Stereoisomerism in Coordination Chemistry

A Laboratory Experiment for Undergraduate Students

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Coordination chemistry is presented to our students, after two obligatory courses in inorganic chemistry, as an optional third one. The eminently experimental character of the subject offers a number of possibilities for laboratory, and the challenge is to choose a few experiments relative to the most relevant aspects of today's coordination chemistry.

Tris-(2,3-butanediamine)cobalt(III) $[Co(2,3\text{-}bn)_3]^{3+}$ is an interesting compound for stereochemical studies; its stereoisomers have been separated and studied in recent years (*1–3*).

The ligand 2,3-butanediamine (bn) exists into two isomeric forms: meso (ms-bn) and racemic (±bn) (Fig. 1). Both of them form five-membered chelate rings upon coordination and give rise to a number of stereoisomers for each complex.

$[Co(ms\text{-}bn)_3]^{3+}$ presents two isomers: facial and meridional (Fig. 2).

Because of the relationship between molecular configuration and ring conformation, there are four possible pairs of enantiomers for $[Co(\pm bn)]^{3+}$ designated as the lel_3, $lel_2\,ob$, $lel\,ob_2$, and ob_3 isomers (Fig. 3). The isomers can be easily separated by ion-exchange chromatography and identified mainly by ^{13}C NMR.

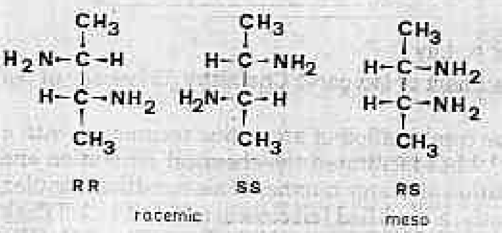

Figure 1. Stereoisomers of 2,3-butanediamine.

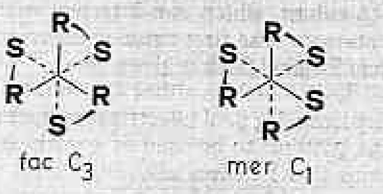

Figure 2. Facial and meridional isomers of $[Co(ms\text{-}bn)_3]^{3+}$ (Δ form).

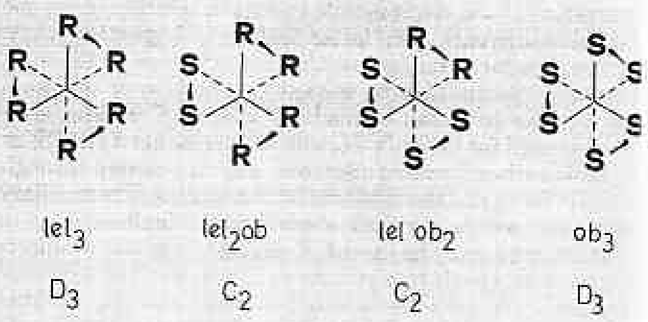

Figure 3. Isomers of $[Co(\pm bn)_3]^{3+}$ (Δ form).

Aims

The general aims of the experiment are:

1. Make the students become acquainted with stereochemical concepts and several techniques used in this field.
2. Incorporate in the learning some of the recent research tasks.

The immediate aim of the experiment is the isolation and characterization of the stereoisomers of a compound.

Background

The students know already the basic stereochemical concepts. They are provided with several key references (*2*, *4–7*) for background and complementary study.

General Method

The work is carried out in groups of two or three students. Usually each group works on the isomers of a single compound and writes a report including theoretical background, method, results, and conclusions. A final general session is dedicated to share their experiences. They are specially invited to communicate how interested they were in this experiment and any conclusions about it.

Experimental

Preparation of the Complexes and Chromatographic Separation

A solution of the appropriate 2,3-butanediamine dihydrochloride salt (3.22 g, 20 mmol) in 20 mL of H_2O is added to a slurry of sodium tris(carbonato) cobaltate(III), $Na_3[Co(CO_3)_3]3H_2O$ (2.18 g, 6 mmol) and charcoal in [illegible] mL of H_2O, and the mixture is stirred and heated at 60 °C for 2 [illegible]ollowing the removal of the charcoal by filtration, the orange s[illegible]ns are chromatographed on SP Sephadex C-25 cation exchange resin by use of a 2.7- × 250-cm glass column for the tris meso compound and a 2.7- × 50-cm glass column for the tris racemic compound. The sample is pipetted carefully onto the drained surface at the top of the column in fractions of 3 mL. The isomers are eluted with aqueous 0.15 M Na_2SO_4 at a flow rate of 1 mL/min. The elution of the tris meso compound gives two orange bands, the first corresponding to the meridional isomer and the second to the facial (*1*). Three well-defined bands, and a very faint fourth one, are obtained upon elution of the tris racemic compound, assigned as the lel_3, $lel_2\,ob$, $lel\,ob_2$, and ob_3 isomers (*3*). The relative isomer abundances are determined from the elution curves plotted from the spectral absorbances at λ_{max}. (Tris meso compound: λ_{max} 475 nm, ϵ_{max} 220. Tris racemic compound: λ_{max} 465 nm, ϵ_{max} 200.) These relative abundances are: meso compound: mer 64.5%, fac

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[2] This experiment does not include separation of optical isomers. See footnote 9 in ref *2* for a discussion of the isomer nomenclature.

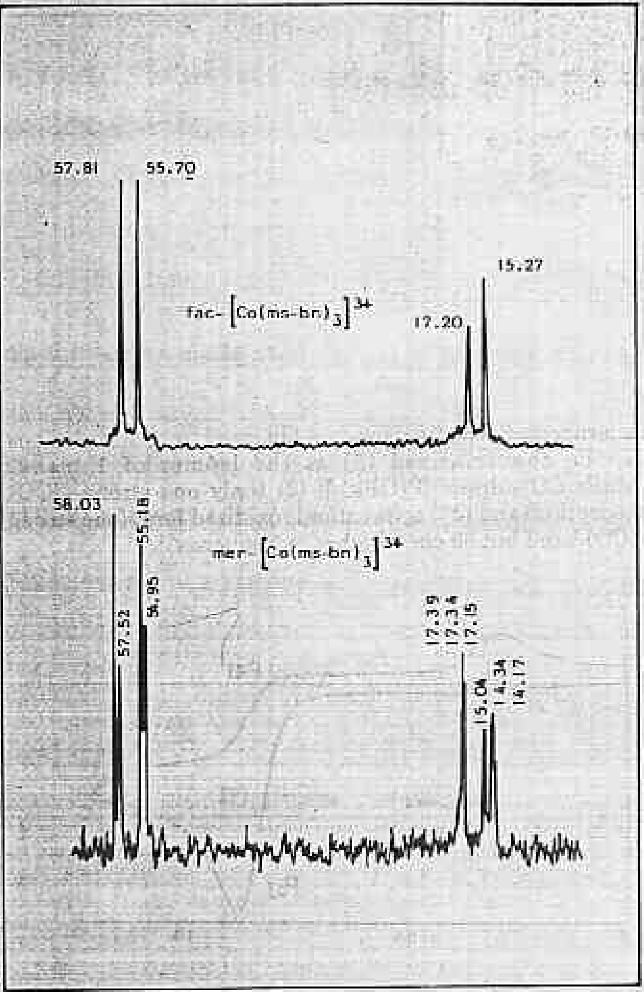

Figure 4. ^{13}C NMR spectra of $[Co(ms\text{-}bn)_3]^{3+}$ isomers.

35.5%; racemic compound: lel$_3$ 50.2%, lel$_2$ ob 33.07%; lel ob$_2$ 12.65%, and ob$_3$ 4.08%.

The addition of methanol to the concentrated chromatographic fractions allows the removal of sodium sulfate. The methanolic solutions are evaporated to dryness under air stream to give the solid isomers as sulfate salts. (Yields: meso compound 85%, racemic compound 88%.)

^{13}C NMR Spectra

In the preparation of the NMR samples, the sulfate salts (60 mg) were dissolved in 0.5 mL of D_2O and placed in a 5-mm sample tube. Me_4Si was employed as an external standard in a coaxial 1-mm tube.

Natural abundance ^{13}C NMR spectra were recorded at ~35 °C on a Varian FT-80A using a 2000-Hz sweep width, 0.5 s acquisition time, proton decoupling, and no pulse delay. Approximately 50,000 acquisitions were taken for each spectrum.

The facial isomer shows two methyl and two methine carbon resonances, as expected for a compound with symmetry C_3, due to the axial and equatorial conformation of methyl groups. The additional peaks observed in the spectrum of the meridional isomer result from its lower symmetry C_1 (Fig. 4).

The four isomers of $[Co(\pm bn)_3]^{3+}$ show the resonances: lel$_3$ and ob$_3$, one for methyl and one for methine groups; lel$_2$ ob and lel ob$_2$, three for methyl and three for methine groups (Fig. 5).

Attainment of Well-developed Crystals

Solid bromide salts are prepared by ion exchange with QAE Sephadex A-25 resin in the bromide form. The concentration of the solution permits the isolation of good crystals with Br as counterion.

IR Spectra

The spectra were collected on a PYE-UNICAM Model SP3-300 spectrophotometer using KBr pellets. The IR spectra of fac and mer isomers as bromide salts are indistinguishable. IR spectra of the isomers of the racemic compound are quite similar, though, as might be expected, the spectral bands found for the isomers of higher symmetry (D_3) lel$_3$ and ob$_3$ are sharper than those determined for the isomers lel$_2$ ob and lel ob$_2$, of lower symmetry (C_2).

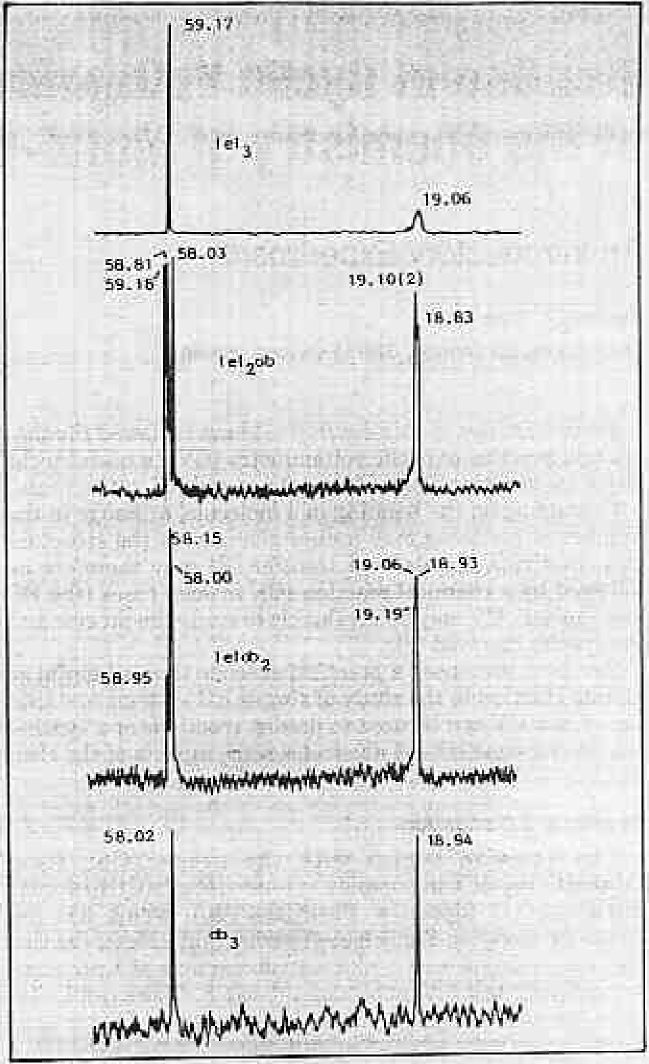

Figure 5. ^{13}C NMR spectra of $[Co(\pm bn)_3]^{3+}$ isomers.

Conclusion

This experiment is quite complete, because the students become acquainted with a number of techniques, such as synthesis, chromatography, IR, UV–vis, and ^{13}C NMR spectroscopy. It is a very interesting practical complement to the theoretical studies on stereochemistry. The use of molecular models allows the student to visualize more easily and clearly the stereochemical concepts.

The results obtained by the different techniques are in good agreement with bibliographic data. It gives didactic value to this experiment; it avoids mistakes and surprises and allows the students to follow it conveniently.

As a teaching aid the experiment has proved to be very successful in stimulating interest both in stereochemistry and laboratory work.

Literature Cited

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