NMR spectroscopy of the solid-state isomerization of nitrito- and nitro-pentamminecobalt(III) chloride¹

Kristopher J. Ooms and Roderick E. Wasylishen

Abstract: Cobalt-59 and nitrogen-15 NMR spectra of the *nitrito*pentamminecobalt(III) chloride, $[(NH_3)_5Co-ONO]Cl_2$, and *nitro*pentamminecobalt(III) chloride, $[(NH_3)_5Co-ONO_2]Cl_2$, isomers in the solid state have been obtained at several applied magnetic field strengths. The ⁵⁹Co NMR line shapes indicate that both the cobalt nuclear quadrupolar coupling constant (C_Q) and the span of the chemical shift tensor (Ω) decrease when the complex isomerizes from $[(NH_3)_5Co-ONO_2]^{2+}$; C_Q decreases from 23 to 10.3 MHz and Ω changes from 1650 to 260 ppm. The ¹⁵N NMR line shapes also show a significant change in the nitrogen magnetic shielding tensor upon isomerization, with Ω decreasing from 710 to 547 ppm; also, an indirect spin-spin coupling, ${}^{1}J({}^{59}Co, {}^{15}N) = 63$ Hz, is observed in the ¹⁵N NMR spectra of the nitro isomer. The NMR parameters are rationalized based on differences in the molecular structure of the two isomers. NMR spectra have also been recorded as the isomerization progresses with time and demonstrate the practicality of the technique for the study of solid-state isomerizations.

Key words: ¹⁵N, ⁵⁹Co, solid-state NMR, linkage isomerization, chemical shift tensor, electric field gradient tensor.

Résumé : Opérant en phase solide et à plusieurs forces de champ magnétique appliqué différentes, on a déterminé les spectres RMN du ⁵⁹Co et du ¹⁵N d'isomères du chlorure de *nitrito*pentamminecobalt(III), $[(NH_3)_5Co-ONO]Cl_2$ et du chlorure de *nitrio*pentamminecobalt(III), $[(NH_3)_5Co-ONO]Cl_2$ et du chlorure de *nitro*pentamminecobalt(III), $[(NH_3)_5Co-NO_2]Cl_2$. Les formes des raies des spectres RMN du ⁵⁹Co indiquent que la constante de couplage quadripolaire nucléaire du cobalt (C_Q) ainsi que l'envergure du tenseur du déplacement chimique (Ω) diminuent toutes les deux lorsque le complexe s'isomérise de $[(NH_3)_5Co-ONO]^{2+}$ à $[(NH_3)_5Co-NO_2]^{2+}$; la valeur de C_Q diminue de 23 à 10,3 MHz alors que la valeur de Ω passe de 1650 à 260 ppm. Lors de l'isomérisation, les formes des raies en RMN du ¹⁵N présentent aussi un changement significatif dans le tenseur de blindage magnétique de l'azote, avec Ω , qui passe de 710 à 547 ppm; de plus, on observe un couplage spin-spin indirect, ${}^{1}J({}^{59}Co,{}^{15}N) = 63$ Hz, dans le spectre RMN du ¹⁵N de l'isomère nitro. Les différences dans les paramètres RMN sont rationalisées sur la base de différences dans la structure moléculaire de chacun des isomères. On a aussi enregistré les spectres RMN alors qu'ils s'isomérisent en fonction du temps et on démontrent que cette technique peut être pratique pour l'étude d'isomérisations à l'état solide.

Mots clés : ¹⁵N, ⁵⁹Co, RMN à l'état solide, isomérisation de liaison, tenseur du déplacement chimique, tenseur du gradient du champ électrique.

[Traduit par la Rédaction]

Introduction

Reactions that occur in the solid state are of interest in many areas of research such as pharmaceutical chemistry (1, 2), organometallic chemistry (3), and organic synthesis (4–6). Linkage isomerizations are one class of solid-state reactions that involve a change in the bond(s) between a ligand and a metal centre. The linkage isomerization involving the nitrite anion (NO_2^{-1}) in *nitrito*pentamminecobalt(III) chloride (nitrito), which isomerizes to form the more thermodynamically stable *nitro*pentamminecobalt(III) chloride (nitro), $[(NH_3)_5Co-ONO]^{2+} \rightarrow [(NH_3)_5Co-NO_2]^{2+}$, has been known

for over 100 years (7). This reaction has been studied in depth by numerous techniques, including solution NMR spectroscopy (8), IR spectroscopy (9–14), single-crystal and powder X-ray diffraction (15–17), and recently, DFT quantum chemical methods (18, 19).

Several studies, primarily employing IR spectroscopy, have determined the rate constants, equilibrium values, and activation energies of the reaction in the solid state (11, 15, 20–23). Typically the isomerization half-life is on the order of hours to days depending on the temperature. One problem with the solid-state investigations to date is that the temperatures at which the kinetic data are measured are usually

Received 21 September 2005. Published on the NRC Research Press Web site at http://canjchem.nrc.ca on 21 March 2006.

Dedicated to Dr. Arthur J. Carty for his contributions to science in Canada.

K.J. Ooms and R.E. Wasylishen.² Department of Chemistry, University of Alberta, Edmonton, AB T6G 2G2, Canada.

¹This article is part of a Special Issue dedicated to Professor Arthur Carty. ²Corresponding author (e-mail: roderick.wasylishen@ualberta.ca). above room temperature, while the X-ray diffraction data has been obtained well below room temperature. This makes it difficult to draw connections between the kinetic data and the crystal structures. In addition, there are significant discrepancies in the rate constants reported by different investigators. In principle, solid-state NMR spectroscopy can provide a valuable link between the structural and thermodynamic properties of this system at the same temperature; however, only the solid-state ⁵⁹Co NMR of the more stable nitro isomer has been reported (24).

In the current study we have determined the ⁵⁹Co and ¹⁵N NMR parameters of both the nitrito and nitro complexes of pentamminecobalt(III) chloride using solid-state NMR. Cobalt-59 is a spin I = 7/2 quadrupolar nucleus and has one of the largest chemical shift ranges in the periodic table, >18 000 ppm (25), making it ideally suited for solid-state NMR investigations of cobalt complexes because of its sensitivity to subtle changes in molecular structure (25–29). Nitrogen-15, which is a spin I = 1/2 nucleus, is well-suited to follow the effect that structural changes have on the NO₂⁻ ligand (30, 31). We present the 59 Co and 15 N solid-state NMR parameters for the [(NH₃)₅Co-ONO]²⁺ isomer followed by those for the $[(NH_3)_5Co-NO_2]^{2+}$ isomer. We have also monitored the thermal isomerization reaction using solid-state ⁵⁹Co and ¹⁵N NMR spectroscopy in an effort to determine whether this technique has the potential to provide the relative amounts of each isomer in the solid state.

Experimental

The pink nitrito, [(NH₃)₅Co-ONO]Cl₂, and yellow nitro, [(NH₃)₅Co-NO₂]Cl₂, isomers were synthesized according to literature methods, and the product purity was verified using IR spectroscopy (10, 12). The isotopically enriched ¹⁵N samples were prepared using 99% ¹⁵N-labelled sodium nitrite obtained from C/D/N Isotopes Inc., Pointe-Claire, Quebec. The precursor compound for the synthesis (chloropentamminecobalt(III) chloride) was synthesized by the addition of 15 mL of concentrated aqueous hydrochloric acid to 5 g of cobalt(II) carbonate in 35 mL of distilled water. The precipitate was filtered twice and 5.05 g of ammonium chloride and 50 mL of concentrated aqueous ammonia were added. The solution was cooled and 80 mL of 6% hydrogen peroxide was slowly added. When bubbling ceased, nitrogen was bubbled through the solution for 1 h. The solution was neutralized with hydrochloric acid, after which an additional 20 mL of concentrated hydrochloric acid were added and the solution was set in a hot water bath for 2 h. The purple precipitate was filtered and washed with water and ethanol, yielding approximately 9 g of sample.

Solid-state NMR spectroscopy was performed on three spectrometers with field strengths of 4.70 T (Chemagnetics CMX Infinity 200), 7.05 T (Bruker Avance 300), and 11.75 T (Bruker Avance 500). Bruker double or triple resonance probes (4 mm o.d. MAS) were used on the Bruker systems, while Chemagnetics double resonance probes (4 mm o.d. MAS and 5 mm o.d. solenoid) were used on the Chemagnetics system. All ⁵⁹Co NMR chemical shifts were referenced with respect to a 1.0 mol/L aqueous solution of $K_3Co(CN)_6$ at 0.0 ppm, while the ¹⁵N NMR chemical shifts were referenced with respect to liquid NH₃ (20 °C) by set-

ting the ammonium peak of labelled, solid $^{15}NH_4NO_3$ to 23.8 ppm (32). Magic angle spinning (MAS) rates were controlled using automated MAS controllers to within ±2 Hz. The ⁵⁹Co nonselective $\pi/2$ pulse lengths were determined for the setup sample (1.0 mol/L $K_3Co(CN)_6$) and were 4.5, 2.0, and 1.9 µs at 4.70, 7.05, and 11.75 T, respectively. A onepulse or echo-pulse sequence was used for acquiring ⁵⁹Co NMR spectra with pulse lengths ($\tau_{p(sel)}$), that selectively excited the central transition $(\tau_{p(sel)} = \tau_{p(nonsel)}/(I + 1/2))$ (33). Nitrogen-15 NMR spectra were acquired using a cross polarization (CP) pulse sequence $(\pi/2(^{1}\text{H}) = 4.5 \,\mu\text{s})$ and a contact time of 8.0 ms, which was initially setup on solid ¹⁵NH₄NO₃ and then optimized for the samples. High-power proton decoupling was performed during the acquisition of all spectra using the TPPM method (34). The sample temperature was determined using a Chemagnetics temperature controller that had been calibrated using the ²⁰⁷Pb NMR peak of solid lead nitrate (32, 35).

Typically, Gaussian line-broadening functions of 20– 50 Hz and 500–3000 Hz were applied when processing the spectra of MAS and stationary samples, respectively. The calculated and experimental spectra were fit by visual inspection using the program WSOLIDS (36).

Ab initio calculations of the nitrogen magnetic shielding tensors were performed using Gaussian 98W (revision A.7) (37) employing the B3LYP method (38, 39) to determine the orientation of the tensor in the molecular frame of reference. Either the 6-311++G(d,p) basis set, or the LANL2DZ basis set with an effective core potential, was used on the cobalt (40); 6-311++G(d,p) basis sets were used on all other atoms. Calculations with both basis sets yielded the same orientation of the magnetic shielding tensor. The calculated magnetic shielding values (σ) were converted to chemical shifts relative to the reference compound, $NH_3(l, 20 \text{ °C})$, by applying the formula $\delta = \sigma_{ref} - \sigma$, where $\sigma_{ref} = 244.6$ ppm (41). The atomic coordinates of the cations used were calculated from the X-ray crystal structures determined by Boldyreva et al. (15) and Grenthe and Nordin (17); chloride ions were not included in the DFT calculations.

Results and discussion

Solid-state NMR results

Nitritopentamminecobalt(III) chloride

Figure 1 shows the ⁵⁹Co NMR spectra for the central transition ($m_1 = 1/2 \leftrightarrow -1/2$) of stationary samples of the nitrito isomer, [(NH₃)₅Co-ONO]²⁺, acquired at 4.70, 7.05, and 11.75 T. The parameters used to calculate the spectra are presented in Table 1 and are defined in the table footnote. The spectra in Fig. 1 are influenced by both the ⁵⁹Co quadrupolar interaction and anisotropic magnetic shielding at all three fields. At 4.70 T the second-order quadrupolar broadening (i.e., the line width without the addition of anisotropic magnetic shielding to the simulation) accounts for approximately 90% of the total breadth, while at 11.75 T it accounts for approximately 33%. The spectra are all between 180 and 220 kHz broad, making uniform excitation of the powder pattern difficult and magic angle spinning impractical.

The ⁵⁹Co isotropic chemical shift (δ_{iso}) of the nitrito isomer in the solid state is 8650 ± 50 ppm, the span is 1650 ±

		⁵⁹ Co NMR parameters							
Isomer	Structure	$\overline{\delta_{iso}}$ (ppm)	Ω (ppm)	κ	$C_{\rm Q}~({\rm MHz})$	η	α (°)	β (°)	γ (°)
Nitrito	[(NH ₃) ₅ Co-ONO] ²⁺	8650±50	1650±100	0.8±0.1	±23±1	0.20±0.05	0±5	0±5	0±2
Nitro	[(NH ₃) ₅ Co-NO ₂] ²⁺	7505±5	260±20	-0.20±0.05	+10.3±0.1	0.35 0.05	90±5	90±5	3±1
		¹⁵ N NMR p	¹⁵ N NMR parameters						
Isomer	Structure	δ_{iso} (ppm)	Ω (ppm)	κ	$^{1}J(^{59}\text{Co},^{15}\text{N})$ (Hz)	α (°)	β (°)		
Nitrito	[(NH ₃) ₅ Co-ONO] ²⁺	611±1	710±6	-0.95±0.05					
Nitro	[(NH ₃) ₅ Co-NO ₂] ²⁺	470±1	547±6	0.5±0.1	±63±2	90±2	90±2		
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Table 1. The experimental chemical shift and EFG parameters determined by fitting the ¹⁵N and ⁵⁹Co NMR spectra for nitrito- and nitro-pentamminecobalt(III) chloride.

Note: The chemical shift parameters are defined as follows: $\delta_{33} \leq \delta_{22} \leq \delta_{11}$, $\delta_{so} = (\delta_{11} + \delta_{22} + \delta_{33})/3$, $\Omega = \delta_{11} - \delta_{33}$, $\kappa = 3(\delta_{22} - \delta_{so})/\Omega$ (62). The components of the chemical shift tensor are $\delta_{ii} = (v_{ii} - v_{ref})/v_{ref}$ (*ii* = 11, 22, 33). The EFG parameters are $C_Q = eQV_{ZZ}/h$ and $\eta_Q = (V_{XX} - V_{YY})/V_{ZZ}$, where $|V_{ZZ}| \geq |V_{YY}| \geq |V_{XX}|$. The Euler angles α , β , and γ describe the rotations illustrated in Fig. 2.

Fig. 1. Calculated and experimental ⁵⁹Co NMR spectra of stationary samples of $[(NH_3)_5Co-ONO]Cl_2$ acquired at 4.70, 7.05, and 11.75 T. Each experimental spectrum is the sum of 10 000 - 50 000 scans collected with a 0.1 s pulse delay. The spectrum acquired at 7.05 T has a small amount of nitro isomer present.



100 ppm, and the skew of the tensor is 0.8 ± 0.1 . Since ⁵⁹Co has a large chemical shift range, the large span is not unexpected. In solution, the chemical shift of the nitrito isomer is 7532 ppm (26), corresponding to an 1118 ppm solution-to-solid shift. This is a large change in δ_{iso} , and highlights the sensitivity of the cobalt chemical shift to changes in the local structure (25, 42).

The cobalt electric field gradient (EFG) tensor is nearly axially symmetric ($\eta_Q = 0.20 \pm 0.05$). The fact that a deviation from axial symmetry is observed can be explained by the deviation from C_4 symmetry in the immediate coordination sphere. The quadrupolar coupling constant (C_Q) is 23 ± 1 MHz. While the error is large, it reflects the fact that the **Fig. 2.** (*a*) The counter-clockwise rotations defined by the Euler angles α , β , and γ required to bring the PAS of the EFG tensor (V_{XX}, V_{YY}, V_{ZZ}) into coincidence with the PAS of the chemical shift tensor $(\delta_{11}, \delta_{22}, \delta_{33})$. (*b*) Relative orientation of the ⁵⁹Co-¹⁵N internuclear vector (*r*) with respect to a tensor.



⁵⁹Co NMR spectra may not be of the pure nitrito form. Any nitro isomer present in the sample would cause a distortion of the low frequency discontinuity, leading to some uncertainty in the analysis. The Euler angles, which describe the relative orientations of the ⁵⁹Co EFG and chemical shift tensors, are also obtained from the experiments and are all 0°, placing δ_{11} along V_{XX} and δ_{33} along V_{ZZ} (Fig. 2*a* shows how the angles are defined, ref. 43).

Figure 3 shows the experimental and calculated ¹⁵N NMR spectra of nitritopentamminecobalt(III) chloride, with 99% ¹⁵N-labelled nitrite, obtained at 4.70 T with MAS rates of 2.0 and 4.0 kHz. The observed spectra were fit with calculated spectra based on the procedure developed by Herzfeld and Berger (44) as implemented in the WSOLIDS program. The experimental and calculated spectra of a stationary sample acquired at 4.70 T are also shown in Fig. 3. Analysis of the spectra yields the experimental NMR parameters listed in Table 1. The tensor is approximately axially symmetric ($\kappa = -0.95 \pm 0.05$), has a span of 710 \pm 6 ppm, and the δ_{iso} (611 \pm 1 ppm) is only slightly less than that of the nitrogen in sodium nitrite (625.4 ppm) (45). The near axial symmetry at the nitrogen of this compound.

Nitropentamminecobalt(III) chloride

The ⁵⁹Co central transition NMR spectra of freshly synthesized nitro isomer, $[(NH_3)_5Co-NO_2]^{2+}$, collected at three fields (4.70, 7.05, and 11.75 T) are shown in Fig. 4; the parameters derived from the calculated spectra are given in Ta**Fig. 3.** Calculated and experimental ¹⁵N NMR spectra of MAS and stationary samples of $[(NH_3)_5Co-ONO]Cl_2$ acquired at 4.70 T using CP. Each experimental spectrum was acquired using a pulse delay of 5.0 s and is the sum of 612 and 6144 scans for the MAS and stationary samples, respectively.



ble 1. The spectra suffered from a general broadening, which obscured some of the features, most likely because of direct and indirect spin-spin coupling to the six directly bonded ¹⁴N nuclei. From the spectrum of an MAS sample, $v_r = 13$ kHz, collected at 7.05 T (Fig. 4*b*), it is straightforward to determine the quadrupolar parameters because the chemical shift anisotropy is averaged by spinning at the magic angle. The values obtained are $C_Q = 10.3 \pm 0.1$ MHz and $\eta_Q = 0.35 \pm 0.05$. This corresponds to a significant decrease in the ⁵⁹Co quadrupolar coupling upon conversion from the nitrito isomer ($C_Q = 23 \pm 1$ MHz). δ_{iso} also changes upon isomerization from 8650 \pm 50 to 7505 \pm 5 ppm.

With the C_Q , η_Q , and δ_{iso} determined from the ⁵⁹Co NMR spectra obtained with MAS, the spectra of the stationary samples (Figs. 4*a* and 4*c*) were analysed, and the chemical shift tensor and its orientation relative to the EFG tensor were determined. The span of the chemical shift tensor is 260 ± 20 ppm and the skew is -0.20 ± 0.05 . The Euler angles are $90 \pm 5^{\circ}$, $90 \pm 5^{\circ}$, and $3 \pm 1^{\circ}$ for α , β , and γ , respectively, making the EFG and chemical shift tensors nearly coincident with δ_{11} parallel to V_{ZZ} and δ_{33} parallel to V_{YY} . These ⁵⁹Co EFG and chemical shift parameters differ from those previously reported (24): $C_Q = 11.25$ MHz, $\eta_Q = 0.55$, $\Omega = 270$ ppm, $\kappa = 0.519$, and $\alpha = 7^{\circ}$, $\beta = 88^{\circ}$, and $\gamma = 7^{\circ}$. The differences can be related primarily to the different C_Q values; in the previous study, measurements of samples under MAS were not carried out.

Figure 5 shows the centre band region of the ¹⁵N NMR spectrum acquired for a sample of the nitro isomer under MAS conditions at 4.70 T. The centre band, as well as the

spinning side bands (not shown), are split by indirect spinspin coupling to the ⁵⁹Co, $|^{1}J(^{59}Co, ^{15}N)|$, which is 63 ± 2 Hz. Previous solid-state ${}^{1}J({}^{59}Co, {}^{15}N)$ values have been reported for a series of cobaloxime complexes with either pyridine-¹⁵N or aniline-¹⁵N ligands; the magnitudes range from 36 to 75 Hz (46). The splitting pattern in the ¹⁵N NMR spectrum is influenced by the cobalt quadrupolar coupling parameters because the ⁵⁹Co-¹⁵N dipolar coupling can not be completely averaged by MAS (46-48). For the ⁵⁹Co-¹⁵N pair, the peaks in the ¹⁵N spectra are split into eight peaks, corresponding to the eight possible spin states of the ⁵⁹Co $(m_{\rm I} = -7/2$ to +7/2). The peak intensities and splittings are dictated by ${}^{1}J({}^{59}\text{Co},{}^{15}\text{N})$, the ${}^{59}\text{Co}-{}^{15}\text{N}$ dipolar coupling constant, $R_{\rm eff}$, the ⁵⁹Co $C_{\rm Q}$, $\eta_{\rm Q}$, and the orientation of the ⁵⁹Co EFG tensor with respect to the ⁵⁹Co-¹⁵N dipolar vector. With the magnitude of the ⁵⁹Co quadrupolar coupling and η_0 determined from the ⁵⁹Co NMR spectra and the value of $R_{\rm eff} = -402$ Hz, calculated based on the Co—N distance obtained from the crystal structure (assuming $\Delta J = 0$), the experimental spectrum in Fig. 5 can be best fit when the sign of C_0 is positive and the Euler angles that orient the Co-N dipolar vector in the PAS of the 59Co EFG are both 0°, placing V_{ZZ} along the dipolar vector (Fig. 2b shows how the angles are defined for a vector with respect to a tensor).

Analysis of the ¹⁵N NMR spectrum of a stationary sample of the nitro isomer (Fig. 6) indicates that the span of the nitrogen chemical shift tensor is 547 ± 6 ppm and that the skew is 0.5 ± 0.1 (Table 1). This is a significant change from the nitrito isomer and is accompanied by a change in δ_{iso} from 611 ± 1 to 470 ± 1 ppm. The ¹⁵N NMR isotropic chemical shift value of the nitrite ligand in the nitro isomer is significantly less than that reported for the nitrite ion in NaNO₂ ($\delta_{iso} = 625.4$ ppm) (45). Also, the span of the nitro nitrogen shielding tensor in the cobalt complex is less than that of the nitrite ion in NaNO₂ ($\Omega = 951$ ppm, $\kappa = 0.37$) (45).

The¹⁵N NMR line shape of a stationary sample of an isolated spin pair, such as ¹⁵N coupled to ⁵⁹Co, depends on the ¹⁵N chemical shift tensor, $R_{\rm eff}$, ¹J(⁵⁹Co,¹⁵N), and the orientation of the dipolar vector in the principal axis system (PAS) of the ¹⁵N chemical shift tensor (46, 49). The angles that relate the Co-N dipolar vector to the ¹⁵N chemical shift tensor, determined from the analysis of the ¹⁵N NMR spectrum in Fig. 6 are $\alpha = 90^{\circ}$ and $\beta = 90^{\circ}$; the δ_{22} component of the nitrogen chemical shift tensor is along the Co—N bond, while δ_{33} is perpendicular to the Co-NO₂ plane.

Relationship between molecular structure and the EFG and chemical shift tensors

To examine the relationship between the molecular structures and the cobalt and nitrogen NMR parameters of the two isomers, it is important to look at the three principal components of the tensors and their orientation in the molecular frame. As mentioned, the magnitude of the cobalt C_Q decreases when the nitrito isomer changes to the nitro form, from 23 to 10.3 MHz. This change indicates that the electronic distribution about the cobalt is more symmetric in the nitro isomer, where the cobalt atom is bonded to six nitrogen atoms, compared with the nitrito isomer, where the cobalt is bonded to five nitrogen atoms and one oxygen atom.

The orientation of the EFG tensors at the cobalt nuclei can

Fig. 4. Cobalt-59 NMR spectra of $[(NH_3)_5Co-NO_2]Cl_2$ acquired at (*a*) 11.75 T, (*b*) 7.05 T, and (*c*) 4.70 T. The spectrum acquired at 7.05 T is of a MAS sample ($v_{rot} = 13$ kHz), while those acquired at the other two fields are ⁵⁹Co NMR spectra of stationary samples. The spectra are the sum of 359, 869, and 6227 scans for the three fields, respectively, with a 0.1 s pulse delay. The distortions in the baseline of the spectrum obtained with MAS are a result of not being able to spin rapidly enough to completely average the second-order quadrupolar interaction and chemical shift anisotropy.



Fig. 5. Calculated and experimental ¹⁵N NMR spectra of a MAS sample of $[(NH_3)_5Co-NO_2]Cl_2$ spinning at 8 kHz obtained using CP acquired at 4.70 T showing the ¹ $J(^{59}Co, ^{15}N)$ coupling to the ⁵⁹Co. The intensities of the spinning side bands were added to the centre band.



be understood based on symmetry arguments. While it was not possible to obtain the orientation of the ⁵⁹Co EFG in the molecular frame from the experimental data of the nitrito isomer, the pseudo- C_4 symmetry of the molecule suggests that the unique component of the EFG (V_{ZZ}) is approximately along the Co—ONO bond, and the two components that are nearly equal in magnitude are perpendicular to this bond. For the nitro isomer, the ¹⁵N spectrum for the sample under MAS indicates that the ⁵⁹Co EFG tensor orientation is the same: the V_{ZZ} component is parallel to the Co— NO_2 bond. The lack of change in the orientation of the EFG tensor and the asymmetry parameter indicates that the isomerization simply results in a scaling of the EFG at the cobalt nucleus.

The orientations of the ⁵⁹Co chemical shift tensors in both isomers can be fixed in the molecular frame based on their relative orientation to the EFG tensor. The Euler angles determined from the ⁵⁹Co stationary line shapes of the nitrito isomer indicate that δ_{11} is along V_{XX} and δ_{33} is along V_{ZZ} . Since the tensor is close to axially symmetric, this places the

Fig. 6. Calculated and experimental ¹⁵N NMR spectra of a stationary sample of $[(NH_3)_5Co-NO_2]Cl_2$ acquired using CP at 4.70 T. The spectrum is the sum of 17 692 scans using a 5.0 s pulse delay.



"unique" component of the cobalt chemical shift tensor along the Co-ONO bond, as would be expected. The component of the cobalt chemical shift along the bond is $7605 \pm$ 50 ppm, while the two components of the chemical shift tensor that lie in the $Co(NH_3)_4$ plane, perpendicular to the Co—ONO bond, are 9255 ± 50 and 9099 ± 50 ppm. The ⁵⁹Co chemical shift tensor of the nitro isomer is oriented such that the direction of least shielding is along the Co- NO_2 bond; δ_{11} has a value of 7643 ± 10 ppm and the two components perpendicular to the bond have values of 7487 ± 10 and 7383 ± 10 ppm. By comparing the values of the components for the two isomers, it is clear that the cobalt shielding along the Co–X bond (δ = 7605 ppm, X = ONO and $\delta = 7643$ ppm, X = NO₂) does not change significantly when the compound isomerizes. In contrast, the shielding perpendicular to the bond increases by approximately 1750 ppm in the nitro isomer.

Correlation of cobalt chemical shifts to octahedral crystal field splitting (Δ_0) has been used for many years to explain the isotropic chemical shifts of octahedral cobalt complexes

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in solution and in the solid state (50-53). The paramagnetic shielding term, as described by Ramsey (54) in his original formalism, depends on the energy difference between electronic states that undergo symmetry-allowed mixing in the presence of a magnetic field and is generally deshielding. The good correlation between the cobalt chemical shifts and the excitation wavelength of the ${}^{1}A_{1g} \rightarrow {}^{1}T_{1g}$ electronic transition in octahedral cobalt(III) complexes was one of the early confirmations of Ramsey's formalism. In the solid state, the correlation can be used for octahedral complexes of high symmetry. Equations describing the dependence of shielding on the transition energies have been derived for numerous symmetries including D_3 , C_{4v} , D_{4v} , C_{2v} , etc. (55, 56). In the present study, however, neither complex has high symmetry at the cobalt atom, which limits the application of the derived equations for determining the individual components or isotropic values of the chemical shift tensor. Despite this, an approximate correlation can be made between the overall shielding that occurs as the complex isomerizes and an increase in the Δ_0 . The change in colour, from the pink nitrito isomer to the yellow nitro isomer, indicates an increase in Δ_0 . The increase in Δ_0 leads to a smaller paramagnetic shielding of the cobalt in the nitro isomer and results in the smaller chemical shift. This change is noticed primarily in the components of the shielding tensor perpendicular to the Co-X bond.

The orientation of the nitrogen chemical shift tensor in the nitrito isomer is unavailable from the NMR experiments. In other two-coordinate nitrogen compounds, such as sodium nitrite and bent nitrosyl compounds (45, 57), the nitrogen chemical shift tensor is oriented such that δ_{22} is approximately along the formal nitrogen lone pair and δ_{33} is perpendicular to the ONO plane. Quantum chemical calculations were performed and predict the same orientation for the nitrito isomer (Fig. 7a). The calculations reproduced the relative magnitudes of the δ_{11} and δ_{22} tensor components to within approximately 100 and 33 ppm, respectively, using both the 6-311++G(d,p) and LANL2DZ basis sets on the cobalt. Given that the chemical shift range of nitrogen is around 1200 ppm, the errors in δ_{11} and δ_{22} are reasonable and lend confidence to the orientations calculated for these two components. The δ_{33} component was underestimated by approximately 250 ppm, which is quite a large discrepancy. The origin of this difference between theory and experiment most likely arises from the neglect of intermolecular effects in the calculations.

The individual components of the nitrogen chemical shift tensor can be related to the electronic states that are responsible for the paramagnetic term in δ . For certain nitrosyl compounds (57), as well as in this case, mixing of the nitrogen *n* and π^* electronic states is expected to be responsible for the paramagnetic shielding term associated with the δ_{11} component of the chemical shift tensor (30). It has also been reported that the orientation of the intermediate component of the nitrogen chemical shift tensor (δ_{22}) is in most cases parallel to the formal nitrogen lone pair for nitrogen atoms bonded to two other atoms such as nitrosyl compounds, oximes, and azides (58–61). The direction of greatest shielding is nearly perpendicular to the ONO plane and arises from the mixing of the in-plane σ and σ^* states (57).

The orientation of the nitrogen chemical shift tensor of

Fig. 7. Orientation of the nitrogen CS tensor in the molecular frame of reference for: (*a*) the nitrito isomer, obtained from DFT calculations, and (*b*) the nitro isomer, obtained from DFT calculations and experiment.



the nitro isomer as determined from the analysis of the ¹⁵N NMR line shape of the stationary sample indicates that δ_{33} is perpendicular to the Co-NO₂ plane and δ_{22} is along the Co-N bond (Fig. 7b). The calculations with both the 6-311++G(d,p) and LANL2DZ basis sets on the Co yielded values for δ_{11} , δ_{22} , and δ_{33} that were in excellent agreement with the experimental values, within 11, 16, and 62 ppm of the experimental values, respectively. The process of coordination to the cobalt metal has the most profound effect on δ_{11} , which decreases by 412 ppm when the isomer changes from the nitrito to the nitro form. This is a result of the changes in the nonbonding molecular orbitals of the nitrito isomer as they coordinate to the cobalt centre to form the Co-N σ bond in the nitro isomer. The chemical shift component along the Co–N bond (δ_{22}) in the nitro isomer changes relatively little as a consequence of the coordination, increasing by 103 ppm with respect to the nitrito isomer. This is expected because the δ_{22} component does not involve mixing with the orbitals that form the Co—N σ bond. Finally, δ_{33} in the nitro isomer decreases by approximately 169 ppm with respect to the nitrito isomer.

Monitoring the isomerization reaction

The isomerization from the nitrito to the nitro isomer was monitored directly using both ¹⁵N and ⁵⁹Co solid-state NMR. The spectra acquired at 4.70 T as the reaction progressed are shown in Figs. 8 and 9 for ¹⁵N and ⁵⁹Co, respectively. For the ¹⁵N MAS spectra a heating scheme was used. The temperature was raised from room temperature (293 K) to 353 K in 5 min, where it was held for 8 min then cooled to room temperature before the spectra were acquired (Fig. 8*a*). In an attempt to drive the reaction to completion, the sample that yielded the top spectrum in Fig. 8*a* was heated at 413 K for 40 min yielding the spectrum in Fig. 8*b*; the sample was allowed to equilibrate at room temperature for 2 h prior to data collection.

The results show the benefit of using NMR to monitor the extent of the reaction. The ¹⁵N peak from the nitrito isomer slowly decreases in intensity while a second peak appears at 470 \pm 3 ppm, corresponding to the formation of the nitro isomer (Fig. 8*a*). It is clear that in the initial preparation there is very little of the nitro isomer present. Due to the breadth of the peak from the nitro isomer there could be as much as 10% of this form that is not detected because of the

Fig. 8. Nitrogen-15 NMR spectra of a MAS sample of the compound, acquired at 4.70 T. The spectra in (*a*) were obtained at room temperature after successive applications of the heating scheme described (see text). The sample that yielded the top spectrum in (*a*) was then heated at 413 K for an additional 40 min to drive the reaction to equilibrium and the NMR spectrum in (*b*) was acquired. Each spectrum in (*a*) is the sum of 612 scans and (*b*) is the sum of 10 050 scans, both using a 5.0 s pulse delay.



baseline noise. This illustrates one drawback to the ¹⁵N NMR of this system; since the peak from the nitro isomer is much broader than that from the nitrito isomer under MAS conditions, when only small amounts of nitro are present it is difficult to get an accurate estimate of the relative amounts of each isomer. However, this is offset by the ability to measure very small quantities of nitrito isomer in a mixture.

While the use of CP generally does not result in completely quantitative peak intensities, the optimal CP parameters were almost identical for the two isomers; hence, it is assumed that the comparison of the integrated peak intensities is a good approximation of the relative amounts of the two isomers. The analysis of the intensities for the spectrum in Fig. 8b shows that a final nitro/nitrito equilibrium ratio of 5.0 is reached after the sample was heated at 413 K. This is in excellent agreement with a previous study that measured the equilibrium values based on the reaction rates (11). From the spectra in Fig. 8a, it is apparent that the reaction is close to equilibrium after the second heating step.

The ⁵⁹Co NMR spectra (Fig. 9) were collected on a second sample preparation without any heating to investigate the sensitivity of the experiment to the isomerization over times consistent with the room temperature rate of reaction. Every 2.75 h a spectrum was acquired over a time of **Fig. 9.** The ⁵⁹Co NMR spectra of a stationary sample of the compound, acquired at 4.70 T, collected at room temperature without heating and with 2.75 h between each spectrum; 10 000 scans were added using a 0.1 s pulse delay.



16.7 min. The ⁵⁹Co NMR spectra show a decrease in the broad nitrito peak, while a new peak from the nitro isomer appears at 7505 \pm 10 ppm. Since the line width of the nitro peak is much smaller than that of the nitrito isomer, the ⁵⁹Co NMR spectra show the opposite sensitivities to those of the ¹⁵N NMR spectra. Whereas the ¹⁵N NMR spectra are sensitive to small amounts of the nitrito isomer and less so to the presence of the nitro isomer, the ⁵⁹Co spectra are more sensitive to the presence of the nitro isomer. These two nuclei therefore offer complementary methods of analyzing the relative quantities of the two isomers.

Conclusions

The ⁵⁹Co and ¹⁵N NMR parameters of nitritopentamminecobalt(III) chloride and nitropentamminecobalt(III) chloride have been determined in the solid state. There is a change in both the ⁵⁹Co quadrupolar coupling constants (23 to 10 MHz), and the spans of the chemical shift tensor (1650 to 260 ppm), for the nitrito and nitro isomers, respectively. The principal components of the ⁵⁹Co chemical shift tensor that are perpendicular to the Co—X (X = ONO or NO_2) bond decrease by approximately 1750 ppm upon isomerization, while the components parallel to the bond are similar in both isomers. The nitrogen chemical shift tensor also shows significant variations; δ_{iso} moves from 611 to 470 ppm and Ω decreases from 710 to 547 ppm as the ligand changes from the nitrito to nitro form. The orientations of the ¹⁵N and ⁵⁹Co chemical shift tensors and the 59Co EFG tensor in the molecular frame have been related to the molecular structure. The isomerization reaction was monitored directly using both ⁵⁹Co and ¹⁵N NMR and the results suggest that solid-state NMR can be used to measure isomer ratios during the reaction. These results highlight the value of solid-state NMR studies and the potential to use NMR to monitor reactions that occur in the solid state.

Acknowledgments

The authors wish to thank members of the solid-state NMR group at the University of Alberta, Edmonton, Alberta, as well as Dr. Klaus Eichele for helpful discussions. Dr. Guy Bernard, in particular, is thanked for his comments. REW is a Canada Research Chair in Physical Chemistry at the University of Alberta and thanks the Natural Sciences and Engineering Research Council of Canada (NSERC), Alberta Ingenuity, and the University of Alberta for research grants. KJO thanks NSERC, the Alberta Ingenuity Fund, and the University of Alberta for post-graduate scholarships.

Finally, REW thanks Arthur Carty for several fruitful scientific collaborations, and personal encouragement dating back to the late 1960s at the University of Waterloo.

References

- S.R. Byrn, R.R. Pfeiffer, G. Stephenson, D.J.W. Grant, and W.B. Gleason. Chem. Mater. 6, 1148 (1994).
- 2. M.C. Lai and E.M. Topp. J. Pharm. Sci. 88, 489 (1999).
- N.J. Coville and L. Cheng. J. Organomet. Chem. 571, 149 (1998).
- S.D.M. Atkinson, M.J. Almond, P. Hollins, and S.L. Jenkins. Spectrochim. Acta Part A, A59, 629 (2003).
- 5. L.R. MacGillivray, J.L. Reid, J.A. Ripmeester, and G.S. Papaefstathiou. Ind. Eng. Chem. Res. **41**, 4494 (2002).
- S.D.M. Atkinson, M.J. Almond, S.J. Hibble, P. Hollins, S.L. Jenkins, M.J. Tobin, and K.S. Wiltshire. Phys. Chem. Chem. Phys. 6, 4 (2004).
- 7. S.M. Jörgenson. Z. Anorg. Allg. Chem. 5, 169 (1894).
- W.G. Jackson, G.A. Lawrence, P.A. Lay, and A.M. Sargeson. J. Chem. Soc. Chem. Commun. 70 (1982).
- W.G. Jackson, G.A. Lawrance, P.A. Lay, and A.M. Sargeson. J. Chem. Educ. 58, 734 (1981).
- R.B. Penland, T.J. Lane, and J.V. Quagliano. J. Am. Chem. Soc. 78, 887 (1956).
- W.M. Phillips, S. Choi, and J.A. Larrabee. J. Chem. Educ. 67, 267 (1990).
- 12. W.H. Hohman. J. Chem. Educ. 51, 553 (1974).
- 13. R.K. Murmann and H. Taube. J. Am. Chem. Soc. 78, 4886 (1956).
- R.G. Pearson, P.M. Henry, J.G. Bergmann, and F. Basolo. J. Am. Chem. Soc. 76, 5920 (1954).
- E.V. Boldyreva, J. Kivikoski, and J.A.K. Howard. Acta Crystallogr. Sect. C: Cryst. Struct. Commun. 53, 523 (1997).
- M. Kubota and S. Ohba. Acta Crystallogr. Sect. B: Struct. Sci. 48, 627 (1992).
- 17. I. Grenthe and E. Nordin. Inorg. Chem. 18, 1869 (1979).
- J.C.C. Chan, P.J. Wilson, S.C.F. Au-Yeung, and G.A. Webb. J. Phys. Chem. A, **101**, 4196 (1997).
- 19. I. Ciofini and C. Adamo. J. Phys. Chem. A, 105, 1086 (2001).
- V.E. Dulepov and E.V. Boldyreva. React. Kinet. Catal. Lett. 53, 289 (1994).
- D.A. Johnson and K.A. Pashman. Inorg. Nucl. Chem. Lett. 11, 23 (1975).
- 22. I.R. Beattie and D.P.N. Satchell. Trans. Faraday Soc. 52, 1590 (1956).
- 23. E.V. Boldyreva. Russ. J. Coord. Chem. 27, 297 (2001).

- 24. C.W. Kirby and W.P. Power. Can. J. Chem. 79, 296 (2001).
- R. Goodfellow. In Multinuclear NMR. Edited by J. Mason. Plenum, New York. 1989. pp. 521.
- J.C.C. Chan and S.C.F. Au-Yeung. J. Chem. Soc. Faraday Trans. 92, 1121 (1996).
- J.C.C. Chan and S.C.F. Au-Yeung. Annu. Rep. NMR Spectrosc. 41, 1 (2000).
- 28. A. Medek and L. Frydman. J. Am. Chem. Soc. 122, 648 (2000).
- W.P. Power, C.W. Kirby, and N.J. Taylor. J. Am. Chem. Soc. 120, 9428 (1998).
- J. Mason. In Nuclear magnetic shielding and molecular structure. Edited by J.A. Tossell. Kluwer Academic Publishers, Dordrecht. 1993. pp. 449.
- J. Mason, L.F. Larkworthy, and E.A. Moore. Chem. Rev. 102, 913 (2002).
- D.L. Bryce, G.M. Bernard, M. Gee, M.D. Lumsden, K. Eichele, and R.E. Wasylishen. Can. J. Anal. Sci. Spectrosc. 46, 46 (2001).
- P.R. Bodart, J.-P. Amoureux, Y. Dumazy, and R. Lefort. Mol. Phys. 98, 1545 (2000).
- A.E. Bennett, C.M. Rienstra, M. Auger, K.V. Lakshmi, and R.G. Griffin. J. Chem. Phys. **103**, 6951 (1995).
- L.C.M. van Gorkom, J.M. Hook, M.B. Logan, J.V. Hanna, and R.E. Wasylishen. Magn. Reson. Chem. 33, 791 (1995).
- K. Eichele and R.E. Wasylishen. WSOLIDS NMR simulation package. Version 1.17.26. 2000.
- M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery, Jr., R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B.G. Johnson, W. Chen, M.W. Wong, J.L. Andres, M. Head-Gordon, E.S. Replogle, and J.A. Pople. Gaussian 98W. Revision A.7 [computer program]. Gaussian Inc., Pittsburgh, Penn. 1998.
- 38. A.D. Becke. J. Chem. Phys. 98, 5648 (1993).
- 39. C. Lee, W. Yang, and R.G. Parr. Phys. Rev. B, 37, 785 (1988).
- 40. W.R. Wadt and P.J. Hay. J. Chem. Phys. 82, 284 (1985).
- P.S. Pregosin. Transition metal nuclear magnetic resonance. Elsevier, Amsterdam. 1991.
- 43. M. Duer (*Editor*). Solid-state NMR spectroscopy: principles and applications. Blackwell Science, Oxford. 2002.
- 44. J. Herzfeld and A.E. Berger. J. Chem. Phys. 73, 6021 (1980).
- 45. P.J. Barrie, C.J. Groombridge, J. Mason, and E.A. Moore. Chem. Phys. Lett. **219**, 491 (1994).
- R.W. Schurko and R.E. Wasylishen. J. Phys. Chem. A, 104, 3410 (2000).
- R.K. Harris and A.C. Olivieri. Prog. Nucl. Magn. Reson. Spectrosc. 24, 435 (1992).
- P. Grondona and A.C. Olivieri. Concepts Magn. Reson. 5, 319 (1993).
- 49. R.E. Wasylishen, R.D. Curtis, K. Eichele, M.D. Lumsden, G.H. Penner, W.P. Power and G. Wu. *In* Nuclear chemical shifts and molecular structure. Nato ASI Series Vol. 386. *Edited by* J.A. Tossel. Kluwer Academic Publishers, Dordrecht. 1993. pp. 297.
- 50. J.S. Griffith and L.E. Orgel. Trans. Faraday Soc. 53, 601 (1957).

- 51. R. Freeman, G.R. Murray, and R.E. Richards. Proc. R. Soc. London. A242, 455 (1957).
- 52. N. Juranić. Coord. Chem. Rev. 96, 253, (1989).
- 53. K. Eichele, J.C.C. Chan, R.E. Wasylishen, and J.F. Britten. J. Phys. Chem. A, **101**, 5423 (1997).
- 54. N.F. Ramsey. Phys. Rev. 78, 699 (1950).
- 55. N. Juranić. J. Serb. Chem. Soc. 56, 723 (1991).
- N. Juranić, M.B. Ćelap, D. Vučelić, M.J. Malinar. and P.N. Radivojša. J. Magn. Reson. 35, 319 (1979).
- 57. M.D. Lumsden, G. Wu, R.E. Wasylishen, and R.D. Curtis. J. Am. Chem. Soc. **115**, 2825 (1993).
- R.D. Curtis, G.H. Penner, W.P. Power, and R.E. Wasylishen. J. Phys. Chem. 94, 4000 (1990).
- 59. R.E. Wasylishen, G.H. Penner, W.P. Power, and R.D. Curtis. J. Am. Chem. Soc. **111**, 6082 (1989).
- 60. D. Schweitzer and H.W. Spiess. J. Magn. Reson. 15, 529 (1974).
- 61. R.E. Wasylishen, W.P. Power, G.H. Penner, and R.D. Curtis. Can. J. Chem. **67**, 1219 (1989).
- 62. J. Mason. Solid State Nucl. Magn. Reson. 2, 285 (1993).

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