

A ^{13}C NMR Study of Some Ammine Complexes of Diethylenetriaminecobalt(III)

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Carbon-13 nuclear magnetic resonance spectroscopy has previously been used to distinguish between *cis*- and *trans*- $\text{CoX}_2(\text{en})_2^+$ isomers [1]. In this paper we describe the use of this technique to establish the configuration of diethylenetriamine in a number of ammine complexes of diethylenetriaminecobalt(III).

Experimental

The commercially available diethylenetriamine (Fluka) was used as supplied to prepare *mer*- $\text{Co}(\text{NO}_2)_3\text{-dien}$ [2-4]. Reaction of this complex with concentrated HCl produces successively $\text{CoCl}(\text{NO}_2)_2\text{-dien}$ (orange, room temperature, overnight), $\text{CoCl}_2(\text{NO}_2)\text{-dien}$ (mud brown, boiling for 5 min) and *mer*- $\text{CoCl}_3\text{-dien}$ [5] (chocolate brown, 80-90 °C for 3 hr). The trichloride was purified as previously described [3], but the crude chloro nitro products were used directly. All complexes were washed with 2-propanol and then ether and air dried, unless otherwise stated. Analytical data are presented in Table I.

mer-Ammine-dichlorodiethylenetriaminecobalt(III) Perchlorate

(CAUTION: Perchlorate salts are potentially explosive). Ammonia ($\rho = 0.800$, 8 mL) was added to a slurry of $\text{CoCl}_3\text{-dien}$ (8 g) and NH_4Cl (8 g) in water (40 mL) and the mixture was heated on a steam bath for 10-15 min until most of the trichloride had dissolved. The filtered solution was added to an equal volume of HCl (12 M) and ZnCl_2 (15 g) was stirred in. Green crystals (7.5 g) deposited overnight and these were recrystallised as the perchlorate salt by dissolving in warm (50-60 °C) dilute HCl (0.1 M, 70 mL) and adding HCl (12 M, 70 mL) and HClO_4 (72%, 20 mL). The yield was 5 g. This complex has been prepared previously [6, 7] using a different route.

mer-Tris(ammine)(diethylenetriamine)cobalt(III) Chloride Tetrachlorozincate(II) and *unsym-fac-cis*-Di(ammine)chloro(diethylenetriamine)cobalt(III) Tetrachlorozincate(II)

A slurry of $\text{CoCl}_3\text{-dien}$ (5 g) in aqueous ammonia ($\rho = 0.880$, 20 mL) was heated on a steam bath for 10-15 min until all the solid had dissolved. Concentrated HCl (30 mL) and ZnCl_2 (10 g) were then added, and the products that deposited were collected in 4 crops over 1 week. Crop 1 (5.6 g, mainly $[\text{Co}(\text{dien})(\text{NH}_3)_3]\text{Cl}\cdot\text{ZnCl}_4$, after 30 min); crops 2 and 3 (0.8 g total, after 12 and 36 hr, respectively, mainly *unsym-fac-cis*- $[\text{CoCl}(\text{dien})(\text{NH}_3)_2]\text{ZnCl}_4$; crop 4 (0.8 g, mixture of di- and tri-ammine, 1 week).

Crop 1 was recrystallised from hot dilute HCl (0.1 M, 40 mL, 60 °C) by the addition of an equal volume of 12 M HCl to give 3 g of yellow *mer*- $[\text{Co}(\text{dien})(\text{NH}_3)_3]\text{Cl}\cdot\text{ZnCl}_4$ on cooling. Two further crops of mainly *unsym-fac-cis*- $[\text{CoCl}(\text{dien})(\text{NH}_3)_2]\text{ZnCl}_4$ (1 g total) were obtained in the addition of ZnCl_2 (10 g). Crops 2 and 3 were combined and recrystallised as above to give 0.6 g of pink *unsym-fac-cis*- $[\text{CoCl}(\text{dien})(\text{NH}_3)_2]\text{ZnCl}_4$.

sym-fac-cis-Di(ammine)chloro(diethylenetriamine)cobalt(III) Chloride Hemihydrate

Crude $\text{CoCl}(\text{NO}_2)_2\text{-dien}$ (29 g) was added to water (125 mL) and ammonia ($\rho = 0.880$, 25 mL) and heated on a steam bath to dryness overnight. Water (100 mL) and HCl (12 M, 100 mL) were added and the solution was heated to boiling. The colour changed from yellow to purple as NO_2 was evolved and red-violet crystals deposited from the boiling solution (20 min). The crude *sym-fac-cis*- $[\text{CoCl}(\text{dien})(\text{NH}_3)_2]\text{Cl}_2\cdot\frac{1}{2}\text{H}_2\text{O}$ (25 g) was collected from the cooled solution and 10 g were recrystallised from hot dilute HCl (80 mL, 0.1 M) by the addition of 12 M HCl (50 mL) to give 6.1 g of the pure isomer. Addition of ZnCl_2 (15 g) to the original mother liquor gave the ZnCl_4^{2-} salts of a 40:60 mixture of the *sym*- and *unsym-fac-cis*-isomers (2 g) which could not be separated by fractional crystallisation.

syn-fac-cis-Di(ammine)bromo(diethylenetriamine)cobalt(III) Bromide Hemihydrate

Crude *sym-fac-cis*- $[\text{CoCl}(\text{dien})(\text{NH}_3)_2]\text{Cl}_2\cdot\frac{1}{2}\text{H}_2\text{O}$ (1 g) was dissolved in 1 M NaOH solution (20 mL) and left at room temperature for 10 min. Concentrated HBr (47%, 20 mL) was added and the solution heated on a steam bath for 1 hr. Purple crystals (0.9 g) deposited and were collected from the cooled solution.

mer-cis-Di(ammine)chloro(diethylenetriamine)cobalt(III) Tetrachlorozincate(II)

A slurry of crude $\text{CoCl}_2(\text{NO}_2)\text{-dien}$ (8 g) and NH_4Cl (8 g) in 40 mL of water was treated with 10 mL

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TABLE I. Analytical Data.

	Co	C	H	N	X ^a	Co	C	H	N	X ^a
<i>mer</i> -[CoCl ₂ (dien)(NH ₃)] ClO ₄	16.86	13.74	4.62	16.03	20.28	16.55	14.17	4.67	16.09	19.70
<i>mer</i> -[Co(dien)(NH ₃) ₃] Cl·ZnCl ₄	12.93	10.53	4.86	18.44	38.88				18.47	39.17
<i>unsym-fac-cis</i> -[CoCl(dien)(NH ₃) ₂] ZnCl ₄	13.43	10.95	4.36	15.96	40.39		11.30	4.26		40.60
<i>sym-fac-cis</i> -[CoCl(dien)(NH ₃) ₂] Cl ₂ · $\frac{1}{2}$ H ₂ O	18.92	15.42	6.15	22.48	34.14	19.10	15.30	6.56	22.25	34.12
<i>sym-fac-cis</i> -[CoBr(dien)(NH ₃) ₂] Br ₂ · $\frac{1}{2}$ H ₂ O	13.24	10.79	4.30	15.74	53.88		10.69	4.81	15.79	53.91
<i>mer-cis</i> -[CoCl(dien)(NH ₃) ₂] ZnCl ₄	13.43	10.95	4.36	15.96	40.39				16.04	40.25

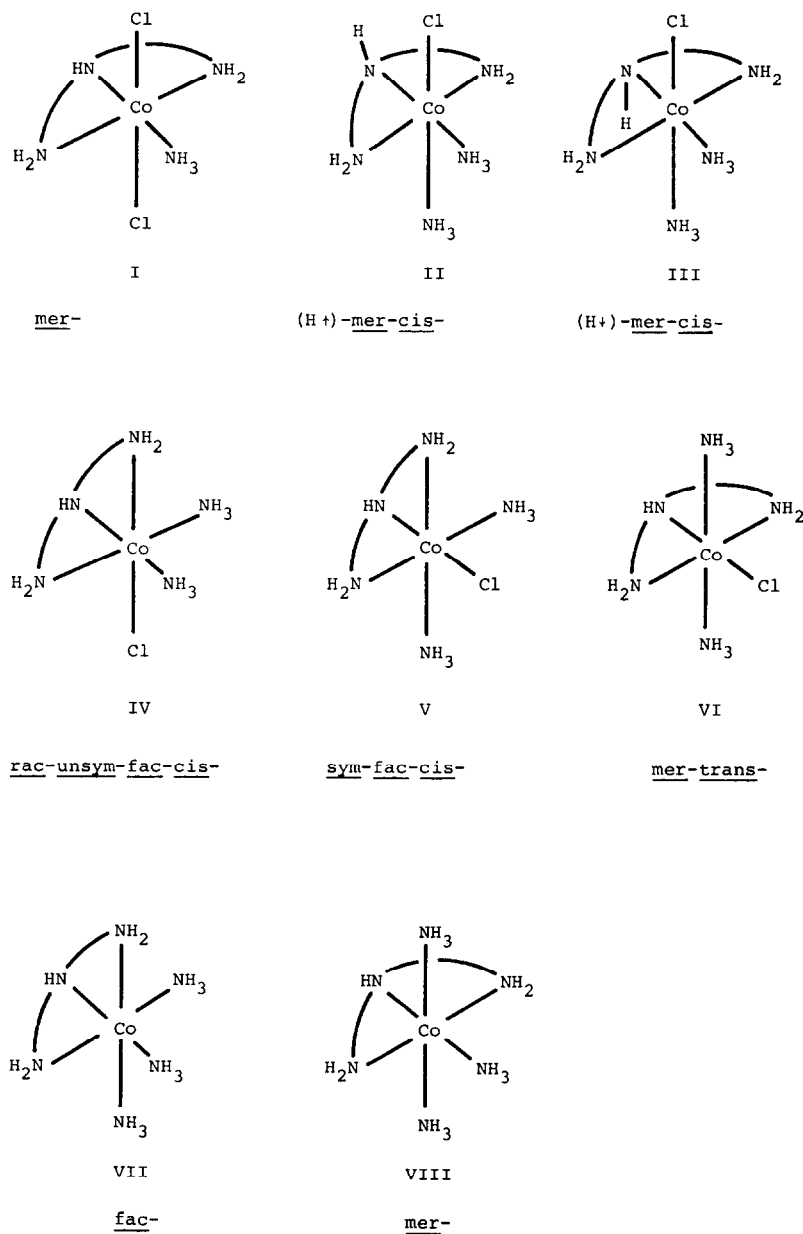
^aX = total halide.Figure 1. Possible configurational and conformational isomers for cobalt(III) ammine complexes of diethylenetriamine (cationic charges are omitted). For the (H⁺), (H⁺) nomenclature see reference [14].

TABLE II. ^{13}C NMR Shielding Data for Some Diethylenetriaminecobalt(III) Ammine Complexes.^a

Complex	Diethylenetriamine-C atoms	
<i>mer</i> -CoCl ₂ (dien)(NH ₃) ³⁺	50.9 ₇	47.9 ₄
<i>mer</i> -Co(dien)(NH ₃) ₃ ³⁺	50.4 ₅	47.7 ₃
<i>unsym-fac-cis</i> -CoCl(dien)(NH ₃) ₂ ²⁺	55.6 ₀	45.0 ₀
	54.6 ₄	44.5 ₅
<i>sym-fac-cis</i> -CoCl(dien)(NH ₃) ₂ ²⁺	55.4 ₅	44.2 ₆
<i>sym-fac-cis</i> -CoBr(dien)(NH ₃) ₂ ²⁺	54.8 ₀	45.1 ₃
<i>mer-cis</i> -CoCl(dien)(NH ₃) ₂ ²⁺	50.9 ₂	48.2 ₄
<i>sym-fac-cis</i> - plus <i>unsym-fac-cis</i> -CoCl(dien)(NH ₃) ₂ ²⁺ (40:60) mixture	55.6 ₀	45.0 ₁
	55.5 ₃	44.5 ₅
	54.6 ₄	44.3 ₄

^aShielding values in ppm relative to $\delta = 0$ for TMS. These values obtained by reference to dioxane as an internal standard, $\delta = 67.4_3$.

of ammonia ($\rho = 0.880$) and the mixture was heated on a steam bath at 70 °C for 15 min. Undissolved starting material (*ca.* 2 g) was removed by filtration and an equal volume of 12 M HCl was added to the filtrate. The orange solution was heated to 70 °C and ZnCl₂ (10 g) was stirred in. Crude orange *mer-cis*-[CoCl(dien)(NH₃)₂]ZnCl₄ (1.5 g) deposited on cooling and was collected after 3 hr at room temperature. A second crop (2 g), which deposited overnight, was a mixture of the *mer-cis*- and *unsym-fac-cis*-isomers and the green dichloro. The first crop was recrystallised as for the *unsym-fac-cis*-isomer to give 1 g of the pure product. An X-ray crystal structure of the chloride perchlorate salt of this isomer has been determined [8].

Spectra

Proton noise-decoupled ^{13}C nuclear magnetic resonance spectra were determined as previously described [1, 3, 9], using water or dimethylformamide (for *mer*-[CoCl₂(dien)(NH₃)]ClO₄) as solvents and dioxane as an internal standard.

Results and Discussion

Figure 1 presents the potential configurational and conformational isomers possible for the cobalt(III) ammine complexes of diethylenetriamine. Of these, I, III, IV, V and VIII have been synthesised and thus the tridentate ligand is found in both the meridional and facial configurations.

Infrared spectroscopy has previously been used to distinguish between these configurations [10–12] but the results from this technique have not always been successful [12, 13]. Carbon-13 NMR spectra (Table II, Figure 2) seem to provide a rapid and apparently unambiguous method for configurational assignment. The *sym-fac-cis*-, *unsym-fac-cis*- and *mer*-configurations (III, IV, V, Figure 2) are easily distin-

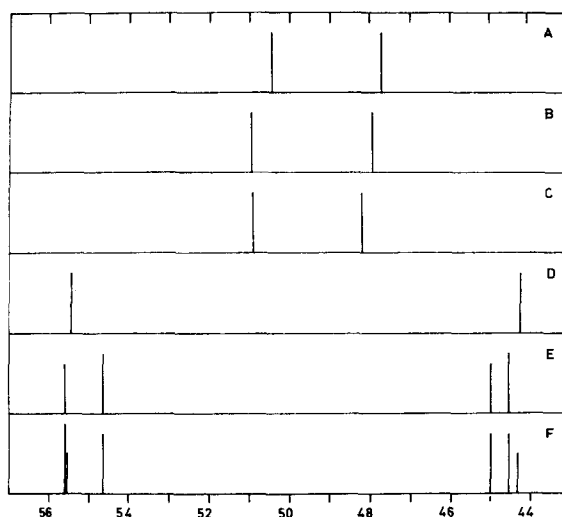


Figure 2. ^{13}C NMR spectra of some ammine complexes of diethylenetriaminecobalt(III) relative to dioxane at 67.4₃ ppm. A, *mer*-Co(dien)(NH₃)₃³⁺; B, *mer*-CoCl₂(dien)(NH₃)₃³⁺; C, *mer-cis*-CoCl(dien)(NH₃)₂²⁺; D, *sym-fac-cis*-CoCl(dien)(NH₃)₂²⁺; E, *rac-unsym-fac-cis*-CoCl(dien)(NH₃)₂²⁺; F, *sym-fac-cis*- plus *rac-unsym-fac-cis*-CoCl(dien)(NH₃)₂²⁺ mixture.

guished (Figure 1) and isomeric mixtures can be identified. In particular, the assignment of the diethylenetriamine configuration in the Co(dien)(NH₃)₃³⁺ isomer isolated would have been difficult in the absence of this technique, as both forms are achiral. A problem that remains (but has not occurred in this study) is to distinguish between the *mer-cis*-CoCl(dien)(NH₃)₂ conformational isomers II and III and to distinguish these from the *mer-trans*-form (VI). It is doubtful if the ^{13}C NMR spectra of these three forms would be different in the present situation. However, the *mer-cis*- and *mer-trans*-CoCl(dien)(NH₂CH₂R)₂²⁺ may be distinguishable, as the monodentate alkylamine ligands are not equivalent in the

mer-cis- configuration [3]. Unfortunately, our efforts to synthesise a *mer-trans*-diamine isomer have not yet been successful.

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