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Triamines of Cobalt(III). 5. Nuclear Magnetic Resonance Characterization of Diethylenetriaminecobalt(III) Complexes and the Structure of Meridional Bis(diethylenetriamine)cobalt(III) Nitrate Monohydrate

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The proton and carbon-13 magnetic resonance spectra of bis(diethylenetriamine)cobalt(III) ion (I) and triazido(diethylenetriamine)cobalt(III) (II) suggest that the tridentate ligand occupies the meridional position of the octahedra about the cobalt(III) metal centers. This configuration is confirmed by crystallographic analysis. The crystal and molecular structure of I was determined by three-dimensional x-ray analysis using monochromatic Mo Kα radiation. The compound is found to be monoclinic, with space group $P2_1/c$ whose unit cell data are a = 8.766 (4) Å, b = 12.167 (6) Å, c = 18.669 (8) Å, β = 103.5 (5)°, Z = 4, d_{calcd} = 2.047 g cm^{-3}, and d_{obsd} = 2.04 g cm^{-3}. The structure was solved by normal Patterson and Fourier methods and refined by conventional full-matrix least-squares techniques to a final discrepancy factor of 0.067. The maximum distortion of the octahedron is 5.6 (7)° from an ideal angle of 90°; and 9.3 (8)° from the expected 180° angle.

Introduction

In the bis(diethylenetriamine)cobalt(III) ion, the diethylenetriamine ligand may coordinate so as to generate three geometrical isomers: meridional, u-facial, and s-facial (Figure 1). These three have been isolated[1,2] and the crystal structures determined for compounds with the u-facial[3] and s-facial[4] configurations.

As part of a systematic study of cobalt(III) triamines, synthesis of *fac*- and *mer*-triazidodiethylenetriaminecobalt(III) (Co(dien)$(N_3)_3$) was attempted by various means. The latter was easily prepared[5,6] while the former could be prepared only from the meridional isomer.[7] When attempts were made to prepare *fac*-Co(dien)$(N_3)_3$ directly from cobalt nitrate, sodium azide, and diethylenetriamine, a large yield of what ultimately proved to be *mer*-(Co(dien)$_2$)$(NO_3)_3\cdot H_2O$ was produced, with little evidence for the formation of the other isomers of (Co(dien)$_2$)$^{3+}$.

Experimental Section

Preparation of Racemic *mer*-(Co$(C_4H_{13}N_3)_2$)$(NO_3)_3\cdot H_2O$. Orange crystals of excellent quality were prepared by mixing 1 mol of cobalt nitrate hexahydrate with 1 mol of diethylenetriamine in water at room temperature (21 °C). This mixture was air oxidized for 1 h and filtered. A small amount of sodium azide had been added in an attempt to prepare the *fac*-Co(dien)$(N_3)_3$; however, only the *mer*-(Co(dien)$_2$)$^{3+}$ ion formed (and in greater yield than when azide was not present). The solution was treated with large amounts of methanol causing a crude yellow product to precipitate. Pure crystals were obtained by recrystallizing the crude product in water and air-drying after separation.

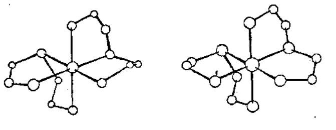
Spectroscopy. Proton magnetic resonance spectra were recorded with Varian A-60 and Varian XL-100 instruments at 60 and 100 MHz, respectively. All samples were dissolved in DMSO-d_6 with a concentration of ca. 5% by weight and run against internal TMS. PMR results are tabulated in Table I.

Carbon-13 resonance frequencies were measured on a Bruker HFX-90 NMR instrument operating in a Fourier transform mode using a Nicolet FT-1083 computer, 8K data table. C_6H_6 was used as a spectrometer lock. All spectrometer operating parameters are identical for the two samples. All samples were run against internal TMS as standard.

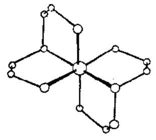
X-Ray Data Collection. The compound prepared as above crystallized as parallelepipeds. A crystal measuring 0.18 × 0.33 × 0.10 mm was chosen from the recrystallized material and mounted with epoxy resin with the "b" axis of the crystal paralleling the glass capillary tube. Weissenberg and oscillation photographs indicated a monoclinic space group with systematic absences: (1) for the $0k0$ reflections, $k = 2n + 1$; (2) for the $h0l$ reflections, $l = 2n + 1$. These absences are characteristic of the assigned space group $P2_1/c$.

The crystal was transferred to a Syntex $P2_1$ automated diffractometer with a graphite monochromator for data collection, the details of which are summarized in Table II.

Solution and Refinement of the Structure. Standard Lorentz and polarization corrections were applied, and absorption corrections were made by the method of Coppens et al.[8a] The grid used for the absorption correction was 4 × 4 × 4 (parallel to a, b, c). Calculated



u-Facial



s-Facial

Figure 1. The u-facial and s-facial isomers of $(Co(dien)_2)^{3+}$ as reported by Kobayashi et. al.[4] and Konno et al.[3] Note that the u-facial isomer can exist in two forms differing only in the orientation of the carbon atoms in the chelate ring system.

Table I

a. Carbon-13 Resonance Frequencies of Some Cobalt(III)-Amine Complexes

Compd	Freq, cm^{-1}	Assignment
$(Co(dien)_2)^{3+}$	46.31	Ethylenic $(CH_2)_n$-NH_2
	47.42	Ethylenic $(CH_2)_n$-NH
$Co(dien)(N_3)_3$	46.88	Ethylenic $(CH_2)_n$-NH_2
	49.20	Ethylenic $(CH_2)_n$-NH
cis-$(Co(en)(NCS)_2)^+$	46.8	
	45.5	Ref 14
trans-$(Co(en)(NCS)_2)^+$	46.0	Ref 14
cis-$(Co(en)(N_3)_2)^+$	45.5	
	44.1	Ref 14

b. ^1H NMR Spectrum of the Amine Resonance in Co(III) Complexes

Compd	Freq, cm^{-1}	Peak height	Assignment
$(Co(dien)_2)^{3+}$	4.21	2	$-NH_2$
	4.75	2	$-NH_2$
	7.50	1	NH
mer-$Co(dien)(N_3)_3$	4.30	2	$-NH_2$
	4.46	2	$-NH_2$
	5.65	1	NH
s-fac-$(Co(dien)_2)^{3+}$	4.80	4	$-NH_2$[4]
	7.12	1	NH
u-fac-$(Co(dien)_2)^{3+}$	4.68	2	$-NH_2$[3]
	5.08	2	$-NH_2$
	6.40	1	NH

transmission coefficients were in the range 0.76–0.66. The linear absorption coefficient was 26.3 cm^{-1}.

The structure was solved using a Patterson calculation and the usual Fourier analyses. The heavy-atom position was deduced from the Patterson calculation and was located at 0.180, 0.750, 0.120. A Fourier calculation phased on the cobalt position alone resulted in a discrepancy index (R_1) of 0.48 where

$$R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$$

Several areas of positive electron density were located about the cobalt atom in the form of an octahedron. Inclusion of these atoms with nitrogen scattering factors associated with each reduced R_1 to 0.40. All of the remaining atoms except the solvent molecule were located. Another electron density calculation including these atoms resulted in a discrepancy index of 0.27.

The structure was initially refined by full-length matrix least squares using a unit weighting scheme. After several cycles of isotropic refinement which converged at $R_1 = 0.136$ and $R_2 = 0.156$ where

$$R_2 = (\Sigma w ||F_o| - |F_c||^2 / \Sigma w |F_o|^2)^{1/2}$$

a difference map was calculated and revealed a rather large area of positive electron density at 0.320, 0.250, 0.228. This peak was assigned an oxygen scattering curve and interpreted to be a water molecule from the solvent used in the recrystallization.

Table II. Experimental Data for the X-Ray Diffraction Study of *mer*-$(Co(dien)_2)(NO_3)_3 \cdot H_2O$

(A) Crystal Parameters (at 22.0 ± 0.5 °C)[a]

Crystal system	Monoclinic	Space group[b]	$P2_1/c$
Vol	1991 (2) $Å^3$	Formula	$(Co(C_4H_{13}N_3)_2)$-$(NO_3)_3H_2O$
a	8.766 (4) Å	Mol wt	451.28
b	12.167 (6) Å	*Z*	4
c	18.669 (8) Å	d_{calcd}[c]	2.047 g cm^{-3}
β	103.5 (5)°	d_{obsd}	2.04 (2) g cm^{-3}

(B) Measurement of Intensity Data

Radiation	λ(Mo Kα) 0.71069 Å
Takeoff angle	6.2°
Attenuators	Not used
Crystal orientation	φ = (010)
Max 2θ	60°
Scan type	Coupled θ(crystal)-2θ(counter)
Scan speed	0.6°/min
Scan length	50 steps for a total scan width of 1°; 2 s/step
Background	Measd for half the total scan time
Std reflections[d]	4 measd for every 100 data points
Reflections collected[e]	4608 unique measurements, of which 2883 were judged to be significantly greater than background[f]

[a] The unit cell parameters are from a least-squares fit of 15 reflections employing Mo Kα radiation (λ 0.71069 Å) and a Syntex $P2_1$ automatic diffractometer system with a graphite monochromator. [b] Weissenberg and oscillation photographs indicated a monoclinic space group with systematic absences: for the 0*k*0 reflection, *k* = 2*n* + 1; for the *h*0*l* reflection, *l* = 2*n* + 1. These absences are characteristic for the assigned space group $P2_1/c$. [c] Neutral bouyancy in CCl_4-1,2-dibromomethane. [d] Scale factors were calculated from the relative intensity of the standards and indicated a maximum of 5% decomposition. [e] Data reduction was performed using the XRAY72 system by Stewart et al.[11] [f] The standard deviation associated with each datum is given by the formula $\sigma = (\text{scan count} + (\Sigma Bg/BgS)^2)^{1/2}$, where Bg = background and BgS = Bg to scan ratio.

At this point in the refinement, the weighting scheme was changed to a modified Cruikshank[8b] weight where

$$w = 1/(A + F_o + BF_o)^2$$

$$A = 2F_{min}$$

$$B = 2/F_{max}$$

The water molecule was added to the structure refinement and convergence was attained at $R_1 = 0.11$ and $R_2 = 0.135$. A second difference Fourier calculation at this point suggested the position of all of the hydrogen atoms except those of the solvent molecule. Inclusion of these hydrogen atoms at calculated positions and several cycles of anisotropic refinement of all atoms except the water oxygen (which showed high thermal motion) and the hydrogen atoms converged (shift/error ≤ 0.25) at the final discrepancy indices of $R_1 = 0.067$ and $R_2 = 0.056$. A final difference synthesis showed no additional peaks exceeding 0.3 e/$Å^3$. A list of observed and calculated structure factors is available (supplementary material). Atomic and thermal parameters appear in Tables III and IV. Table V presents the bond lengths and angles.

Atomic scattering factors for all atoms were taken from Cromer and Waber.[9] The real (Co(III), N, C, O, H) and anomalous Co(III) contributions to the scattering atoms were obtained from ref 10. The least-squares and Fourier programs were those included in the XRAY72 system,[11] while the remaining programs were written by the authors.[7]

Results and Discussion

The coordination complex $(Co(dien)_2)(NO_3)_3 \cdot H_2O$ (where dien = diethylenetriamine) consists of a cobalt(III) atom surrounded by six nitrogen atoms of the two diethylenetriamine ligands in an octahedral configuration. Initially, the meridional configuration had been assigned to this complex by the similarity of its nuclear magnetic resonance spectra with that

Table III. Atom Table for $(Co(dien)_2)(NO_3)_3 \cdot H_2O$

Atom	x	y	z
Co	0.1823 (2)	0.7525 (1)	0.1215 (1)
O(1)	0.0210 (11)	0.5634 (8)	0.4236 (4)
O(2)	0.2560 (11)	0.7352 (8)	0.3901 (6)
O(3)	0.0378 (10)	0.1079 (9)	0.1922 (5)
O(4)	0.3675 (12)	0.6377 (9)	0.3283 (4)
O(5)	0.4300 (12)	0.4659 (7)	0.3351 (6)
O(6)	0.4055 (12)	0.0783 (9)	0.1102 (7)
O(7)	0.2034 (10)	0.0543 (7)	0.3700 (4)
O(8)	0.1405 (7)	0.9887 (6)	0.4669 (4)
O(9)	0.3485 (10)	0.9319 (9)	0.4363 (4)
N(1)	0.3397 (11)	0.8050 (8)	0.2081 (4)
N(2)	0.0402 (12)	0.8510 (8)	0.1563 (5)
N(3)	0.0017 (11)	0.7140 (8)	0.0409 (4)
N(4)	0.1400 (11)	0.6231 (7)	0.1782 (3)
N(5)	0.3275 (9)	0.6565 (6)	0.0865 (3)
N(6)	0.2506 (12)	0.8655 (7)	0.0612 (4)
N(7)	0.0042 (12)	0.6351 (7)	0.3746 (4)
N(8)	0.4613 (14)	0.5614 (8)	0.3501 (4)
N(9)	0.2306 (11)	0.9908 (6)	0.4230 (4)
C(1)	0.2664 (16)	0.8861 (11)	0.2509 (6)
C(2)	0.0919 (16)	0.8628 (11)	0.2373 (7)
C(3)	0.1272 (16)	0.3142 (11)	0.3485 (6)
C(4)	0.1337 (13)	0.2869 (10)	0.4537 (6)
C(5)	0.2265 (15)	0.5252 (10)	0.1579 (6)
C(6)	0.3750 (17)	0.5625 (11)	0.1397 (6)
C(7)	0.4536 (17)	0.7253 (12)	0.0683 (8)
C(8)	0.3719 (16)	0.8152 (13)	0.0248 (7)
O(10)[a]	0.3243 (12)	0.2437 (14)	0.2280 (14)

[a] For O(10), $B = 18.1$ Å^2.

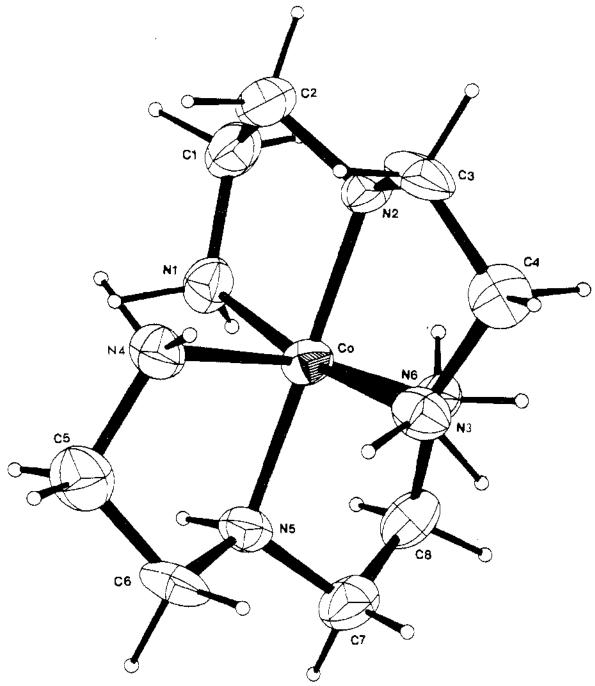


Figure 2. An ORTEP illustration of $(Co(dien)_2)^{3+}$. The nonhydrogen atoms are drawn to the 50% inclusion level, while the hydrogen atoms are drawn as spheres of arbitrary size. Note the orientation of the diethylenetriamine ligand in the meridional configuration.

of *mer*-$Co(dien)(N_3)_3$ whose structure was assigned by x-ray diffraction analysis.[6]

The carbon-13 magnetic resonance spectrum of the $(Co(dien)_2)^{3+}$ ion is tabulated in Table I along with the frequencies observed for some other cobalt(III) complexes. The spectrum of *mer*-$(Co(dien)_2)^{3+}$ is similar to that of *mer*-$Co(dien)(N_3)_3$; only two resonance frequencies are observed, indicating that only two independent types of carbon atoms are present. Ideally this can occur if *mer*-$(Co(dien)_2)^{3+}$ exhibits an internal twofold rotation and a local mirror plane through the secondary amine nitrogen atom. Thus, only two different types of carbon atoms would be present: those adjacent to the secondary amine and those adjacent to the primary amine. In *mer*-$Co(dien)(N_3)_3$, such a mirror plane was found to exist.

The proton magnetic resonance spectra of these two complexes are also similar. In the *mer*-$(Co(dien)_2)^{3+}$ ion and in *mer*-$Co(dien)(N_3)_3$, one set of protons from each of the terminal amines ($-NH_2$) is directed toward the remaining ligands (dien in the former complex, azide in the latter) while the second set is directed away from the complex. Thus, the

Table IV. Final Anisotropic Thermal Parameters ($\times 10^4$) for $(Co(dien)_2)(NO_3)_3 \cdot H_2O$[a]

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co	20.4 (5)	36.5 (7)	22.5 (5)	−0.7 (8)	−0.2 (8)	4.3 (4)
O(1)	63 (5)	46 (5)	38 (4)	−12 (5)	16 (4)	−15 (4)
O(2)	71 (5)	45 (5)	35 (4)	4 (4)	7 (4)	0.2 (4)
O(3)	75 (5)	58 (5)	30 (4)	−17 (4)	9 (4)	−15 (4)
O(4)	55 (5)	61 (5)	51 (4)	−26 (5)	33 (4)	−19 (4)
O(5)	48 (5)	127 (6)	39 (4)	15 (6)	12 (4)	3 (4)
O(6)	66 (5)	76 (5)	49 (4)	−44 (5)	2 (4)	−8 (4)
O(7)	47 (5)	83 (6)	55 (5)	−30 (4)	18 (4)	−25 (4)
O(8)	77 (7)	81 (7)	100 (6)	−11 (6)	11 (5)	−10 (5)
O(9)	67 (6)	144 (9)	109 (7)	100 (6)	−38 (5)	1 (6)
N(1)	21 (4)	40 (5)	23 (4)	−1 (4)	1 (4)	8 (4)
N(2)	23 (5)	37 (5)	28 (5)	−13 (4)	5 (4)	14 (4)
N(3)	25 (4)	29 (5)	32 (4)	6 (4)	16 (4)	2 (3)
N(4)	38 (5)	32 (5)	36 (5)	−4 (4)	13 (4)	5 (4)
N(5)	29 (5)	25 (5)	34 (5)	6 (4)	4 (4)	−3 (4)
N(6)	17 (4)	27 (5)	26 (4)	7 (4)	−1 (3)	1 (3)
N(7)	51 (5)	67 (6)	17 (4)	1 (5)	1 (4)	−7 (4)
N(8)	38 (5)	42 (6)	26 (5)	28 (5)	9 (4)	−1 (4)
N(9)	67 (7)	57 (7)	62 (6)	−1 (6)	13 (5)	5 (5)
C(1)	30 (6)	54 (7)	49 (6)	−12 (5)	4 (5)	−20 (5)
C(2)	45 (6)	25 (6)	33 (6)	4 (5)	−13 (5)	−20 (5)
C(3)	34 (6)	46 (7)	40 (6)	18 (6)	8 (5)	−3 (6)
C(4)	58 (7)	47 (7)	27 (6)	−9 (6)	21 (5)	10 (5)
C(5)	23 (6)	35 (6)	60 (6)	6 (5)	20 (5)	−2 (5)
C(6)	24 (6)	53 (8)	52 (6)	−1 (5)	5 (4)	10 (5)
C(7)	47 (7)	58 (8)	28 (6)	7 (6)	8 (6)	3 (6)
C(8)	25 (5)	51 (9)	45 (6)	1 (5)	7 (5)	12 (5)

[a] The anisotropic temperature factor has the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{23}klb^*c^* \cos \gamma^*)]$. The standard deviations are given following each parameter in parentheses.

Table V. Bond Lengths and Angles for *mer*-(Co(dien)$_2$)(NO$_3$)$_3$·H$_2$O (Standard Deviations in Parentheses)

(a) Bond Lengths, Å

Co–N(1)	1.971 (8)	N(2)–C(3)	1.517 (17)
Co–N(2)	1.946 (8)	C(3)–C(4)	1.518 (18)
Co–N(3)	1.969 (8)	N(3)–C(4)	1.504 (14)
Co–N(4)	1.980 (7)	N(4)–C(5)	1.507 (16)
Co–N(5)	1.949 (7)	C(5)–C(6)	1.491 (19)
Co–N(6)	1.957 (9)	N(5)–C(6)	1.508 (16)
N(1)–C(1)	1.505 (17)	N(5)–C(7)	1.488 (17)
C(1)–C(2)	1.518 (19)	C(7)–C(8)	1.488 (19)
N(2)–C(2)	1.481 (17)	N(6)–C(8)	1.518 (17)

(b) Bond Angles, Deg

N(1)–Co–N(2)	84.6 (4)	Co–N(1)–C(1)	110.1 (6)
N(1)–Co–N(3)	171.1 (4)	N(1)–C(1)–C(2)	109.1 (9)
N(1)–Co–N(4)	90.1 (3)	C(1)–C(2)–N(2)	104.0 (9)
N(1)–Co–N(5)	94.7 (3)	C(2)–N(2)–C(3)	98.6 (8)
N(1)–Co–N(6)	89.7 (4)	N(2)–C(3)–C(4)	84.9 (7)
N(2)–Co–N(3)	86.5 (4)	C(3)–C(4)–N(3)	108.3 (9)
N(2)–Co–N(4)	95.6 (3)	C(4)–N(3)–Co	108.3 (5)
N(2)–Co–N(5)	178.8 (3)	Co–N(4)–C(5)	109.0 (6)
N(2)–Co–N(6)	93.7 (4)	N(4)–C(5)–C(6)	109.5 (9)
N(3)–Co–N(4)	90.1 (3)	C(5)–C(6)–N(5)	105.0 (9)
N(3)–Co–N(5)	94.2 (3)	C(6)–N(5)–C(7)	118.1 (8)
N(3)–Co–N(6)	91.5 (4)	C(7)–N(5)–Co	108.5 (6)
N(4)–Co–N(5)	85.3 (3)	N(5)–C(7)–C(8)	104.9 (9)
N(4)–Co–N(6)	170.7 (4)	C(7)–C(8)–N(6)	111.1 (9)
N(5)–Co–N(6)	85.2 (4)	C(8)–N(6)–Co	108.3 (9)

two NH$_2$ moieties of each diethylenetriamine are not equivalent to each other.

The results of the x-ray analysis of the (Co(dien)$_2$)(NO$_3$)$_3$·H$_2$O complex are presented in Figure 2. Neglecting the distortion of the octahedron about the cobalt atom, the molecule contains the ideal twofold symmetry. Furthermore, the decided asymmetry of the amine (–NH$_2$) hydrogens and existence of a local mirror plane through the secondary amine nitrogen is clearly apparent.

The bond angles within the octahedron are in agreement with the values expected and are similar to those obtained for the other geometrical isomers of this complex.[3,4] The maximum distortion of the octahedron occurs at the N(4)–Co–N(6) angle which is 170.7 (4)° rather than the expected angle of 180°. The average bond length of 1.97 (1) Å is similar to that found in Co(dien)(N$_3$)$_3$. The secondary amine to cobalt distance, 1.95 (1) Å, is similar to that previously reported and values reported by other observers.[12] The shortened metal to secondary nitrogen distance has been observed in complexes where diethylenetriamine is coordinated about metals other than cobalt. *trans*-Bis(diethylenetriamine)copper(II) bromide hydrate and *trans*-bis(diethylenetriamine)copper(II) nitrate[13] each show distortion about the copper atoms and each show shorter secondary nitrogen to metal distances when compared to the primary amine to copper distances.

The *mer*-(Co(dien)$_2$)(NO$_3$)$_3$·H$_2$O crystalline lattice contains some hydrogen-bonding characteristics. Hydrogen bonding distances (in Å) are as follows: O(1)–N(1), 2.97; O(1)–N(2), 2.99; O(2)–N(3), 2.94; O(4)–N(6), 2.99; O(4)–N(5), 3.04; O(5)–N(6), 3.05; O(6)–N(2), 2.97; O(7)–N(5), 3.05; O(8)–N(3), 3.00; O(8)–N(4), 3.01.

In summary, it is apparent from the data presented that carbon-13 NMR provides a rapid method of identification of the symmetry present in certain types of chelates. This spectroscopic technique in combination with conventional ^{1}H NMR spectroscopy allows one to arrive at an accurate approximation of the structure of a coordination complex which may be confirmed by x-ray structure analysis.

Registry No. *mer*-(Co(dien)$_2$)(NO$_3$)$_3$, 58957-78-1; *mer*-(Co(dien)(N$_3$)$_3$), 26493-63-0; ^{13}C, 14762-74-4.

Supplementary Material Available: Listing of structure factor amplitudes (13 pages). Ordering information is given on any current masthead page.

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