

Proton-Deuterium Isotope Shifts in ^{59}Co N.M.R.

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Abstract

An isotope shift of 5 ppm per deuterium atom has been observed for the ^{59}Co resonance of tris(ethylenediamine)cobalt(III) chloride ($[\text{Co}(\text{en})_3]\text{Cl}_3$) and hexaamminecobalt(III) chloride ($[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$) after exchange of hydrogen for deuterium. The upfield direction of the shift can be readily understood as changes in the ligand-field strength causing changes in the nuclear paramagnetic screening.

We always observe a downfield shoulder on the ^{59}Co resonance of tris(ethylenediamine)cobalt(III) chloride ($[\text{Co}(\text{en})_3]\text{Cl}_3$) in D_2O solvent. In the past we assigned this shoulder to an impurity. However, n.m.r. of a freshly dissolved sample showed transient spectra of up to nine equally spaced resonances. The transient nature of these spectra lead us to conclude that it was a hydrogen-deuterium exchange phenomenon. A detailed study has confirmed this.

Spectra of $[\text{Co}(\text{en})_3]\text{Cl}_3$ in H_2O , D_2O and various H_2O - D_2O mixtures, after hydrogen-deuterium exchange had reached equilibrium, are illustrated in Fig. 1a. The high purity of the $[\text{Co}(\text{en})_3]\text{Cl}_3$ is illustrated by the single-line spectrum in H_2O solvent. With increasing amounts of D_2O present a multiplicity of resonances are produced, upfield of the resonance in solvent water, corresponding to partially deuterated $[\text{Co}(\text{en})_3]\text{Cl}_3$ species. In 99.8% D_2O solvent a single resonance of fully deuterated $[\text{Co}(\text{en})_3]\text{Cl}_3$ is observed with a downfield shoulder corresponding to d_{11} - $[\text{Co}(\text{en})_3]\text{Cl}_3$. As $[\text{Co}(\text{en})_3]\text{Cl}_3$ contains 12 exchangeable hydrogen atoms per molecule, 13 discrete resonances are expected for this complex and its partially and fully deuterated derivatives, and these are observed. This was confirmed by mixing equilibrium samples of $[\text{Co}(\text{en})_3]\text{Cl}_3$ in H_2O , 25% D_2O , 50% D_2O , 75% D_2O , and 99.8% D_2O at 273 K and obtaining a spectrum at 280 K where the amount of deuterium exchange is quite small during the few minutes required to obtain a spectrum. The resulting spectrum is illustrated in Fig. 1b. The shift per exchanged hydrogen atom is 4.7 ppm upfield. It might be expected that, for instance, the shift of d_2 - $[\text{Co}(\text{en})_3]\text{Cl}_3$ would be different depending on whether the deuterium atoms are geminal or further apart. This type of difference, if any, is sufficiently small so that

the various resonances are not resolved. Of course, to observe discrete resonances at all, slow chemical exchange must prevail.

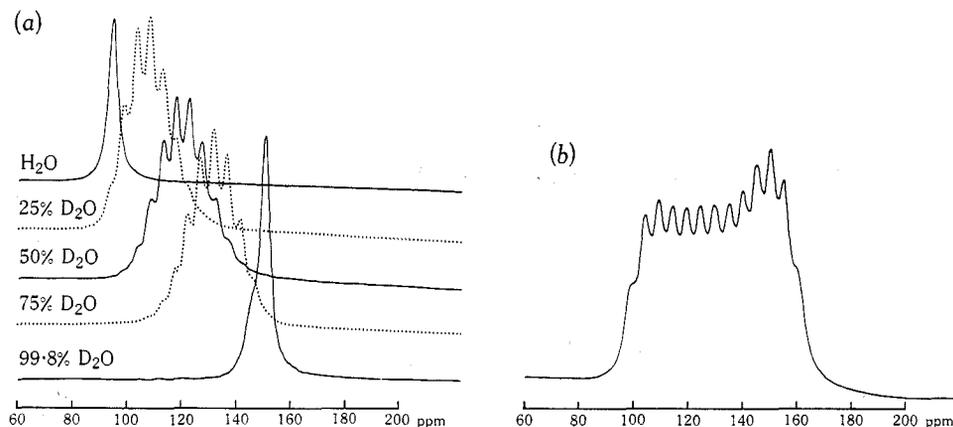


Fig. 1. ^{59}Co spectra of (a) $[\text{Co}(\text{en})_3]\text{Cl}_3$ (200 mg) in H_2O (0.5 ml), 25% (v/v) D_2O - H_2O (0.5 ml), 50% (v/v) D_2O - H_2O (0.5 ml) and 75% (v/v) D_2O - H_2O (0.5 ml) and of $[\text{Co}(\text{en})_3]\text{Cl}_3$ (20 mg) in 99.8% D_2O (0.5 ml). The sample temperature was 310 K in each case. (b) Approximately equal volumes of $[\text{Co}(\text{en})_3]\text{Cl}_3$ (200 mg) in H_2O (0.5 ml), 25% (v/v) D_2O - H_2O (0.5 ml), 50% (v/v) D_2O - H_2O (0.5 ml), 75% (v/v) D_2O - H_2O (0.5 ml) and 99.8% D_2O mixed at 273 K and determined at 280 K.

A large isotope shift may be expected for any NH group bonded to cobalt. Spectra of hexaamminecobalt(III) chloride ($[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$) in H_2O , 50% D_2O , and 99.8% D_2O (Fig. 2) again illustrate the phenomenon. Seventeen discrete resonances are expected for the partially deuterated derivatives but these are not resolved due to the large linewidth of each resonance (180 Hz for $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ in solvent H_2O). Calculation using the shift between $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ and d_{18} - $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ yields an isotope shift of 5.2 ppm upfield per exchanged hydrogen atom.

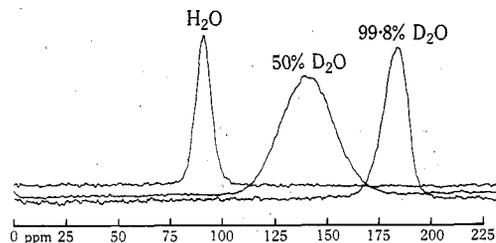


Fig. 2. ^{59}Co spectra of saturated solutions of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ in H_2O , 50% (v/v) D_2O - H_2O and 99.8% D_2O , prepared at 293 K and determined at 310 K.

Theoretically, isotope effects on nuclear shielding are not well understood although bond length changes and polarity effects have been considered.¹ The effects are, however, larger for nuclei where paramagnetic effects dominate the nuclear screening² and this is undoubtedly the case for ^{59}Co . A number of previous

¹ Batiz-Hernandez, H., and Berheim, R. A., *Prog. Nucl. Magn. Reson. Spectrosc.*, 1967, 3, 63; *J. Chem. Phys.*, 1966, 45, 2261.

² Doddrell, D. M., and Burfitt, I., *Aust. J. Chem.*, 1972, 25, 2239.

workers have demonstrated the good inverse correlation between the ^{59}Co chemical shift and the magnetically allowed $^1\text{A}_{1g} \rightarrow ^1\text{T}_{1g}$ electronic transition, a requirement for paramagnetic screening.³ Within this context, the upfield deuterium isotope shift on ^{59}Co n.m.r. is readily understood. RND_2 is a stronger base than RNH_2 ⁴ (e.g. the dipole moment of ND_3 is larger than that of NH_3 ⁴ and $K_{\text{H}}/K_{\text{D}}$ for NH_4^+ and ND_4^+ is 4⁵). Consequently RND_2 will produce a stronger ligand field thereby increasing the $^1\text{A}_{1g} \rightarrow ^1\text{T}_{1g}$ energy gap separations. This results in a smaller paramagnetic contribution to the nuclear screening and an upfield shift.

Experimental

^{59}Co spectra were determined at 2.1 T on a Bruker HX-90 n.m.r. spectrometer. 21.5-MHz radiation was generated by mixing the 90-MHz signal with a 68.5-MHz signal generated by a Schomandl ND 100 M 300 Hz-100 MHz frequency synthesizer and amplified with a Bruker 2-45 MHz broad-band pulsed amplifier. 90° pulses (length 17 μs) were applied to the sample by a Bruker multinuclear probe and a 20-37-MHz, 10-mm head. External D_2O contained in a 10-mm tube provided the lock signal and the sample was contained in a coaxial 5-mm tube. Spectra were obtained as described in Figs 1 and 2. Shifts are positive upfield and are relative to a carrier frequency of 21.508731 MHz for $[\text{Co}(\text{en})_3]\text{Cl}_3$ and 21.530731 MHz for $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ given that the field was locked to the upfield D sideband (centre-band frequency 13.810950 MHz, modulation frequency 4.16 kHz) by a time-sharing mode.

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³ Freeman, R., Murray, G. R., and Richards, R. E., *Proc. R. Soc. London, Ser. A*, 1957, **242**, 455.

⁴ Simon, H., and Palm, D., *Angew. Chem.*, 1966, **5**, 920.

⁵ Salomaa, P., Schaleger, L. L., and Long, F. A., *J. Phys. Chem.*, 1964, **68**, 410.