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Experiments with Tris(ethylenediamine)cobalt(III) Compounds: ^{59}Co NMR and the Resolution of Enantiomeric $[\text{Co}(\text{en})_3]^{3+}$ Ion and Analysis by Formation of Diastereomeric Ion Pairs

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Background

Cobalt(III) complexes are used in upper-division undergraduate inorganic laboratory to demonstrate techniques in coordination chemistry. The experiment described in this report involves the synthesis and resolution (1) of enantiomeric tris(ethylenediamine)cobalt(III) compounds and the analysis of enantiomeric purity by optical rotation and ^{59}Co NMR spectroscopy through the formation of diastereomeric ion pairs (2).

Cobalt-59 has a nuclear spin number, I , of 7/2, an isotopic abundance of 100%, and resonance frequency of 71 MHz at 7.0 T, which makes ^{59}Co NMR spectroscopy a practical and rapid experiment. The only caveat stems from the nuclear quadrupole moment of ^{59}Co , which requires the cobalt atom to occupy a highly symmetric environment in order to yield line widths of 100–200 Hz. The cobalt ion in the cobalt complex $[\text{Co}(\text{en})_3]^{3+}$ resides in an octahedrally symmetric environment and meets the symmetry criterion for a relatively narrow ^{59}Co NMR line width. Although a line width of 100–200 Hz is much larger than the 0.5–1.0 Hz of ^1H and ^{13}C NMR, the cobalt NMR line width is not a problem at 7.0 T, as the cobalt(III) chemical shift range is on the order of 15,000 ppm (3). This extremely large chemical shift range implies an extreme sensitivity of the chemical shift of a cobalt atom to small perturbations in its environment. Indeed, the cobalt chemical shift for the cobalt atom in $[\text{Co}(\text{en})_3]^{3+}$ hydrogen–deuterium isotopomers show about 5 ppm shift for each hydrogen atom that is replaced by a deuterium atom (4).

Iida et al. reported that racemic $[\text{Co}(\text{en})_3]^{3+}$ ion pairs with *d*-tartrate ion, resulting in diastereomeric ion pairs having clearly separated ^{59}Co NMR resonances that differ in chemical shift by about 5–6 ppm (2). Figure 1 shows the ^{59}Co NMR spectrum of 10 mM (+/-)- $[\text{Co}(\text{en})_3]^{3+}$ ion and Figure 2 shows the two ^{59}Co NMR resonances that result from the addition of sodium *d*-tartrate to a concentration of 50 mM. The spectrum reflects the rapid equilibrium between the free ions and the ion paired species, which results in mole fraction weighted averaged chemical shift values, as described in eqs 1 and 2. Equation 3 gives the ion pair association constant, K .

$$M_f + T_f = M^*T_{ip} \quad (1)$$

$$\delta_{\text{obs}} = N_f\delta_f + N_{ip}\delta_{ip} \quad (2)$$

$$K = \frac{[M^*T_{ip}]}{[M_f][T_f]} \quad (3)$$

where the subscripts f and ip denote free and ion-paired species,

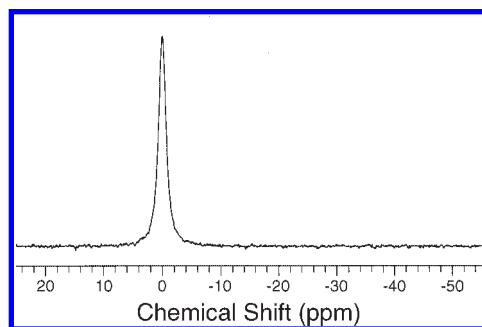


Figure 1. ^{59}Co NMR spectrum of 10 mM (+/-)- $[\text{Co}(\text{en})_3]\text{Cl}_3$ solution.

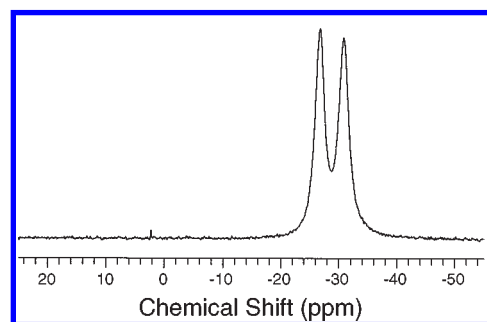


Figure 2. ^{59}Co NMR spectrum of 10 mM (+/-)- $[\text{Co}(\text{en})_3]\text{Cl}_3$ solution that is 50 mM in sodium *d*-tartrate.

M is (+)- or (-)- $[\text{Co}(\text{en})_3]^{3+}$, T is *d*-tartrate ion, M^*T is the $[\text{Co}(\text{en})_3]^{3+}$ -*d*-tartrate ion paired species, δ is the chemical shift and δ_{obs} the observed chemical shift, N is the ion or ion pair mole fraction, and K is the ion pair association constant.

The ion pairs between *d*-tartrate ion and (+)- $[\text{Co}(\text{en})_3]^{3+}$ and (-)- $[\text{Co}(\text{en})_3]^{3+}$ ions are diastereomeric and would be expected to have different association constants, $K_{(+)}$ and $K_{(-)}$, respectively, and ^{59}Co chemical shifts, δ_{ip} . The association constants (5; Settlege, R. E.; Russell, J. G.; Bryant, R. G. unpublished results) are on the order of 20–60 and the ratio $K_{(+)}/K_{(-)}$ is approximately equal to 1.1, indicating that ion pair formation between *d*-tartrate and (+)- $[\text{Co}(\text{en})_3]^{3+}$ is favored slightly but at 0.1–1.0 M tartrate ion more than one tartrate associates with the $[\text{Co}(\text{en})_3]^{3+}$ ion (2). This multiple association of $[\text{Co}(\text{en})_3]^{3+}$ with the tartrate counter ion does not affect the application described here and we are not attempting to calculate K or $K_{(+)}/K_{(-)}$.

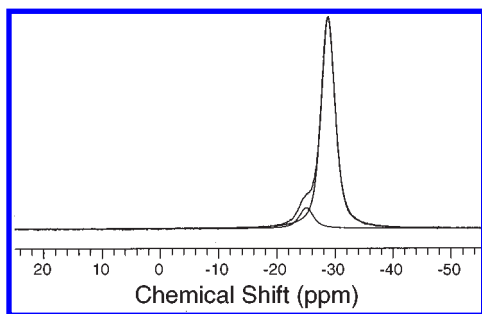


Figure 3. ^{59}Co NMR spectrum of sample 5-d, 10 mM (+)-[Co(en) $_3$] *d*-tartrate Cl to which sufficient sodium *d*-tartrate was added to give a solution 50 mM in *d*-tartrate ion. The resonances from both diastereomeric ion pairs are seen, showing 92% (+)-enantiomer. The resolution was incomplete.

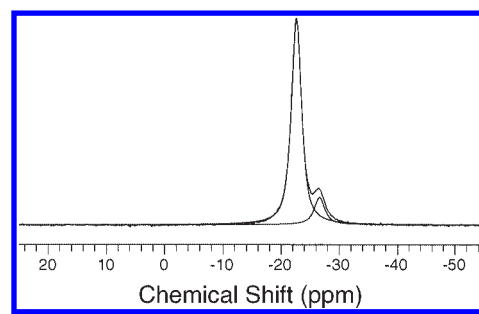


Figure 4. ^{59}Co NMR spectrum of sample 5-1, 10 mM (-)-[Co(en) $_3$]I $_3$ to which sufficient sodium *d*-tartrate was added to give a solution 50 mM in *d*-tartrate ion. The spectrum shows the resonances from both diastereomeric ion pairs, with 88% (-)-enantiomer. Resolution was incomplete.

The ^{59}Co chemical shift of the *d*-tartrate-(+)-[Co(en) $_3$] $^{3+}$ ion pair is chemically shifted more from the ^{59}Co chemical shift for reference of 10 mM (+/-)-[Co(en) $_3$]Cl $_3$ solution than is the ^{59}Co chemical shift of the *d*-tartrate-(-)-[Co(en) $_3$] $^{3+}$ ion pair (2). This is reflected in Figure 2, which shows a -30 ppm shift on addition of sodium *d*-tartrate to 10 mM (+/-)-[Co(en) $_3$]Cl $_3$ solution (cf. Fig. 1). Of the two ^{59}Co NMR resonances shown in Figure 2, the more chemically shifted one at -30.85 ppm is that of the ion pair between *d*-tartrate ion and (+)-[Co(en) $_3$] $^{3+}$; the resonance at -26.74 ppm is that of the ion pair between *d*-tartrate ion and (-)-[Co(en) $_3$] $^{3+}$, in agreement with the reported assignment (2). This can be verified by comparing Figures 3 and 4, which show the ^{59}Co NMR spectra of incompletely resolved (+)-[Co(en) $_3$] $\cdot d$ -tartrate $\cdot \text{Cl} \cdot 5\text{H}_2\text{O}$ with sodium *d*-tartrate added and incompletely resolved (-)-[Co(en) $_3$]I $_3$ with sodium *d*-tartrate added. The spectrum of the solution containing mostly (+)-[Co(en) $_3$] $^{3+}$ ion shows a larger, more chemically shifted peak that can be assigned to the ^{59}Co resonance of the (+)-[Co(en) $_3$] $^{3+}$ -containing species, as the specific rotation, $[\alpha]$, is positive for the cobalt complex solute. The ^{59}Co NMR spectrum of the solution containing mostly (-)-[Co(en) $_3$] $^{3+}$ ion can similarly be assigned. The larger, less chemically shifted peak is assigned to the (-)-[Co(en) $_3$] $^{3+}$ -containing species.

The percent enantiomeric purity of a tris(ethylenediamine)cobalt(III) sample can be obtained from the *d*-tartrate ion pair solutions using ^{59}Co NMR peak areas, which are obtained using a line-fitting routine. The observation of two ^{59}Co NMR peaks provides a concrete corroboration of enantiomeric purity calculated from optical rotation.

Experimental Procedure

Synthesis

The cobalt compounds were synthesized and resolved according to known procedures (1).

NMR Spectra

The NMR samples were 10 mM in cobalt complex to which sufficient sodium *d*-tartrate was added to give a solution 50 mM in *d*-tartrate ion. The ^{59}Co NMR spectra were acquired

at 71 MHz on stationary samples with outfield-frequency lock using a Bruker AC-300 equipped with a 10-mm broadband probe temperature-controlled at 298 K. The spectra were acquired by signal averaging 256 scans obtained with a 90° pulse, 80-ms pulse recycle time, 50 kHz spectral width, and 8 k data points zero-filled to 32 k points. The resulting spectra were processed on a PC using NUTS.¹ The relative peak areas were obtained by the NUTS line-fitting routine after fitting and flattening the spectrum baseline. The ^{59}Co chemical shifts are referenced to an external 10 mM (+/-)-[Co(en) $_3$]Cl $_3$ solution.

NMR spectrometers operating at a field strength of approximately 7.0 T and equipped with 5- or 10-mm broad band probes are common even at undergraduate institutions. The high field strength is required for resolution of the broad ^{59}Co NMR lines. A broad band NMR spectrometer based on an electromagnet will not have a high enough magnetic field strength to adequately resolve the broad ^{59}Co NMR lines. To accommodate those with electromagnet systems, we have made several cobalt spectra FID files available online.^u

Optical Rotation

The optical rotation of the resolved cobalt complexes were determined using a Rudolph Auto polarimeter, 1-dm sample cells, and solutions containing approximately 0.025 g of cobalt compound per 1.0 mL of solution.

Hazards

Wear protective eyewear and gloves at all times. Keep flammable liquids away from open flames. All reactions should be carried out in a hood or well-ventilated area. Exercise caution when handling ethylenediamine and the barium compounds. Barium sulfate and cobalt wastes must be put in separate receptacles in the hood.

Results

The optical rotation results for several student samples of (+)-[Co(en) $_3$] $\cdot d$ -tartrate $\cdot \text{Cl} \cdot 5\text{H}_2\text{O}$ and (-)-[Co(en) $_3$]I $_3$ are collected in Tables 1 and 2, respectively. The percent optical purity, %op, and the percent enantiomer purity, %enant, were

calculated from the experimental specific rotation, $[\alpha]_{\text{exptl}}$, using eqs 4 and 5, respectively (6):

$$\% \text{op} = \frac{[\alpha]_{\text{exptl}}}{[\alpha]_{\text{lit}}} \times 100 \quad (4)$$

$$\% \text{enant} = \% \text{op} + \frac{100 - \% \text{op}}{2} \quad (5)$$

where $[\alpha]_{\text{lit}}$ is the literature value (l) of $+102^\circ$ for the specific rotation for (+)-[Co(en)₃] $\cdot d$ -tartrate $\cdot \text{Cl} \cdot 5\text{H}_2\text{O}$ and -90° for (-)-[Co(en)₃]I₃.

Typical ^{59}Co NMR spectra after the addition of sodium d -tartrate to a student sample making a solution 50 mM in d -tartrate ion are shown in Figures 3 and 4. Figure 3, the spectrum of (+)-[Co(en)₃] $\cdot d$ -tartrate $\cdot \text{Cl} \cdot 5\text{H}_2\text{O}$ with added tartrate ion, sample 1- d , shows the experimental spectrum and the two calculated peaks that were fitted to it. Similarly, Figure 4 shows the experimental spectrum of (-)-[Co(en)₃]I₃ with added tartrate ion, sample number 5- l , and the two calculated peaks that were fitted to it. The NMR data and percent enantiomeric purity for (+)-[Co(en)₃] $\cdot d$ -tartrate $\cdot \text{Cl} \cdot 5\text{H}_2\text{O}$ and (-)-[Co(en)₃]I₃ with added tartrate ion are collected in Tables 3 and 4, respectively. The sample numbers of the NMR data and results correspond to the sample numbers for the optical rotation results collected in Tables 1 and 2.

Discussion

A comparison of the percent enantiomeric purity in Tables 1 and 2 and Tables 3 and 4, calculated from the specific rotation data and the ^{59}Co NMR relative peak areas, are within $\pm 2\%$ of each other, in good agreement. The detection limit of the ^{59}Co NMR peak area is estimated to be 2–3% of the minor enantiomer for peaks with widths at half-height in the range of 150–200 Hz and chemical shift differences of 4 ppm.

For each set of diastereomeric ion samples there is a range of chemical shifts. For example, the d -tartrate ion pairs derived from (+)-[Co(en)₃] $\cdot d$ -tartrate $\cdot \text{Cl} \cdot 5\text{H}_2\text{O}$ show a shift of -28.75 to -31.64 ppm on the addition of sodium d -tartrate, and (-)-[Co(en)₃]I₃ samples have a range of -20.35 to -22.59 ppm. The range of shifts may be due to the solutions' having different pH values, which would affect the concentration of the tartrate ion. However, it was not necessary to adjust the pH of the sample solutions for this analysis.

The ion-pair ^{59}Co NMR spectra obtained from [Co(en)₃]I₃ samples are not chemically shifted as much as those of the [Co(en)₃]Cl₃ reference or [Co(en)₃] $\cdot d$ -tartrate $\cdot \text{Cl} \cdot 5\text{H}_2\text{O}$. The chemical shift of the d -tartrate (+)-[Co(en)₃]³⁺ ion pair in the [Co(en)₃]Cl₃ reference sample is -30.85 ppm, while the minor amount of ion-paired (+)-[Co(en)₃]³⁺ in the (-)-[Co(en)₃]I₃ samples has chemical shifts ranging from -24.21 to -26.59 ppm. The chloride and iodide ions in these samples interact to different degrees with the [Co(en)₃]³⁺, and in the d -tartrate ion-paired solutions they compete with the tartrate ion for the [Co(en)₃]³⁺, though not as effectively as the tartrate ion. The ^{59}Co chemical shift of 6.7 ppm for 10 mM (-)-[Co(en)₃]I₃ before addition of d -tartrate is evidence for the different degree of interaction of chloride and iodide with [Co(en)₃]³⁺.

Table 1. Student Optical Rotation Data for (+)-[Co(en)₃] $\cdot d$ -Tartrate $\cdot \text{Cl} \cdot 5\text{H}_2\text{O}$

Sample No.	$[\alpha]_{\text{exptl}}$ (deg)	Optical Purity (%)	(+)-Enantiomer Purity (%)
1- d	+88	86	93
2- d	+101	99	100
3- d	+103	100	100
4- d	+100	98	99
5- d	+87	87	93
6- d	+92	90	95

Table 2. Student Optical Rotation Data for (-)-[Co(en)₃]I₃

Sample No.	$[\alpha]_{\text{exptl}}$ (deg)	Optical Purity (%)	(-)-Enantiomer Purity (%)
1- l	-90	100	100
2- l	-35	39	69
3- l	-70	78	89
4- l	-45	50	75
5- l	-71	79	90
6- l	-20	22	61

Table 3. Student ^{59}Co NMR Data for (+)-[Co(en)₃] $\cdot d$ -Tartrate $\cdot \text{Cl} \cdot 5\text{H}_2\text{O}$ with Na₂[d -Tartrate]

Sample No.	(+)-[Co(en) ₃] ³⁺		(-)-[Co(en) ₃] ³⁺		(+)Enantiomer (%)
	δ (ppm)	Relative Peak Area	δ (ppm)	Relative Peak Area	
1- d	-28.79	1.00	-24.79	0.08	93
2- d	-29.38	1.00	—	nil	100
3- d	-29.10	1.00	—	nil	100
4- d	-28.75	1.00	—	nil	100
5- d	-31.64	1.00	-27.56	0.09	92
6- d	-30.75	1.00	-26.70	0.06	94

Table 4. Student ^{59}Co NMR Data for (-)-[Co(en)₃]I₃ with Na₂[d -Tartrate]

Sample No.	(-)-[Co(en) ₃] ³⁺		(+)Enantiomer (%)	
	δ (ppm)	Relative Peak Area	δ (ppm)	Relative Peak Area
1- l	-20.88	1.00	—	nil
2- l	-20.35	1.00	-24.21	0.46
3- l	-21.58	1.00	-25.47	0.13
4- l	-20.96	1.00	-24.87	0.30
5- l	-22.59	1.00	-26.59	0.13
6- l	-21.22	1.00	-25.15	0.45

These experiments using polarimetry and NMR spectroscopy are an excellent addition to experiments of synthesis and resolution of Co complexes in an upper-division chemistry laboratory (7). Students can assess their laboratory techniques by determining the degree of resolution achieved on the cobalt samples. Students profit from analyzing data that have been collected from more than one type of instrumentation. Critical thinking skills must be used for interpretation and integration of data. Students who have “less-than-perfect” data usually gain the most understanding from this experiment.

Acknowledgment

Partial support for the purchase of the Bruker AC-300 NMR spectrometer was provided by the National Science Foundation under grant USE-9051141.

^WSupplemental Material

Several cobalt spectra FID files and instructions for students on conducting the experiment and preparing the lab report are available in this issue of *JCE Online*.

Note

1. Acorn NMR Inc., 46560 Fremont Blvd #418, Fremont, CA 94538-6491; <http://www.acornnmr.com/>.

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