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Conformational Ordering Effects in the Proton Nuclear Magnetic Resonance Spectra of the Tris-Ethylenediamine Complexes of Cobalt(III) and Rhodium(III)[1,2]

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Pmr spectra of the $Co(en)_3{}^{3+}$ and $Rh(en)_3{}^{3+}$ ions in D_2O solutions of phosphate, selenate, and selenite ions and of the Co(III) complex in D_2O solutions of trifluoroacetic acid (TFA) show changes in the CH_2 resonance consistent with directional association which favors the chelate ring conformations of the lel form. Added monovalent ions such as Cl^-, Br^-, I^-, and OH^- have little effect on the CH_2 resonance for the Co(III) complex. The pmr CH_2 pattern for the Rh(III) complex is a narrow resonance band which is not temperature dependent in the range 4–82°. The CH_2 resonance for the Co(III) complex is broad and has a distinct temperature dependence, consistent with a shift of distribution among the possible conformational isomers. The Co(III) and Rh(III) complex chlorides give identical band shapes in TFA, suggesting that both complexes have similar distributions of conformers in TFA, with the lel form strongly favored.

Introduction

Knowledge of chelate ring conformations is important in assigning sources of rotatory power, and this information, in principle, can be obtained from pmr data. The tris-ethylenediamine complexes are particularly appropriate to pmr studies, since conformational changes alter the symmetry of the complex ion decisively ($D_3 \rightleftarrows C_2$).

In aqueous solution at 25° the $\Lambda(+)_{589}Co(en)_3{}^{3+}$ ion exists[3,4] in conformational equilibrium. Thermodynamic data[5] obtained for the $Co(en)_x((-)pn)_{3-x}{}^{3+}$ system, where specific conformational forms are stabilized by the pn chelate rings, suggest the following proportions for the conformational isomers of the $Co(en)_3{}^{3+}$ ion:[6,7] 59% (δδδ)lel,[7] 29% (δδλ), 8% (δλλ), and 4% (λλλ)ob. These proportions suggest that only the first two species, of D_3 and C_2 symmetry, respectively, contribute significantly to the pmr pattern observed for the $Co(en)_3{}^{3+}$ ion. For the lel conformer (D_3 symmetry) the chelate rings are equivalent, and the resulting pmr pattern should be AA′BB′. Inversion of one of the chelate rings, yielding the (δδλ) conformer of C_2 symmetry, results in only two equivalent rings, and the pmr pattern should be more complicated. Depending upon the rate of conformational interchange,[8] the values of the various coupling constants, the chemical shifts, and the transverse relaxation times, this pattern might range from a single resonance band of variable width to about 20 observable nonzero-intensity lines[9] *symmetrically* disposed about a midpoint.

It has been proposed from changes in the circular dichroism (CD) spectra of some tris(diamine)cobalt(III) complexes in the presence of various oxyanions[4,10] that ion pairing with tetrahedral or trigonal anions is sterically favored for the lel isomer, thus shifting the conformational equilibrium of $Co(en)_3{}^{3+}$ in aqueous solution toward the lel isomer, effectively ordering the conformations. The pmr spectrum of $Co(en)_3{}^{3+}$ in the presence of $PO_4{}^{3-}$ was reported[3] to show little difference from that without added phosphate ion, so that no conclusions regarding conformations could be directly obtained. In this work, the pmr spectra of $Co(en)_3{}^{3+}$ and $Rh(en)_3{}^{3+}$ have been recorded at various temperatures and in the presence of some molecules and anions which have a large effect on the CD spectrum of the Co(III) complex, including phosphate ion. Correlation of these pmr spectra provides evidence consistent with preferential stabilization of the lel isomer through molecular association which favors the conformations of the lel form.

Experimental Section

Tris(ethylenediamine)cobalt(III) Salts.—The chloride salt was prepared by standard methods.[11] The bromide, iodide, and perchlorate salts were prepared by recrystallizing the racemic chloride salt in the presence of excess KBr, NaI, or $Ba(ClO_4)_2$, respectively. The racemic chloride, bromide, iodide, and perchlorate salts were characterized by their molar absorptivities in the visible region. The chloride, bromide, and iodide salts gave acceptable analyses for elemental nitrogen, and the perchlorate salt gave no cloudiness in $AgNO_3$ solution.

Tris(ethylenediamine)rhodium(III) Salts.—The chloride salt was prepared from rhodium trichloride trihydrate (Alfa Inorganics, Inc.) by the method of Watt and Crum[12] (88% yield). The chloride salt was isolated by addition of isopropyl alcohol to the reaction solution. The iodide and perchlorate salts were prepared by the addition of solid KI or an aqueous solution of $AgClO_4$, respectively, to aqueous solutions of the chloride salt (94% yield for conversion to the iodide and 80% yield for con-

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[1] This work was supported by Research Grant GM 10829 from the Division of General Medical Studies, U. S. Public Health Service. Presented at the 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969; see Abstracts, No. INOR 11.

[2] The nmr instrumentation used in this study was maintained under Grant FR 00292-03 from the National Institutes of Health.

[3] A. M. Sargeson, *Transition Metal Chem.*, **3**, 303 (1966).

[4] A. J. McCaffery, S. F. Mason, and B. J. Norman, *Chem. Commun.*, 49 (1965).

[5] A. M. Sargeson in "Chelating Agents and Metal Chelates," F. P. Dwyer and D. P. Mellor, Ed., Academic Press, New York, N. Y., 1964, p 183; *cf.* ref 3

[6] These percentages may be calculated from the equilibrium ratio data in Table I of ref 3. They may also be calculated as a Boltzmann distribution of the free energy differences[7] among the conformational isomers when degeneracy is neglected.

[7] E. J. Corey and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **81**, 2620 (1959).

[8] H. Elsbernd and J. K. Beattie, *ibid.*, **91**, 4573 (1969).

[9] K. B. Wiberg and B. J. Nist, "The Interpretation of NMR Spectra," W. A. Benjamin, Inc., New York, N. Y., 1962, p 309.

[10] R. Larsson, S. F. Mason, and B. J. Norman, *J. Chem. Soc.*, *A*, 301 (1966); S. F. Mason and B. J. Norman, *ibid.*, *A*, 307 (1966).

[11] J. B. Work, *Inorg. Syn.*, **2**, 221 (1946).

[12] G. W. Watt and J. K. Crum, *J. Am. Chem. Soc.*, **87**, 5366 (1965).

version to the perchlorate). A small amount of KI impurity was removed from the iodide salt by stirring in absolute ethanol and filtering (75% final yield). The chloride and iodide salts were characterized by analyses for elemental nitrogen, while the perchlorate salt gave negative tests with $AgNO_3$ and NaCl solutions. All three salts gave acceptable molar absorptivities[13] in the uv–visible region.

Tris(trimethylenediamine)cobalt(III) chloride was provided by Dr. Randall L. Russell of this laboratory.

Analyses for elemental nitrogen were obtained using a Coleman Model 29 analyzer.

Spectra.—Absorption spectra were measured at room temperature for *ca.* 10^{-3} *M* solutions using a Cary Model 14 recording spectrophotometer with 1-cm quartz cells. Pmr spectra were measured using a Varian A-60 analytical spectrometer with a variable-temperature probe coupled to a V-6040 nmr temperature controller. Unless specified, the spectra reported were recorded at the ambient temperature of the probe, *ca.* 35°. Samples for pmr studies were prepared by dissolving 0.05 g of complex in 0.5 ml of solvent. The materials used for preparing solutions were: TFA (Eastman Organic Chemicals); perdeuteriodimethyl sulfoxide (DMSO-d_6; Mallinckrodt); 1% dideuteriosulfuric acid (diluted from 98% D_2SO_4; Diaprep, Inc.); Na_2SeO_4, sodium selenate, and Na_2SeO_3, sodium selenite (Alfa Inorganics, Inc.); K_3PO_4, potassium phosphate (Baker Analyzed reagent); and D_2O deuterium oxide (Diaprep, Inc.). DSS (sodium 2,2-dimethyl-2-silapentane-5-sulfonate) was used as an internal standard in most solutions after it was determined that its presence had no effect on the spectral patterns. No significant chemical shift differences were observed in any of the series of solutions. The band width at half-height for each of the resonance patterns was measured regardless of band shape for comparing spectra.

Results and Discussion

Pmr spectra of the chloride, bromide, iodide, and perchlorate salts of $Co(en)_3^{3+}$ and also the chloride, iodide, and perchlorate salts of $Rh(en)_3^{3+}$ (Figure 1) exhibit no significant differences in chemical shift or band width for both the methylene and amine bands of each series of complex salts. The Co(III) complex shows a single amine band (34–37 Hz at δ 4.84 ppm) for all the salts and a single methylene band of 19–21 Hz (at δ 2.85 ppm) which sharpens to only 17–19 Hz when the amine hydrogens are replaced by deuterium. The series of Rh(III) complex salts is likewise consistent, but the band shapes are quite different. In 1% D_2SO_4 in D_2O an AB type of amine pattern arises. This is probably due to the greater field gradient of the Rh(III) ion and subsequent greater difference between the hydrogen nuclei of each NH_2 group. A smaller difference in the pairs of amine hydrogen nuclei for the Co(III) complex would be consistent with the observation of only one amine band in the 60-MHz spectrum and two amine bands at 100 MHz.[3,14] The methylene resonance has little or no fine structure and a band width of 8–9 Hz (at δ 2.92 ppm). In D_2O alone the methylene resonance sharpens to 2.5–3.0 Hz indicative of extensive N–H and C–H coupling and rapid averaging, as by conformational interchange.[15] Coupling of the ^{103}Rh (spin $^1/_2$) nucleus to the chelate ring protons was not observed.

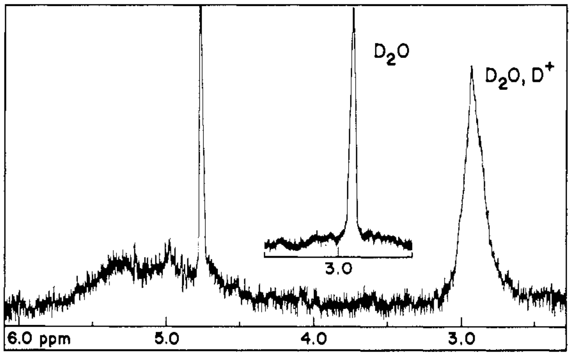

Figure 1.—Pmr spectra of $[Rh(en)_3](ClO_4)_3$ in D_2O and in 1% D_2SO_4–D_2O (D_2O, D^+) at 60 MHz (HOD resonance at 4.7 ppm).

A pmr temperature study of $[Co(en)_3](ClO_4)_3$ and $[Rh(en)_3](ClO_4)_3$ in D_2O solutions has been carried out (Figure 2). The temperature study of the spectral pattern for the Rh(III) complex showed essentially no change, indicating rapid conformational averaging[15] which is not significantly affected in the range of temperatures studied. The trend in the band width data for the Co(III) complex (Figure 2) indicates a unique temperature dependence. The band width of the methylene resonance pattern broadens *unsymmetrically* with increasing temperature. The broadening is opposite to the influence expected from quadrupolar effects.[16] (An opposite, smaller trend is observed in trifluoroacetic acid solution,[17] consistent with quadrupolar effects.) Assuming that the rate of conformational interchange is very rapid and is not significantly altered in the range of temperatures studied, this temperature dependence is probably due to variation in the chemical

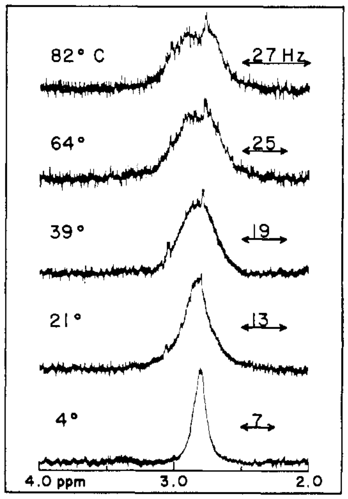

Figure 2.—Pmr temperature study of $[Co(en)_3](ClO_4)_3$ in D_2O solution at 60 MHz after deuterium exchange. Band widths at half-height are listed on the arrows. Temperature accuracy is ±2°.

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[13] C. K. Jørgensen, *Acta Chem. Scand.*, **10**, 500 (1956).

[14] S. T. Spees, Jr., L. J. Durham, and A. M. Sargeson, *Inorg. Chem.*, **5**, 2103 (1966).

[15] It has been suggested that the simplicity of the CH_2 resonance could be due to a lower anisotropy for the ^{103}Rh–N bond as compared to the ^{59}Co–N bond in these complexes: B. M. Fung, personal communication, 1969; *J. Phys. Chem.*, **72**, 4708 (1968).

[16] J. D. Roberts, *J. Am. Chem. Soc.*, **78**, 4495 (1956).

[17] H. Yoneda and Y. Morimoto, *Bull. Chem. Soc. Japan*, **39**, 2180 (1966).

shifts with temperature. However, further consideration yields some interesting information. The unsymmetrical CH_2 resonance at 82° can be rationalized as being made up of two symmetrical components, a higher field narrow peak and a lower field broad peak. Assuming a distribution of conformational isomers, the higher field narrow peak can be assigned to more symmetrical species, the lel conformers which should possess a simpler pmr pattern because of the higher symmetry (D_3). The lower field peak can be assigned to species of lower symmetry, the less stable conformers of C_2 symmetry. If the same distribution of conformational isomers is maintained in the temperature range, then the coalescence of resonance patterns at lower temperatures should result in a pattern which is still broad, *ca.* 20 Hz. The band width at 4° (7 Hz) indicates that the total pattern becomes narrow (with some broadening at the base) indicative of a predominance of a more symmetrical species, the lel conformer.

Ion pairing of multiply charged oxyanions to the $Co(en)_3^{3+}$ ion has been deduced as being predominantly directional in nature while that for monovalent anions such as Cl^-, Br^-, and I^- is nondirectional in nature.[4,10,18] The model proposed for ion pairing by oxyanions which favors the lel conformer[4,10] is not sterically favored for ion pairing by monovalent anions. Consequently, while changes are expected in the pmr spectrum for directional modes of ion pairing which impose restrictions on the conformations of the chelate rings, little or no change is expected for the nondirectional modes (Figure 3, Table I). The Co(III) and Rh(III) complexes in phosphate solutions are cited as examples consistent with the ordered model, and almost identical results are obtained in comparable solutions of selenate and selenite ions (Table I). The data indicate that with increasing phosphate concentration the band width of the CH_2 resonance for the Rh(III) complex increases while that for the Co(III) complex first decreases and then increases. Since the conformational equilibrium for the Co(III) complex is a dynamic one and since the nmr experiment records an equilibrium situation compared to the CD experiment, the observed trend in the band width data for the Co(III) complex is consistent with a shift of the conformational equilibrium toward the lel conformer of higher symmetry and narrower band width. Only broadening is observed in the CH_2 resonance of the Rh(III) complex, but the Co(III) and Rh(III) complexes give identical CH_2 patterns in 0.5 and 1.8 *m* K_3PO_4. It might be expected that the nmr pattern of the Co(III) complex should broaden continually with ion pairing and the deterred motion of the chelate rings. This need not be the case, especially in the more dilute phosphate solutions, if the rate of ring inversion remains fast but the distribution of conformational isomers is shifted toward the lel isomer. There is also the possibility that band sharpening is due to an acid–base type of reaction between phosphate species and the complex ion which relaxes the barrier to ring inversion through proton exchange. The probability that this mechanism is operative is small, however, since D_2O is a much stronger acid than the complex ion. Also, a pmr spectrum of the $Co(en)_3^{3+}$ ion in NaOD–D_2O (pH *ca.* 13) showed some sharpening of the resonance pattern (16–17 Hz), but this does not compare with the band width of 8 Hz in 0.1 or 0.5 *m* K_3PO_4 in D_2O. The effects of ion pairing with monovalent anions are small in the CD spectrum for $[Co(en)_3]Cl_3$[10,18] and the effects in the pmr spectrum (Table I) are also small. This is consistent with the prediction that nondirectional ion pairing is associated with negligible shifts in the distribution of conformational isomers.

TABLE I

BAND WIDTHS AT HALF-HEIGHT ($W/2$) FOR COMPLEXES IN VARIOUS D_2O–SALT SOLUTIONS

Complex	Salt soln	$W/2$ of CH_2, Hz
$[Co(en)_3]Cl_3$	D_2O alone	17
	0.1 *m* Na_2SeO_4	14
	0.5 *m* Na_2SeO_4	10
	1.8 *m* Na_2SeO_4	13
	0.1 *m* Na_2SeO_3	11
	0.5 *m* Na_2SeO_3	8
	1.9 *m* Na_2SeO_3	11
	1.1 *m* NaCl	16
$[Co(en)_3)Br_3$	D_2O alone	19
	0.1 *m* NaBr	17
	0.5 *m* NaBr[a]	16
$[Co(en)_3]I_3$	D_2O alone	19
	0.1 *m* KI[a]	17
$[Rh(en)_3]Cl_3$	D_2O alone	3
	1.8 *m* Na_2SeO_4	7
	1.9 *m* Na_2SeO_3	10

[a] Solubility limitations prevented the study of more concentrated solutions.

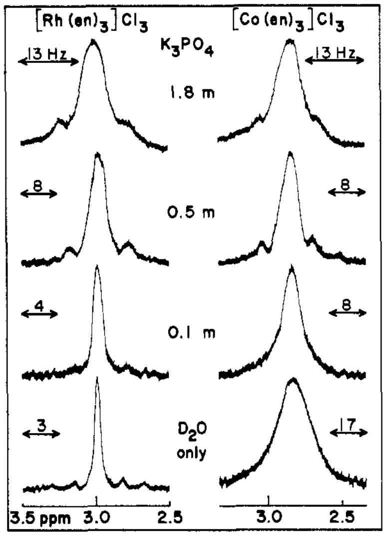

Figure 3.—Pmr spectra of $[Co(en)_3]Cl_3$ and $[Rh(en)_3]Cl_3$ in deuterium oxide solutions of potassium phosphate at 60 MHz. Band widths at half-height are listed on the arrows.

Pmr spectra of the complexes in the hydrogen-bonding solvents trifluoroacetic acid (TFA) and per-

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[18] H. L. Smith and B. E. Douglas, *Inorg. Chem.*, **5**, 784 (1966); *J. Am. Chem. Soc.*, **86**, 3885 (1964).

deuteriodimethyl sulfoxide (DMSO-d_6) also show changes ascribed to conformational ordering. It has been shown[19] that solvent association with the Co(III) complex in DMSO-d_6 solution gives an activation energy for ring inversion of *ca.* 10.5 kcal/mol. The high barrier to ring inversion is attributed to the formation of a secondary coordination shell and "frozen conformers" in solution. It has been suggested[20] that ring inversion is rapid for this complex in DMSO-d_6 but this conclusion was based on the observation of a singlet amine resonance, which has been observed as at least a doublet in this and other[19] work. The solvent impurity resonance of DMSO-d_5 is superimposed upon the methylene resonance for the Co(III) complex so that evaluation of the band width is difficult (*ca.* 20 Hz total band width). The CH_2 peak for the Rh(III) complex is separated from the DMSO-d_5 resonance well enough to yield the reasonably accurate band width of 15 Hz. This unfortunate situation gives no indication as to whether the Co(III) and Rh(III) chelate rings are in common environments in solution, but the spectra in TFA are much more informative in this respect. Except for their chemical shifts, the Co(III) and Rh(III) complexes give identical spectra in TFA solution. The spectrum for the Co(III) complex is shown in Figure 4. Both complexes possess CH_2 resonances with the common band width of 10 Hz and broadened AB-type amine resonances of comparable width. The peaks for the Rh(III) complex occur slightly further downfield, and this might be expected considering the larger radius of the Rh(III) ion and larger field gradient surrounding the ^{103}Rh nucleus. The narrow CH_2 resonance of the Co(III) complex in D_2O at low temperatures was attributed to the lel conformer. The narrow CH_2 resonance in TFA suggests a predominance of the lel conformer in this solvent. It was hoped that the deuterated complexes in TFA would yield even smaller widths for the CH_2 resonances with the removal of N–H and C–H coupling, but the band widths were observed to broaden slightly (Table II). The expected sharpening with the deuterated Co(III) complex in TFA has been reported[17] but was not observed in this work.

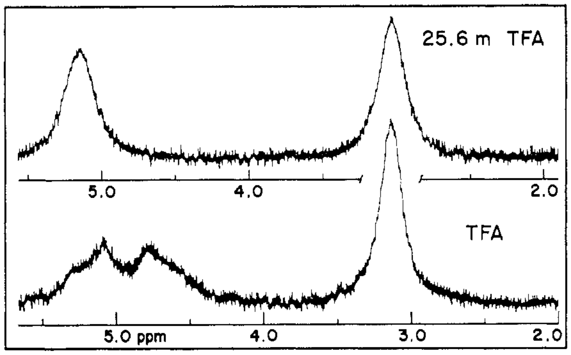

Figure 4.—Pmr spectra of $[Co(en)_3]Cl_3$ in trifluoroacetic acid (TFA) and 25.6 *m* TFA in D_2O (note chemical shift indices).

Table II

Band Widths at Half-Weight ($W/2$) for the Complexes $[Co(en)_3]Cl_3$ and $[Rh(en)_3]Cl_3$ in Hydrogen-Bonding Solvents (Chemical Shifts *vs.* DSS Are Given in Parentheses)

Complex	Solvent soln	$W/2$ of CH_2, Hz (δ, ppm)	$W/2$ of NH_2, Hz (δ, ppm)
$[Co(en)_3]Cl_3$	D_2O, D^+	19 (2.86)	36 (4.84)
	0.1 *m* TFA in D_2O	19 (2.82)	36 (4.88)
	0.5 *m* TFA in D_2O	18 (2.83)	30 (4.88)
	2.0 *m* TFA in D_2O	17 (2.86)	24 (5.0)
	9.8 *m* TFA in D_2O	14 (2.95)	15 (5.14)
	25.6 *m* TFA in D_2O	13 (3.02)	15 (5.14)
	TFA	10 (3.22)	*Ca.* 30 (4.71)[a]
			Ca. 30 (5.04)
	DMSO-d_6	*Ca.* 20[b] (2.57)	*Ca.* 34 (5.39)[a]
			Ca. 25 (5.75)
$[Co(en\text{-}d_4)_3]Cl_3$	TFA	17 (3.24)	
$[Rh(en)_3]Cl_3$	D_2O, D^+	9 (2.92)	*Ca.* 25 (5.0)[a]
			Ca. 25 (5.3)
	0.1 *m* TFA in D_2O	8	*Ca.* 25[a]
			Ca. 25
	TFA	10 (3.17)	*Ca.* 25 (5.15)[a]
			Ca. 25 (5.36)
	DMSO-d_6	15 (2.67)	*Ca.* 24 (5.74)[a]
			Ca. 30 (5.96)
$[Rh(en\text{-}d_4)_3]Cl_3$ (partially deuterated)	TFA	11 (3.15)	

[a] Two overlapping bands. [b] DMSO-d_5 resonance superimposed.

To investigate the possibility that the reduced band width of the Co(III) complex in TFA might be due only to solvent effects on the chemical shifts and therefore not to the lel conformer alone, pmr spectra of the complex were recorded in a series of TFA–D_2O solutions (Figure 4, Table II). Just as with the various salt solutions, the band width of the CH_2 resonance was observed to decrease with increasing TFA concentration. The change was not as pronounced as in the salt solutions but there was also no comparable charge effect in the TFA solutions. An interesting aspect of this series of spectra is that the single amine band sharpened with increasing TFA concentration instead of broadening toward the two amine bands observed in pure TFA. This trend does not necessarily reflect a lack of conformational ordering effects since a concentrated solution of Na_2SeO_4 in 1% D_2SO_4–D_2O gave the same result for the band widths of the CH_2 (16 Hz) and NH_2 (18 Hz) patterns.

The larger chelate rings of the tris(trimethylenediamine)cobalt(III) ion have far more mobility than en chelate rings. This mobility is reflected in the pmr spectra obtained in TFA,[17] D_2O, 1% D_2SO_4 in D_2O, and 1.8 *m* K_3PO_4 in D_2O. While large differences in the CH_2 resonance were noted in the $(en)_3$ complexes in these solvents, only minor differences in fine structure were evident in the CH_2 resonances of the $Co(tn)_3^{3+}$ ion (two protons at *ca.* 1.9 ppm, half-width 17–19 Hz; four protons at *ca.* 2.6 ppm, half-width 14–18 Hz).

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(19) B. M. Fung, *J. Am. Chem. Soc.*, **89**, 5788 (1967).

(20) H. Yoneda, M. T. Emerson, and Y. Morimoto, *Inorg. Chem.*, **8**, 2214 (1969).