¹⁵ Thus, for operator l/r^3 all terms are dropped except those on the atom for which σ^p is sought. We chose to calculate the shielding on a ligator in position 5 (see Figure 5), so that only excitations along the x and y axes of the complex contribute to σ^p , i.e.,

$$\sigma_{av}^p = \frac{1}{3}(\sigma_{xx}^p + \sigma_{yy}^p)$$

Because $\psi_{t_{2g}}$ and ψ_{e_g} are antibonding orbitals, shielding along the y axis is

$$\sigma_{yy}^p(5) = -\frac{8\beta^2}{\Delta E} \left\langle \psi_{z^2}^a \left| \frac{l_y}{r^3(5)} \right| \psi_{xz}^a \right\rangle \langle \psi_{xz}^a | l_y | \psi_{z^2}^a \rangle \quad (A3)$$

where (see Figure 5)

$$\psi_{z^2}^a = a_{\sigma} d_{z^2} - \frac{b_{\sigma}}{2\sqrt{3}}(p_x^{(1)} + p_y^{(2)} - p_x^{(3)} - p_y^{(4)} - 2p_z^{(5)} + 2p_z^{(6)})$$

$$\psi_{xz}^a = a_{\pi} d_{xz} - \frac{b_{\pi}}{2}(p_z^{(1)} - p_z^{(3)} + p_x^{(5)} - p_x^{(6)})$$

For operator l_y it is necessary to keep the terms on all atoms. However, if overlap effects are neglected local origins are properly used for l_y and a good estimation may be obtained by considering only local terms.¹⁵ With this procedure it follows that

$$\left\langle \psi_{z^2}^a \left| \frac{l_y}{r^3(5)} \right| \psi_{xz}^a \right\rangle = i \frac{b_{\sigma} b_{\pi}}{2(3)^{1/2}} \langle r^{-3} \rangle_L \quad (A4)$$

where $\langle r^{-3} \rangle_L$ is the mean reciprocal cubic distance of ligator p electrons from the ligator nucleus. The same values are obtained for shielding along the x axis so that additional shielding of the ligator nucleus from the Cornwell-Santry effect is given by

$$\sigma_{av}^p(L) = \frac{8\beta^2}{3} \frac{\langle r^{-3} \rangle_L}{\Delta E} b_{\sigma} b_{\pi} \left(a_{\sigma} a_{\pi} - \frac{1}{2} b_{\sigma} b_{\pi} \right) \quad (A5)$$

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Solution Structure of Tris[hydridotris(pyrazol-1-yl)borato]ytterbium(III): Rare Example of Solution Rigid Lanthanide Complex

Matthew V. R. Stainer* and Josef Takats*

Contribution from the Department of Chemistry, The University of Alberta, Edmonton, Alberta, Canada T6G 2G2. Received June 11, 1982

Abstract: The ¹H, ¹³C, and ¹¹B NMR spectra of Lu(HBPz₃)₃ and Yb(HBPz₃)₃ (Pz = pyrazolyl, C₃N₂H₃) complexes have been recorded. The complexes are stereochemically rigid on the NMR scale with solution structure approximating the known solid-state structure of Yb(HBPz₃)₃. The molecules have C₃ symmetry in solution, and accordingly, the ytterbium complex gives rise to 21, 18, and 3 well-separated and lanthanide-shifted resonances in the ¹H, ¹³C, and ¹¹B NMR spectrum, respectively. Least-squares fits of the lanthanide-induced shifts in the paramagnetic Yb(HBPz₃)₃ complex to the solid-state structural data, using the full form of the McConnell-Robertson expression for the dipolar shifts, gave the molecular susceptibility anisotropies of the complex and the orientation of the magnetic axes in the complex. The C₃ molecular symmetry fixes the z magnetic axis perpendicular to the mirror plane, while the magnetic x axis refines to a position close to the pseudo-C₂ axis of the coordination polyhedron, which has approximate C_{2v} symmetry. The close agreement between calculated dipolar shifts and experimentally observed lanthanide-induced shifts confirms that the solid-state molecular structure remains essentially unchanged on dissolution and shows that contributions to the induced shifts in the ytterbium complex by a Fermi contact mechanism are minimal.

In the course of our studies on lanthanide complexes containing the potentially tridentate HBPz₃⁻ (Pz = pyrazolyl, C₃N₂H₃) ligand, we prepared the tris[hydridotris(pyrazol-1-yl)borato]lanthanide complexes, Ln(HBPz₃)₃.¹ An X-ray structure determination²

of the ytterbium complex revealed that the complex is eight-coordinate, with one free uncoordinated pyrazolyl group directed away from the metal center in a fashion which appeared to preclude its participation in an intramolecular ligand exchange

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