Inorganica Chimica Acta, 32 (1979) L5–L8
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A ^{13}C NMR Study of Some Ammine Complexes of Diethylenetriaminecobalt(III)

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Received October 4, 1978

Carbon-13 nuclear magnetic resonance spectroscopy has previously been used to distinguish between *cis*- and *trans*-$CoX_2(en)_2^+$ 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*-$Co(NO_2)_3$-dien [2–4]. Reaction of this complex with concentrated HCl produces successively $CoCl(NO_2)_2$dien (orange, room temperature, overnight), $CoCl_2(NO_2)$(dien) (mud brown, boiling for 5 min) and *mer*-$CoCl_3$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-*Amminedichlorodiethylenetriaminecobalt(III) Perchlorate*

(CAUTION: Perchlorate salts are potentially explosive). Ammonia (ρ = 0.800, 8 mL) was added to a slurry of $CoCl_3$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 $CoCl_3$dien (5 g) in aqueous ammonia (ρ = 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 $[Co(dien)(NH_3)_3]Cl\cdot ZnCl_4$, after 30 min); crops 2 and 3 (0.8 g total, after 12 and 36 hr, respectively, mainly *unsym-fac-cis*-$[CoCl(dien)(NH_3)_2]ZnCl_4$); 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*-$[Co(dien)(NH_3)_3]Cl\cdot ZnCl_4$ on cooling. Two further crops of mainly *unsym-fac-cis*-$[CoCl(dien)(NH_3)_2]$-$ZnCl_4$ (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*-$[CoCl(dien)(NH_3)_2]ZnCl_4$.

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

Crude $CoCl(NO_2)_2$dien (29 g) was added to water (125 mL) and ammonia (ρ = 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*-$[CoCl(dien)(NH_3)_2]Cl_2\cdot\frac{1}{2}H_2O$ (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*-$[CoCl(dien)(NH_3)_2]Cl_2\cdot\frac{1}{2}H_2O$ (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 $CoCl_2(NO_2)$dien (8 g) and NH_4Cl (8 g) in 40 mL of water was treated with 10 mL

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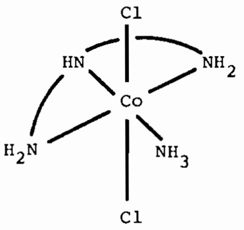
TABLE I. Analytical Data.

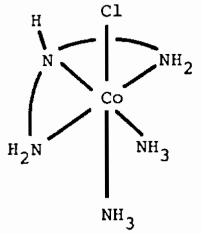
	Co	C	H	N	X[a]	Co	C	H	N	X[a]
mer-[CoCl$_2$(dien)(NH$_3$)]ClO$_4$	16.86	13.74	4.62	16.03	20.28	16.55	14.17	4.67	16.09	19.70
mer-[Co(dien)(NH$_3$)$_3$]Cl·ZnCl$_4$	12.93	10.53	4.86	18.44	38.88				18.47	39.17
unsym-fac-cis-[CoCl(dien)(NH$_3$)$_2$]ZnCl$_4$	13.43	10.95	4.36	15.96	40.39		11.30	4.26		40.60
sym-fac-cis-[CoCl(dien)(NH$_3$)$_2$]Cl$_2$$\cdot\frac{1}{2}H_2$O	18.92	15.42	6.15	22.48	34.14	19.10	15.30	6.56	22.25	34.12
sym-fac-cis-[CoBr(dien)(NH$_3$)$_2$Br$_2$$\cdot\frac{1}{2}H_2$O	13.24	10.79	4.30	15.74	53.88		10.69	4.81	15.79	53.91
mer-cis-[CoCl(dien)(NH$_3$)$_2$]ZnCl$_4$	13.43	10.95	4.36	15.96	40.39				16.04	40.25

[a] X = total halide.



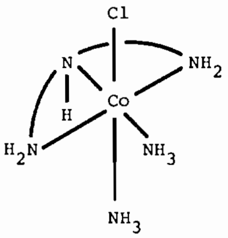
I

mer-



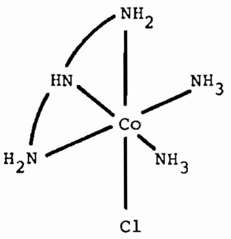
II

(H↑)-*mer-cis*-



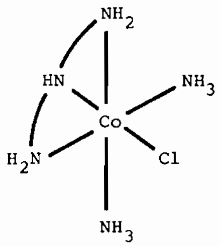
III

(H↓)-*mer-cis*-



IV

rac-unsym-fac-cis-



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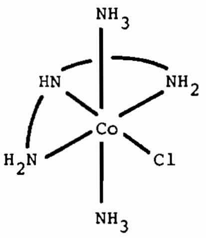
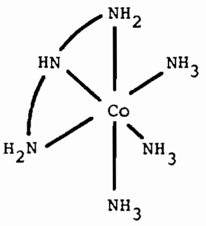
sym-fac-cis-



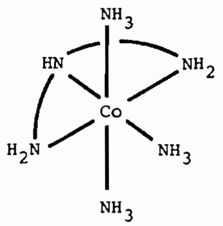
VI

mer-trans-



VII

fac-



VIII

mer-

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	
mer-$CoCl_2(dien)(NH_3)^+$	50.9_7	47.9_4
mer-$Co(dien)(NH_3)_3^{3+}$	50.4_5	47.7_3
unsym-fac-cis-$CoCl(dien)(NH_3)_2^{2+}$	55.6_0	45.0_0
	54.6_4	44.5_5
sym-fac-cis-$CoCl(dien)(NH_3)_2^{2+}$	55.4_5	44.2_6
sym-fac-cis-$CoBr(dien)(NH_3)_2^{2+}$	54.8_0	45.1_3
mer-cis-$CoCl(dien)(NH_3)_2^{2+}$	50.9_2	48.2_4
sym-fac-cis- plus *unsym-fac-cis*-$CoCl(dien(NH_3)_2^{2+}$ (40:60) mixture	55.6_0	45.0_1
	55.5_3	44.5_5
	54.6_4	44.3_4

[a] Shielding 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 $ZnCl_2$ (10 g) was stirred in. Crude orange *mer-cis*-$[CoCl(dien)(NH_3)_2]ZnCl_4$ (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*-$[CoCl_2(dien)(NH_3)]ClO_4$) 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 distinguished (Figure 1) and isomeric mixtures can be identified. In particular, the assignment of the diethylenetriamine configuration in the $Co(dien)(NH_3)_3^{3+}$ 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*-$CoCl(dien)(NH_3)_2$ 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*-$CoCl(dien)(NH_2CH_2R)_2^{2+}$ may be distinguishable, as the monodentate alkylamine ligands are not equivalent in the

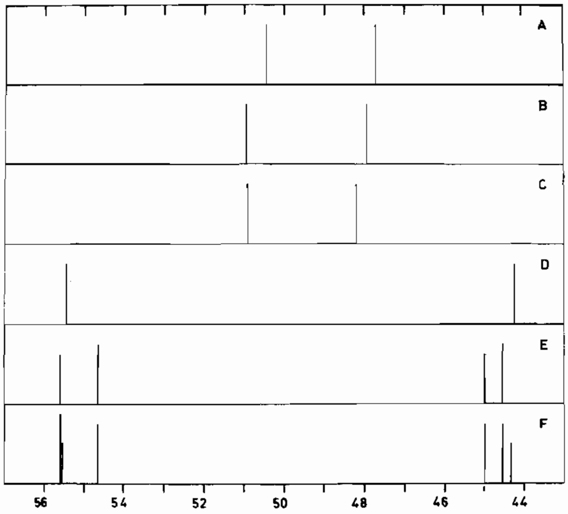


Figure 2. ^{13}C NMR spectra of some ammine complexes of diethylenetriaminecobalt(III) relative to dioxane at 67.4_3 ppm. A, *mer*-$Co(dien)(NH_3)_3^{3+}$; B, *mer*-$CoCl_2(dien)(NH_3)^+$; C, *mer-cis*-$CoCl(dien)(NH_3)_2^{2+}$; D, *sym-fac-cis*-$CoCl(dien)(NH_3)_2^{2+}$; E, *rac-unsym-fac-cis*-$CoCl(dien)(NH_3)_2^{2+}$; F, *sym-fac-cis*- plus *rac-unsym-fac-cis*-$CoCl(dien)(NH_3)_2^{2+}$ mixture.

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

Acknowledgements

We thank the New Zealand Universities Grants Committee for funds to purchase instruments used in this research.

References

1 D. A. House and J. W. Blunt, *Inorg. Nucl. Chem. Lett.*, *11*, 219 (1975).

2 Y. Kushi, K. Watanabe and H. Kunoya, *Bull. Chem. Soc. Japan*, *40*, 2985 (1967).

3 Foo Chuk Ha and D. A. House, *Inorg. Chim. Acta*, (1979) in press.

4 B. Bosnich and F. P. Dwyer, *Australian J. Chem.*, *19*, 2045 (1966).

5 A. D. Fowlie, D. A. House, W. T. Robinson and S. Sheat Rumball, *J. Chem. Soc. A*, 803 (1970).

6 M. C. Couldwell and D. A. House, *Inorg. Chem.*, *12*, 2949 (1974).

7 A. V. Ablov and E. V. Popa, *Russ. J. Inorg. Chem. (Eng. trans.)*, *16*, 1615 (1971); *17*, 388 (1972).

8 R. G. Holloway, D. A. House and B. R. Penfold, *Cryst. Struct. Comm.*, *7*, 139 (1978).

9 D. A. House and R. S. Visser, *J. Inorg. Nucl. Chem.*, *38*, 1157 (1976).

10 D. A. House, *Inorg. Nucl. Chem. Lett.*, *3*, 67 (1967).

11 H. H. Schmidtke and D. Garthoff, *Inorg. Chim. Acta*, *2*, 357 (1968).

12 A. R. Gainsford and D. A. House, *Inorg. Chim. Acta*, *3*, 367 (1969).

13 A. R. Gainsford and D. A. House, *Inorg. Chim. Acta*, *5*, 544 (1971).

14 Lim Say Dong, A. R. Gainsford and D. A. House, *Inorg. Chim. Acta*, *30*, 271 (1978).