Conformational Analysis of Trisethylenediamine and Tris-*R*-propylenediamine Complexes of Cobalt(III) by 251-MHz Proton Magnetic Resonance with Cobalt-59 Decoupling

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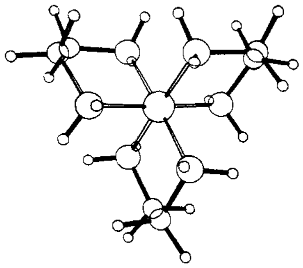
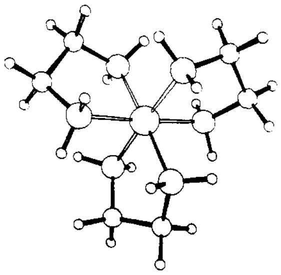
Abstract: Proton magnetic resonance spectra of N-deuterated $Co(en)_3{}^{3+}$ and $Co(R\text{-pn})_3{}^{3+}$ in D_2O at various temperatures and phosphate concentrations were obtained at 251 MHz with spin decoupling of cobalt-59. From the coupling constants obtained by analysis of the $Co(en)_3{}^{3+}$ AA′BB spectra, the fraction of time spent by an ethylenediamine ring in each conformational state (*i.e.*, with carbon–carbon bonds perpendicular or parallel to the C_3 axis) is determined. The molecular species having one carbon–carbon bond perpendicular and two carbon–carbon bonds parallel to the C_3 axis (*e.g.*, Δ-$\delta\lambda\lambda$) is more abundant than the species having all three carbon–carbon bonds parallel to the C_3 axis (*e.g.*, $\Delta\lambda\lambda\lambda$). However, the population of Δ-$\lambda\lambda\lambda$ exceeds that of Δ-$\delta\lambda\lambda$ at high phosphate concentrations. For efficient cobalt-59 decoupling, the extent of N-deuteration must be extremely high because of large deuterium isotope effects on cobalt-59 chemical shifts, as shown by cobalt-59 magnetic resonance spectra. Nonequivalent methyl resonances and nonequivalent methylene resonances were resolved in the 250-MHz pmr spectra of $Co(R\text{-pn})_3{}^{3+}$ (cis–trans mixture), and approximate chemical shifts and coupling constants were obtained by first-order analysis.

Conformational analysis of trisethylenediamine metal complexes has been a favorite topic in coordination chemistry over the past decade. In a recent report[2] we included a review of previous conformational studies of diamagnetic trisethylenediamine metal complexes.

Each five-membered ethylenediamine ring is puckered and can adopt one of two favored conformations—the one with the carbon–carbon bond *parallel* to the threefold axis, I, or the one with the carbon–carbon bond roughly *perpendicular* to the threefold axis, II. It has long been accepted that the $Co(en)_3{}^{3+}$ species having all three carbon–carbon bonds parallel to the C_3 axis is the most stable one, and that it "costs" approximately 0.5 kcal/mol in free energy for each ring flipped with the carbon–carbon bond perpendicular to the C_3 axis. The fractions of species having zero, one, two, and three carbon–carbon bonds perpendicular to the C_3 axis have been widely quoted as 59, 29, 8, and 4%, respectively. In our previous report,[2] by reexamining earlier data from equilibration–separation experiments, we showed that the above notions do not represent a true interpretation of the existing data for $Co(en)_3{}^{3+}$.



I



II

We established a method for using proton spin–spin coupling constants obtained from pmr spectral analysis to determine the position of the conformational equilibrium for a given chelate ring. We also showed previously[3] the necessity for cobalt-59 decoupling in order to provide sufficient resolution for spectral analysis.

In the present work, the high magnetic field strength of a superconducting solenoid and cobalt-59 decoupling make possible the first detailed analysis of the $Co(en)_3{}^{3+}$ pmr spectrum, providing new evidence on the conformational analysis of this compound. The effect of the phosphate ion on the ring conformations of $Co(en)_3{}^{3+}$ was investigated because of the marked influence on the ORD, CD, and pmr spectra[2-7] of trisdiamines.

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[1] To whom correspondence should be directed at the Department of Chemistry, University of California, Riverside, Calif. 92502.

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[3] J. L. Sudmeier and G. L. Blackmer, *J. Amer. Chem. Soc.*, **92**, 5238 (1970).

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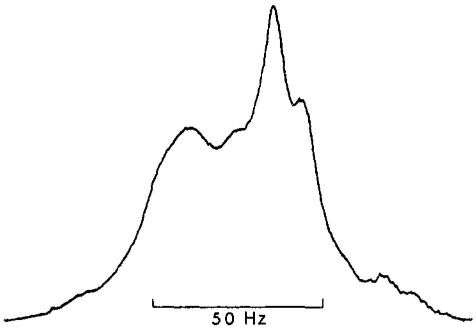

Figure 1. Observed 251-MHz pmr spectrum of Co(en)$_3{}^{3+}$ in D$_2$O at 17°.

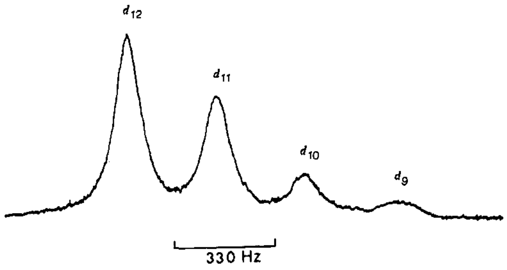

Figure 2. Observed 59.976-MHz cobalt-59 nmr spectrum at 17° after dissolving solid Co(en)$_3{}^{3+}$ in 99.5% D$_2$O.

The cobalt(III) tris-*R*-propylenediamine sample was a mixture of cis and trans geometrical isomers (the statistical cis-to-trans ratio is 1:3). With the aid of the superconducting nmr spectrometer and cobalt decoupling, it was of interest to try to resolve the cis and trans isomers and to determine the chemical shifts and coupling constants. The presence of equatorial methyl groups strongly favors a single conformation of each ring, in contrast to the mixture of rapidly equilibrating conformers postulated for Co(en)$_3{}^{3+}$.

Experimental Section

Preparation of Complexes. The cobalt(III) trisdiamine complexes used in this study were prepared as described in the literature.[8,9] Drop quantities of a stock phosphate solution (1 *M*) in D$_2$O were added to 1-ml samples of 0.15*M* N-deuterated Co(en)$_3{}^{3+}$ in D$_2$O. Phosphate/complex ratios up to 3:1 were studied. Higher degrees of N-deuteration were achieved by dissolving the trisdiamine complexes in neutral D$_2$O, evaporating to dryness, and redissolving. This procedure was repeated at least four times so that deuteration was virtually complete, as revealed by cobalt-59 nmr.

Instrumentation. Spectra were obtained on a 59-kG superconducting solenoid nmr spectrometer.[10] All spectra were obtained by frequency sweeps and samples were contained in standard 5-mm nmr tubes. Sample temperatures were measured with a thermocouple in the probe situated at about 2.5 cm below the center of the receiver coil and directly in contact with the temperature regulating gas.

Results

Co(en)$_3{}^{3+}$. Figure 1 shows the 250-MHz pmr spectrum of N-deuterated Λ-Co(en)$_3{}^{3+}$ in D$_2$O at 17°. The asymmetry of this pattern is due to greater spin coupling of Co-59 ($I = {}^7/_2$, 100% abundant) to the low-field (equatorial) proton than to the high-field (axial) proton. This phenomenon has been pointed out for several diamine chelates,[2,3,11] with greater M-N-C-H spin couplings occurring for equatorial than for axial protons. Little additional information can be obtained from a spectrum of this sort without the resolution enhancement produced by spin decoupling cobalt-59.[3] When certain difficulties were encountered in locating the cobalt-59 resonance frequency which produced the maximum decoupling efficiency, we decided to observe the cobalt-59 resonance directly. Figure 2 shows the cobalt-59 nmr spectrum (59.976 MHz) obtained after dissolving solid Co(en)$_3{}^{3+}$ in 99.5% isotopically pure D$_2$O. The spectrum consists of four broad resonances separated by ~300 Hz between successive peaks. These peaks are attributed to the proton impurities in the solvent, giving rise to species having varying degrees of N-deuteration and are labeled d_{12}-Co(en)$_3{}^{3+}$, d_{11}-Co(en)$_3{}^{3+}$, d_{10}-Co(en)$_3{}^{3+}$, etc. This was demonstrated by a redistribution of peak intensities into the d_{12} peak with an increasing extent of deuteration through exchange-evaporation cycles. The isotope effects upon the cobalt-59 resonances are strikingly large. Although N-deuteration of Co(en)$_3{}^{3+}$ is complete in minutes at room temperature in neutral D$_2$O, the cobalt-59 nmr shows that all species undergo "slow exchange," since the various cobalt resonances are distinct. The lifetimes of the various deuterated species are greater than ($\pi \times$ line widths)$^{-1}$, *i.e.*, about 3 msec. Before efficient spin decoupling of cobalt-59 could be obtained, complete conversion of all samples to the d_{12} species as described in the Experimental Section was required.

Figure 3A shows the effect of irradiating cobalt-59 upon the 251-MHz pmr spectrum of the completely N-deuterated complex at 17°, the ambient probe temperature. The advantages derived from cobalt-59 decoupling and higher spectrometer frequencies are self-evident.

Figure 3B shows the 251-MHz pmr spectrum of N-deuterated Co(en)$_3{}^{3+}$ obtained at 93°. The increased resolution obtained at higher temperatures is attributed to increased spin relaxation times T_1 and T_2 with decreased viscosity.

Figure 3C shows the 251-MHz pmr spectrum of a Co(en)$_3{}^{3+}$ sample containing 0.3 *M* K$_3$PO$_4$ at 17°. Increased axial-equatorial chemical shift difference and increased line widths are readily apparent. This pattern, like those in Figures 3A,B and 4A, is slightly unsymmetrical, probably due to unresolved spin coupling of N-deuterons to the C-H protons. Spin decoupling of H^2 (and perhaps N^{14}), together with cobalt-59 decoupling, might yield even better resolution, but these capabilities were not available with the present instrumentation.

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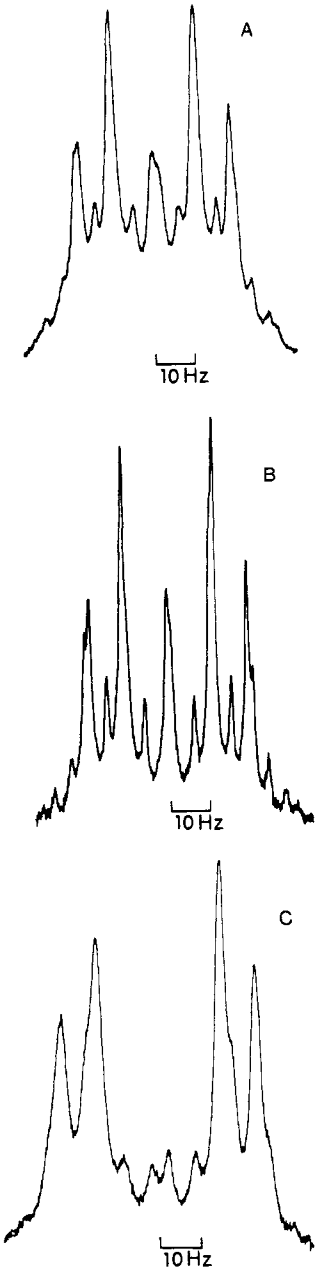

Figure 3. (A) Observed 251-MHz pmr spectrum of completely N-deuterated sample of $Co(en)_3^{3+}$ at 17° with cobalt-59 decoupling. (B) Pmr spectrum (251 MHz) of N-deuterated $co(en)_3^{3+}$ at 93° with Co-59 decoupling. (C) Observed 251-MHz pmr spectrum of 0.15 *M* N-deuterated $Co(en)_3^{3+}$ in D_2O containing 0.3 *M* K_3PO_4 at 17°.

Figure 4A shows the 251-MHz pmr spectrum of N-deuterated 0.15 *M* $Co(en)_3^{3+}$ in D_2O at 60° after addition of 0.3 *M* K_3PO_4. Higher temperatures (~90°) with 0.3 *M* phosphate could not be studied owing to the precipitation of crystalline $[Co(en)_3]PO_4$.[12] Very high phosphate concentrations (≫0.3 *M*) at lower temperatures caused severe line broadening probably attributable to viscosity effects.

All pmr spectra were analyzed by well-known techniques with the aid of LAOCOON III.[13] Each case was treated as a four-spin AA′BB′ problem using only the high-field (right hand) side of the spectrum. Overlapping lines were avoided or eliminated because of their greater uncertainties. Computed spectra from LAOCOON III gave excellent agreement with the observed spectra, both in line positions and intensities, as exemplified by Figure 4B, produced by a Cal-Comp plotter. Calculated chemical shifts and coupling constants are given in Table I with estimated random errors.

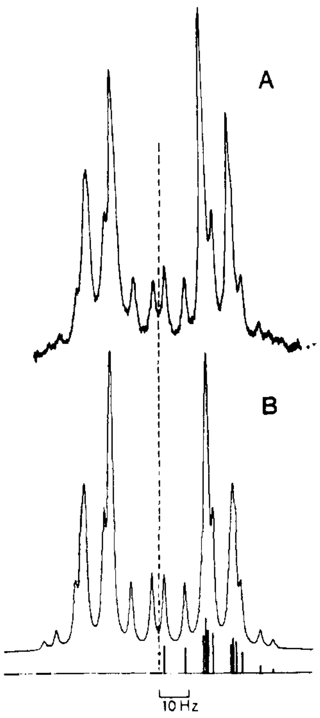

Figure 4. (A) Observed 251-MHz pmr spectrum of 0.15 *M* N-deuterated $Co(en)_3^{3+}$ in D_2O containing 0.3 *M* K_3PO_4 at 60°. (B) Calculated spectrum.

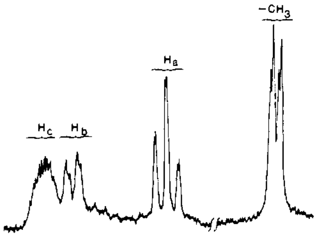

Figure 5. Observed 251-MHz pmr spectrum of N-deuterated Δ-Co(*R*-pn)$_3$ at 93° with Co-59 decoupling.

Co(*R*-pn)$_3^{3+}$. Figure 5 shows the 251-MHz pmr spectrum of N-deuterated Δ-Co(*R*-pn)$_3^{3+}$ at 93° in D_2O with cobalt-59 decoupling. The resonances assigned to protons H_c and H_b, III, occurring at 3.07 ppm and 2.91 ppm, respectively, are for the first time clearly separated and distinguishable, in contrast to the 100-MHz spectrum reported earlier.[3] The H_c proton resonance is highly split due to spin coupling with protons H_a, H_b, and methyl protons of each propylenediamine ring. Proton H_b appears roughly as a doublet of

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(12) An X-ray crystallographic study of Λ-$[Co(en)_3]PO_4$ is currently underway in the UCR laboratories.

(13) LAOCOON III is an improved version of the least-squares nmr spectral-fitting computer program described by S. Castellano and A. A. Bothner-By, *J. Chem. Phys.*, 41, 8363 (1964).

Table I. Calculated Spectral and Conformational Parameters for $Co(en)_3^{3+}$

Case	$[PO_4^{3-}]$	Temp, °C	Line width, Hz	$\Delta\delta_{AB}$, ppm	J_{12}, Hz	J_{13}, Hz	J_{34}, Hz	J_{14}, Hz	ω, deg	J (trans), Hz	J (gauche), Hz	f_λ
I	0.0	93	1.2	0.146	9.9[a]	4.3	4.5	−13.5	56	11.8	3.4	0.79 ± 0.03
II	0.0	60	1.6	0.139	9.4[b]	4.7	4.8	−13.2	54	12.0	3.4	0.74 ± 0.03
III	0.0	17	3.0	0.138	9.2[c]	5.2	4.4	−12.3	52	11.9	3.4	0.75 ± 0.07
IV	0.1	17	1.6	0.143	10.1[b]	3.8	4.9	−13.8	58	11.9	3.4	0.79 ± 0.04
V	0.3	60	1.6	0.173	11.0[b]	4.1	4.2	−12.7	58	12.3	3.5	0.87 ± 0.04
IV	0.3	17	2.0	0.171	11.1[d]	3.2	4.1	−11.8	61	11.7	3.3	0.93 ± 0.08

[a] Random error estimated as ±0.1 for all spin-coupling constants in this case. [b] Random error estimated as ±0.15 for all spin-coupling constants in this case. [c] Random error estimated as ±0.3 for all spin-coupling constants in this case. [d] Random error estimated as ±0.2 for all spin-coupling constants in this case.

doublets arising from spin coupling with H_a and H_c ($J_{ab} = -12.3, J_{bc} = 4.2$ Hz). The resonance of proton H_a appears at 2.53 ppm and consists of a doublet of doublets (roughly a triplet), due to couplings with H_b and H_c ($J_{ab} = -12.3$, $J_{ac} = 12.2$ Hz). These spin-coupling constants, obtained by first-order analysis, are in excellent agreement with results for $Co(R\text{-pn})(CN)_4^-$,[14] where values of $J_{ab} = -12.4$, $J_{ac} = 12.4$, and $J_{bc} = 4.4$ Hz were given. The analysis is complicated by additional fine structure, shown clearly in the H_a resonance and the methyl doublet (1.37 ppm, $J = 5.9$ Hz) and less evident in the resonances of protons H_b and H_c. This additional fine structure is attributed to nonequivalent propylenediamine rings arising from the presence of cis and trans geometrical isomers (statistical ratio = 1:3) and/or the fact that all three rings in the trans isomer are nonequivalent. The methyl resonance appears as two doublets of roughly 2:3 in intensities. The separation, 2.2 Hz, is strongly dependent on the phosphate concentration, presumably due to changes in the nature of the solvent. Additional insight into the spectral assignments may be gained by fractional crystallization, which has been reported[15] to separate the cis and trans isomers.

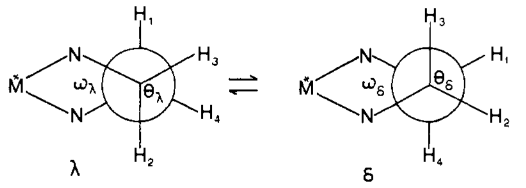
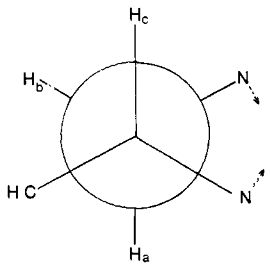


Figure 6. Conformational equilibrium for each ring of a metal-trisethylenediamine complex.



III

As in the case of $Rh(en)_3^{3+}$ shown previously,[2] the pmr spectra of $Co(en)_3^{3+}$ are best interpreted in terms of conformationally labile chelate rings. Using the same arguments, assumptions, and mathematical treatment given earlier,[2] the position of the λ–δ conformational equilibrium (Figure 6) of each ring can be determined.

A brief review of these assumptions is that: (1) for simplifying the discussion, only the Δ configuration is present in the sample; (2) the Δ-λλλ species is more stable than the Δ-δδδ species; (3) $\theta_\lambda = \theta_\delta = 120°$; (4) $\omega_\lambda = \omega_\delta$, but not necessarily equal to 60°; (5) vicinal coupling constants J_{12}, J_{13}, and J_{34} obey Karplus equations[16] of the form $J = A \cos^2\varphi$, where φ is the dihedral angle and A is a constant having a value of A_1 in the range $0° < \varphi < 90°$ and a value of A_2 in the range of $90° < \varphi < 180°$; and (6) the ratio A_1/A_2 equals 4/3.5, or equivalently J(trans)/J(gauche) = 3.5.

Using these assumptions, a computer program[2] was written to solve each set of coupling constants for f_λ, the fraction of time spent by each ring in the λ conformation, and f_δ, which equals simply $1 - f_\lambda$. The computed values of f_λ and its random errors are all given in Table I, along with calculated values of ω, J(trans), and J(gauche).

Discussion

While f_λ values of $Co(en)_3^{3+}$ may be interesting, most previous investigations have focused upon the relative populations of the molecular species depicted in IV. As we have shown previously for $Rh(en)_3^{3+}$, the mole fractions of species A, B, C, and D deter-

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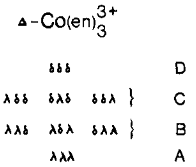
mined from f_λ values range from indeterminate at worst to highly imprecise at best, depending on the individual case.



IV

We showed that D probably amounts to less than a few per cent and could be discarded. If we also discard species C, we can obtain solutions for species A and B, but risk the introduction of systematic errors which could be 20% or larger. Species B is favored over species A by the statistical entropy term $\Delta S_{BA} = R \ln 3$. Neglecting additional entropy contributions, we find that discarding species C leads to an interpolated ΔG_{BA} value of -0.5 ± 0.3 kcal/mol (A = 30%, B = 70%) at 25°. The result that B lies below A in free energy contrasts with nearly all previous studies of Co(en)$_3{}^{3+}$.[17]

In 0.3 M K_3PO_4, we find that $\Delta G_{BA} = +0.5 \pm 0.3$ kcal/mol, indicating a reversal in the population of species A and B (A = 70%, B = 30%).

These very crude calculations seem to bear out the tendency of phosphate ion to preferentially stabilize species A, which has been attributed to hydrogen bonding.[4–7] A plot of $\Delta\delta_{AB}$ *vs.* f_λ leads to a rather poor linear least-squares fit.

The conformational problem is clearly underdetermined, and we do not presume to have given a full solution from these pmr data. However, the f_λ values obtained from the pmr studies should prove useful in conjunction with strain-energy calculations or additional experimental results.

Acknowledgments. This research was supported by U. S. Public Health Service Grants No. R01-ES00477-04 and R01-GM12769-04. We are grateful to the UCLA Campus Computing Network for their generous support of the computational work. Professor R. M. Wing provided the drawings used in structures I and II.

[17] A recent reexamination of R-pn and en data for Co(III), however, has resulted in a similar conclusion (B favored over A): C. Hawkins, "Absolute Configuration of Metal Complexes," Wiley-Interscience, New York, N. Y., 1971, pp 102–104.

Metal Ion–Aromatic Complexes. XIII. Trigonal-Planar Silver(I) in the Structure of Indene Silver Perchlorate

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Abstract: The crystal and molecular structure of indene silver perchlorate has been determined by single-crystal X-ray diffraction from 882 counter-measured intensities at room temperature. The structure was refined by full-matrix least-squares methods to a final conventional R of 0.066. Crystals of $C_9H_8 \cdot AgClO_4$ are orthorhombic, *Pbnm*, $Z = 8$, $d_c = 2.15$ g cm^{-3}, $a = 15.390$ (2) Å, $b = 8.525$ (1) Å, $c = 15.213$ (1) Å. The structure consists of isolated dimeric units (indene·AgClO$_4$)$_2$ in a half-open hinge (99°) arrangement where the leaves of the hinge are the organic groups and the pin corresponds to the silver ions with their associated perchlorate groups. The silver, chlorine, and two oxygen atoms of each perchlorate group lie in a crystallographic mirror plane. This same mirror interrelates the rest of the molecule. Such an arrangement leads to one silver atom bound to only olefin parts of the molecule in a distorted linear configuration. The other silver is in a trigonal-planar arrangement with the two aromatic parts [Ag–C = 2.47 (2) Å] and an oxygen of a perchlorate [Ag–O = 2.46 (2) Å]. This is the first reported instance of a trigonal-planar Ag(I) coordination involving aromatic ligands.

In earlier publications[1] we have postulated that a fundamental distinction exists between the nature of the metal–carbon bond in silver–aromatic complexes and silver–olefin complexes.[2] In general, a "short" silver–carbon distance of 2.47 ± 0.02 Å has been found in the silver(I)–aromatic complexes regardless of stoichiometry, anion, and packing considerations.[2–6] The next shortest silver–carbon distance varies over wide limits from 2.56 to 2.94 Å. The silver–carbon distances found for silver–olefin complexes, on the other

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[1] For a general review of the literature and a historical introduction, see ref 3a.

[2] I. F. Taylor, Jr., E. A. Hall, and E. L. Amma, *J. Amer. Chem. Soc.*, **91**, 5745 (1969).

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