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Anionopentaaminecobalt(III) Complexes with Polyamine Ligands. XIII. The Synthesis and Characterisation of Some Isomers of Chloro(diethylenetriamine)bis(monoamine)cobalt(III) Complexes

FOO CHUK HA, DONALD A. HOUSE and JOHN W. BLUNT

Department of Chemistry, University of Canterbury, Christchurch, New Zealand

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The reaction of mer-*$CoCl_3$(dien) with greater than 2.5 mol equivalents of several monoamines, A (A = methylamine, ethylamine, n-propylamine, n-butylamine, i-butylamine, n-pentylamine, n-hexylamine, benzylamine, cyclohexylamine, cyclohexylmethylamine, pyridine, 3,5-dimethylpyridine, 3-ethyl-4-methylpyridine, 4-benzylpyridine and 4-n-propylpyridine) in aqueous or aqueous methanol solution produces various amounts of* rac-unsym-fac-X-a,bcf,de-*CoCl(dien)$(A)_2^{2+}$,* mer-cis-a,bcd,ef-*CoCl(dien)$(A)_2^{2+}$ and* trans-af,bcd,e-*$ClCl_2$(dien)$(A)^+$. The chloropentaaminecobalt(III) complexes were isolated as $ZnCl_4^{2-}$ salts and the green* trans-*dichloro complexes as the perchlorates. The isomeric purity and composition was established on the basis of C-13 NMR and i.r. spectra and the* unsym-fac-cis- *geometry was confirmed by resolution of the complexes with A = n-pentylamine and pyridine.*

Introduction

Aninopentaaminecobalt(III) complexes [1, 2] are known for a variety of $CoCl(N_5)^{2+}$ systems, where N_5 varies from $CoCl(NH_3)_5^{2+}$ through $CoCl(en)_2(A)^{2+}$ and $CoCl(trien)(A)^{2+}$ [3–7] to $CoCl(tetren)^{2+}$ [8–13]. In this paper, we describe a series of CoCl(dien)$(A)_2^{2+}$ complexes where A is an aliphatic NH_2CH_2R amine, or a pyridine type ligand. These compounds provide a link between $CoCl(tetren)^{2+}$ and CoCl(trien)$(A)^{2+}$ and are also some of the few examples of Co(III) complexes with more than one coordinated monoamine other than ammonia.

Experimental

The commercially available amines were used without further purification: other chemicals were A.R. or the best reagent grade available. All complexes were washed with isopropanol and then ether and air dried unless otherwise stated. Analytical data are presented in Table I.

CAUTION: Although we have experienced no difficulties with the perchlorate salts of the complexes mentioned herein, these compounds should be treated as potentially explosive and handled with care.

mer-Trichloro(diethylenetriamine)cobalt(III): *mer*-$CoCl_3$(dien). Although the preparation of this complex has been described previously [14–16] the following is more suitable on a large scale. Diethylenetriamine (57 mL, 0.5 mol) was added to a solution of $Co(NO_3)_2 \cdot 6H_2O$ (146 g, 0.5 mol) in water (600 mL) containing glacial acetic acid (40 mL). A solution of $NaNO_2$ (200 g, 2.9 mol) in water (400 mL) was then added and a stream of air was passed through the mixture for about 6 ks with ice cooling over the last 2 ks. Orange crystals of $Co(NO_2)_3$(dien) (137 g, 0.42 mol, 84% yield) deposited during the course of the reaction. The trinitro (0.42 mol) was suspended in 12 *M* HCl (700 mL) and the temperature slowly raised (*care, effervescence and NO_2* fumes) to just below boiling. The colour of the suspension changed from orange to purple to red-brown to dark chocolate brown and heating at 350–360 K was maintained for about 3 ks.

The crude $CoCl_3$(dien) (containing some CoCl$(NO_2)_2$(dien)) was collected and recrystallised from twice its weight of water containing half its weight of NaOH. The red-violet solution was warmed at 313K for about 1 ks, filtered and poured into an equal volume of 12 *M* HCl. This solution was heated at 350–360 K for about 2 ks during which time pure chocolate brown, nitro-free (by i.r.) $CoCl_3$(dien) deposited. The product (100–110 g, 0.37–0.41 mol, 74–82% yield based on the starting material) was collected from the ice cooled solution.

Chloro(diethylenetriamine)bis(aliphatic amine)cobalt(III) Tetrachlorozincate(II) and Dichloro(diethylenetriamine)(aliphatic amine)cobalt(III) Perchlorate Salts

TABLE 1. Analytical Data.[a]

	Calc.						Found				
	FW	C	H	N	Co	Cl	C	H	N	Co	Cl
fac-[CoCl(dien)(MeNH$_2$)$_2$]ZnCl$_4$	466.8	15.42	4.96	15.00	12.6	37.97	15.95	5.95	14.76	12.7	37.90
mer-[CoCl(dien)(MeNH$_2$)$_2$]ZnCl$_4$	466.8	15.42	4.96	15.00	12.6	37.97	15.73	5.24	15.16	12.1	37.85
fac-[CoCl(dien)(EtNH$_2$)$_2$]ZnCl$_4$	494.8	19.40	5.46	14.15	11.9	35.82	19.73	5.82	14.12	11.9	36.29
mer-[CoCl(dien)(EtNH$_2$)$_2$]ZnCl$_4$·H$_2$O	512.8	18.72	5.70	13.65	11.5	34.57	19.02	5.79	13.46	11.5	34.80
fac-[CoCl(dien)(nPrNH$_2$)$_2$]ZnCl$_4$	522.8				11.3	33.90				11.1	33.31
fac-[CoCl(dien)nBuNH$_2$)$_2$]ZnCl$_4$	550.8				10.7	32.18				10.8	32.91
mer-[CoCl(dien)(nBuNH$_2$)$_2$]ZnCl$_4$·H$_2$O	568.8				10.4	31.12				10.4	31.31
fac-[CoCl(dien)(iBuNH$_2$)$_2$]ZnCl$_4$	550.8	26.14	6.40	12.54	10.7	32.18	26.38	6.54	12.57	10.7	32.23
fac-[CoCl(dien)(nPentNH$_2$)$_2$]ZnCl$_4$	578.8	29.02	6.79	12.09		30.62	29.45	7.09	12.09		30.40
(–)-*fac*-[CoCl(dien)(nPentNH$_2$)$_2$]ZnCl$_4$	578.8					30.62					30.72
fac-[CoCl(dien)(nHexNH$_2$)$_2$]ZnCl$_4$	606.8					29.21					29.23
fac-[CoCl(dien)(BzNH$_2$)$_2$]ZnCl$_4$	618.8				9.52	28.64				9.18	29.00
fac-[CoCl(dien)(cyclohexCH$_2$NH$_2$)$_2$]ZnCl$_4$	630.8				9.34					9.68	
fac-[CoCl(dien)(py)$_2$]ZnCl$_4$	562.8				10.4	31.49				10.5	31.18
fac-[CoCl(dien(4-nPrpy)$_2$]ZnCl$_4$·2H$_2$O	682.8				8.63	25.96				8.42	25.32
fac-[CoCl(dien)(4-Bzpy)$_2$]ZnCl$_4$·2H$_2$O	719.8					22.79					22.48
fac-[CoCl(dien)(3,5-Me$_2$py)$_2$]ZnCl$_4$	618.8				9.52	28.64				9.77	28.42
fac-[CoCl(dien)(3-Et,4-Mepy)$_2$]ZnCl$_4$	646.8				9.10	27.40				9.10	27.12
mer-[CoCl$_2$(dien)(MeNH$_2$)]ClO$_4$·H$_2$O	381.4				15.4	18.62				15.5	18.52
mer-[CoCl$_2$(dien)(EtNH$_2$)]ClO$_4$·H$_2$O	395.4				14.9	17.96				14.5	17.77
mer-[CoCl$_2$(dien)(nPrNH$_2$)]ClO$_4$	391.4				15.0	18.14				14.8	18.63
mer-[CoCl$_2$(dien)(nBuNH$_2$)]ClO$_4$	405.4				14.5	17.51				14.5	17.10
mer-[CoCl$_2$(dien)(cyclohexNH$_2$)]ClO$_4$·2H$_2$O	467.4				12.6	15.2				12.6	15.3
mer-[CoCl$_2$(dien)(cyclohexCH$_2$NH$_2$)]ClO$_4$·2H$_2$O	481.4				12.2	14.7				12.4	14.5

[a] *fac*- is the *unsym-fac-cis*- configuration. [b] Total non-perchlorate chloride.

mer-$CoCl_3$(dien) (7 g) was suspended in water (7 mL) containing 5 mol equivalents of the mono-amine. The mixture was refluxed for about 2 ks, cooled and filtered. The now red-violet solution was warmed to about 320 K and an equal volume of 12 *M* HCl containing $ZnCl_2$ (10 g) was added. The monochloro tetrachlorozincate(II) product(s) (2–4 g) deposited from the hot solution or on cooling and were collected after about 10 ks at room temperature. $HClO_4$ (10 mL, 70%) was added to the mother liquor and any green dichloro perchlorate (1–3 g) was collected after 0.1–0.3 Ms.

In the case of A = $EtNH_2$, the first crop of monochloro was the *mer-cis-* isomer (1.2 g). The *unsym-fac-cis-* form (1.2 g) was isolated from the mother liquor on evaporation under an air stream. No green dichloro perchlorate was isolated under these conditions, but this was the only product (2 g) when the initial $CoCl_3$(dien) to $EtNH_2$ ratio was reduced to 1:2.5 mol equivalents.

The 13-C NMR spectrum of the crude monochloro $ZnCl_4$ salts showed that isomeric mixtures were formed where A = $MeNH_2$, $nPrNH_2$, $nBuNH_2$ and $iBuNH_2$ (Table II). One half of the crude products (1–3 g) were recrystallised as the $ZnCl_4^{2-}$ salts by dissolving in the minimum volume (20–50 mL) of 330 K 0.1 *M* HCl and adding 12 *M* HCl (10–20 mL) containing $ZnCl_2$ (5–10 g). The *mer-cis-* isomer was obtained for A = $nBuNH_2$ and $iBuNH_2$, the *unsym-fac-cis-* for A = $nPrNH_2$ and a mixture for A = $MeNH_2$. The other half of the crude $ZnCl_4^{2-}$ salts (1–3 g) were recrystallised as dithionates by dissolving in the minimum volume (20–50 mL) of 0.1 *M* HCl and adding $Na_2S_2O_6$ (2–3 g). The products that deposited (1–2 g) were recrystallised as the $ZnCl_4^{2-}$ salts as above. The *unsym-fac-cis-* isomers were isolated for A = $MeNH_2$, $nBuNH_2$ and $iBuNH_2$. Addition of 12 *M* HCl containing $ZnCl_2$ to the mother liquor from the dithionate recrystallisation for A = $MeNH_2$ gave a product enriched in the *mer-cis* form and two further recrystallisations as the $ZnCl_4^{2-}$ salt yielded the pure (by 13-C NMR) *mer-cis-* isomer.

The green dichloro perchlorates were recrystallised by dissolving in the minimum volume (20–50 mL) of 330 K 0.1 *M* HCl and adding an equal volume of 12 *M* HCl followed by 10 mL of 70% $HClO_4$.

Chloro(diethylenetriamine)bis(pyridine type)cobalt(III) Tetrachlorozincate(II) Salts

The preparative procedure was similar to that described for the aliphatic amines except that the $CoCl_3$(dien): pyridine type ligand ratio was 1:2.5 mol equivalents and the solutions were heated to about 330 K until most of the trichloro complex had dissolved [19]. About 4–6 g of the *unsym-fac-cis-* isomers were isolated as the $ZnCl_4^{2-}$ salts and recrystallised as above.

Resolution of rac-unsym-fac-cis-*CoCl(dien)(py)*$_2^{2+}$

The resolution is difficult because of the similar solubilities of the arsenyl-(+)-tartrate salts in water.

A solution of *rac-unsym-fac-cis-*[CoCl(dien)(py)$_2$](ClO_4)$_2$ (prepared by metathesis from the $ZnCl_4^{2-}$ salt) (3.0 g) in 0.1 *M* (+)-tartaric acid (100 ml) was warmed to 313 K and 5.0 g of Na[(+)AsOT] [2, 17] was stirred in. A pink precipitate (4.5 g, slight negative CD at 470 nm) deposited over 0.2 Ms at room temperature.

This precipitate was dissolved in 0.1 *M* (+)-tartaric acid (100 ml) at 313 K and 2.0 g of Na[(+)-AsOT] was added. A more crystalline product (1.0 g, crop 1, strong negative CD at 470 nm) was collected after 11 ks at room temperature and a second crop (1.0 g) was collected after 65 ks. This latter material was a mixture of two crystal forms. The smaller crystals gave a strong negative CD at 470 nm while the CD of larger irregular shaped crystals was strongly positive at this wavelength. $\Delta\epsilon(470)$ for crop 1, small and large crystals of crop 2 are −1.83, −1.43 and +1.21 (M^{-1} cm^{-1}) respectively (see Table IV).

Resolution of rac-unsym-fac-cis-*CoCl(dien)(pent-NH*$_2$*)*$_2^{2+}$

A solution of the racemic $ZnCl_4^{2-}$ salt (2.0 g) in 0.1 *M* (+)-tartaric acid solution (50 mL) was heated to 313 K and solid Na[(+)AsOT] (2.0 g) was added. A precipitate of the less-soluble diasteroisomeride deposited almost immediately (negative CD at 470 nm) and was collected from the cooled solution. Addition of HCl (50 mL, 12 *M*) and $ZnCl_2$ (5 g) to the mother liquor precipitated the $ZnCl_4^{2-}$ salt of the other chiral form (positive CD at 470 nm, see Table IV). The $\{-\}_{470}$ (+)AsOT salt was dissolved in 20 ml of warm 6 *M* HCl and the $\{-\}_{470}$ $ZnCl_4^{2-}$ salt precipitated by the addition of $ZnCl_2$ (3 g).

Instrumentation

Spectra were recorded using the following instruments: i.r. (KBr discs), Shimadzu IR-27G; visible absorption (*ca.* 2 m*M* aqueous acidic solutions, using 5.00 cm silica cells), Varian Super Scan 3; ORD, CD (*ca.* 10 m*M* aqueous acidic solutions, 1.00 cm silica cells), JASCO ORD/UV/CD 5; C-13 NMR (H_2O or DMF solutions, 0.1–0.2 g/5 mL plus dioxane), Varian CFT 20; Atomic absorption, Varian Techtron AA5.

Analyses

C, H and N data were provided by Dr A. D. Campbell's microanalytical laboratory, University of Otago. Co was determined by atomic absorption using [CoCl(en)(dien)]$ZnCl_4$ as a standard for Co and Cl^- by potentiometric titration with standard Ag^+ solutions, the complexes being decomposed with NaOH and acidified prior to titration.

TABLE II. Products Isolated from the Reaction of $CoCl_3$(dien) with Monoamines.[a]

A	Isomeric Composition of the First Formed [CoCl(dien)$(A)_2$]$ZnCl_4$ salts	[$CoCl_2$(dien)(A)]ClO_4 Salt Isolated
NH_3	*mer-cis-*[b]	yes[c]
$MeNH_2$	mixt: 30% *mer-cis-*	yes
$EtNH_2$	*mer-cis-*[d]	yes
$nPrNH_2$	mixt: 16% *mer-cis-*	yes
$nBuNH_2$	mixt: 44% *mer-cis-*	yes
$iBuNH_2$	mixt: 56% *mer-cis-*	no
$nPentNH_2$	*unsym-fac-cis-*	no
$nHexNH_2$	*unsym-fac-cis-*	no
$BzNH_2$	*unsym-fac-cis-*	yes
$cyclohexNH_2$	none	yes
$cyclohexCH_2NH_2$	*unsym-fac-cis-*	yes
py	*unsym-fac-cis-*	yes
4-nPrpy	*unsym-fac-cis-*	no
4-Bzpy	*unsym-fac-cis-*	no
3,5-Me_2py	*unsym-fac-cis-*	yes
3-Et,4-Mepy	*unsym-fac-cis-*	no

[a] Reaction conditions: see *Experimental*. [b] Reference [22]. [c] Reference [23]. [d] Pure *unsym-fac-cis-* was isolated from the mother liquor as a second crop.

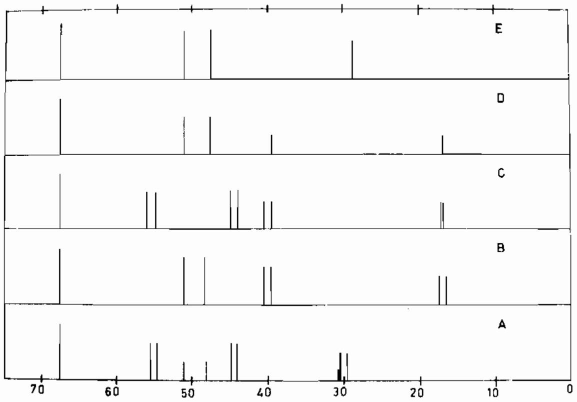

Fig. 1. 13-C NMR spectra of some [CoCl(dien)$(A)_2$]$ZnCl_4$ (in water) and [$CoCl_2$(dien)(A)]ClO_4 (in DMF) salts relative to dioxane at 67.43 ppm. A, *mer-cis-* plus *unsym-fac-cis-*CoCl(dien)$(MeNH_2)_2^{2+}$ mixture; B, *mer-cis-*CoCl(dien)$(EtNH_2)_2^{2+}$; C, *unsym-fac-cis-*CoCl(dien)$(EtNH_2)_2^{2+}$; D, *trans-mer-*$CoCl_2$(dien)$(EtNH_2)^+$; E, *trans-mer-*$CoCl_2$(dien)$(MeNH_2)^+$. Arbitrary intensity units, and DMF resonances are omitted.

Results

The products isolated from the reaction of *mer-*$CoCl_3$(dien) with 15 monoamines are summarised in Table II. Of the monoamines used, only cyclohexylamine failed to form a bis(monoamine) complex, and no green *trans*-dichloro complexes were isolated for A = $iBuNH_2$, $nPentylNH_2$, $nHexylNH_2$, 4-Bzpy, 4-nPrpy or 3-Et,4-Mepy. Isomeric mixtures of *unsym-fac-cis-* and *mer-cis-*bis(monoamine) complexes were obtained for A = $MeNH_2$, $EtNH_2$, $nPrNH_2$, $nBuNH_2$ and $iBuNH_2$ but only the *unsym-fac-cis-* isomer was detected with the others.

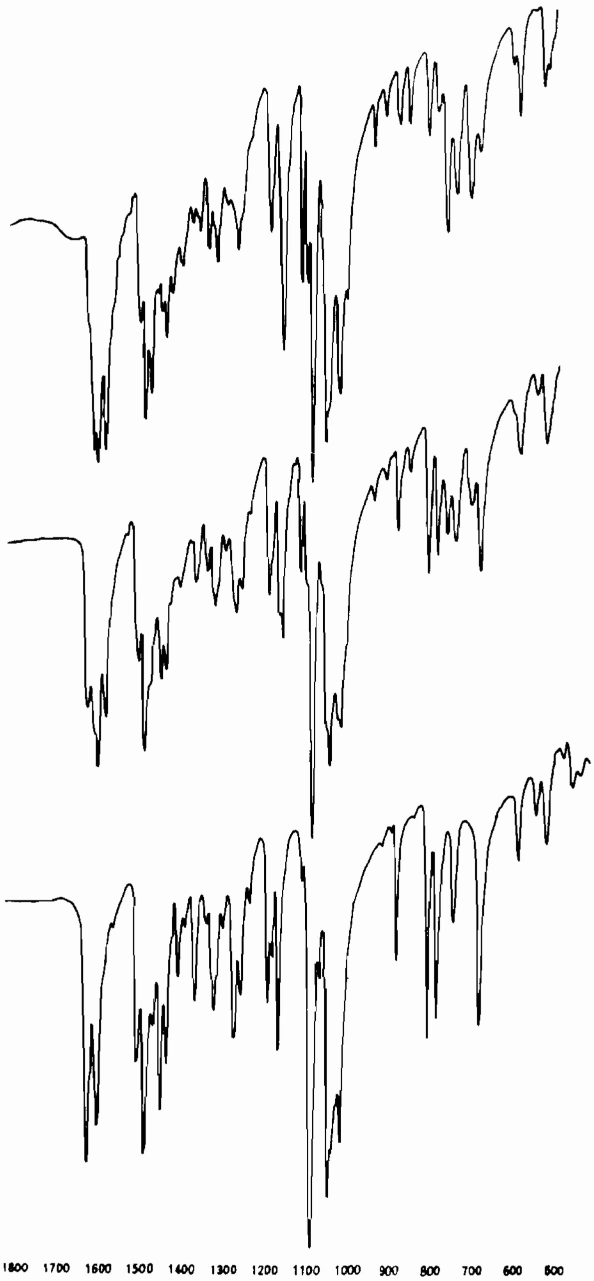

Fig. 2. I.r. spectra (KBr disc) of *mer-cis-* (top) *mer-cis-* plus *unsym-fac-cis-* mixture (center) and *unsym-fac-cis-* [CoCl(dien)$(MeNH_2)_2$]$ZnCl_4$ (bottom).

TABLE III. 13-C NMR Data for $[CoCl(dien)(A)_2]ZnCl_4$[a] and $[CoCl_2(dien)(A)]ClO_4$[b] Salts.

A	Carbon Atom	*unsym-fac-cis* + *mer-cis*[c]	*unsym-fac-cis-*	*mer-cis-*	*trans-mer-*
$MeNH_2$	dien	*fac* 55.81, 54.52	55.92, 54.62		51.11
		mer 51.08, 48.00 (30%)[d]			47.52
		fac 44.61, 43.94	44.73, 44.06		
	C(1)[e]	30.70, 30.45, 29.40	30.57, 29.51		29.12
$EtNH_2$	dien		55.95, 54.71	51.01	51.02
			44.85, 44.11	48.18	47.62
	C(2)		40.31, 39.43	40.42, 39.43	39.48
	C(1)		17.29, 17.15	17.43, 16.59	16.98
$nPrNH_2$	dien	*fac* 55.86, 54.61	55.90, 54.60		
		mer 51.05, 48.20 (16%)			
		fac 44.82, 44.02	44.79, 44.01		
	C(3)	47.10, 46.21	47.08, 46.24		
	C(2)	25.48, 25.35	25.44, 25.33		
	C(1)	11.43	11.40		
$nBuNH_2$	dien	*fac* 55.95, 54.52	55.89, 54.60		51.08
		mer 50.97, 48.15 (44%)		51.09, 48.47	47.57
		fac 44.78, 43.96	44.81, 44.03		
	C(4)	45.07, 44.20	45.11, 44.18	45.17, 44.25	44.34
	C(3)	34.15, 34.02	34.20, 34.09	34.20, 33.83	34.09
	C(2)	20.25	20.30	20.30	20.17
	C(1)	13.89	13.95	13.90	13.63
$iBuNH_2$	dien	*fac* 55.91, 54.54	55.94, 54.55		
		mer 51.08, 48.20 (56%)			
		fac 44.85, 43.88	44.88, 43.90		
	C(3)	30.53, 30.25	30.57, 30.45		
	C(2)	52.92, 52.72, 51.93, 51.66	52.75, 51.94		
	C(1)	20.24	20.22		
$nPentNH_2$	dien		55.86, 54.55		
			44.02, 44.39		
	C(5)		45.33, 44.77		
	C(4)		31.73, 31.59		
	C(3)		29.04		
	C(2)		22.52		
	C(1)		14.11		
$nHexNH_2$	dien		55.84, 54.53		
			44.01, 43.38		
	C(6)		43.30, 44.78		
	C(5)		31.96, 31.83		
	C(4)		31.50		
	C(3)		26.48		
	C(2)		22.68		
	C(1)		14.17		
$BzNH_2$	dien		56.10, 55.46		51.19
			44.76, 43.80		47.60
	CH_2		48.45, 47.87		48.54
	C_6H_5		139.28, 139.13		140.00
			129.51, 129.39		129.25
			129.27		128.74
			128.46		128.21

(continued overleaf)

TABLE III. *(continued)*

A	Carbon Atom	*unsym-fac-cis + mer-cis*[c]	*unsym-fac-cis-*	*mer-cis-*	*trans-mer-*
cyclohexNH$_2$	dien				50.91
					47.59
	CH				53.25
	CH$_2$				34.75
					25.65
					24.98
cyclohexCH$_2$NH$_2$[b]	dien		55.72, 54.69		51.18
			44.60, 43.47		47.51
	CH or CH$_2$		50.90, 50.28		50.78
	CH$_2$		39.71		39.70
			30.98		30.14
			26.69		26.70
			26.07		25.94
py	dien		55.29, 54.28		51.76
			43.61, 42.64		47.51
	aromatic C$_2$		156.29, 155.62		156.38
	C$_4$		141.54, 141.37		139.88
	C$_3$		127.39, 126.97		125.34
4-nPrpy[b]	dien		55.09, 54.00		
			43.35, 42.51		
	C(3)		36.75		
	C(2)		23.43		
	C(1)		13.64		
	aromatic C$_4$		157.62, 157.35		
	C$_2$		155.51, 154.82		
	C$_3$		127.23, 126.79		
4-Bzpy[b,f,g]	dien		55, 54		
			43, 42		
	CH$_2$		40.96		
	aromatic		155 ± 2 (9 bands)		
			139 (2 bands)		
			129 ± 0.5 (5 bands)		
			127 (2 bands)		
3,5-Me$_2$py[b]	dien		55.33, 54.04		51.65
			43.32, 42.84		47.45
	CH$_3$		18.15		17.82
	aromatic C$_2$		153.53, 152.76		153.68
	C$_4$		142.31, 141.98		140.66
	C$_3$		136.73, 136.15		134.54
3Et, 4Mepy[b]	dien		54.93, 53.92		
			43.36, 42.21		
	CH$_3$		18,23, 146.1, 13.85		
	CH$_2$		23.81		
	aromatic		154.60, 153.96,		
			153.15, 152.54,		
			151.50, 151.19		
			141.80, 141.10		
			128.09, 127.66		

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[a] 150–200 mg in H$_2$O with dioxane as an internal standard. [b] 150–200 mg in DMF with dioxane as an internal standard. [c] Isomeric mixture of first formed ZnCl$_4^{2-}$ salt. [d] Percentage of *mer-cis-* isomer as calculated from the 13-C intensities. [e] Carbon atom numbering is remote from the NH$_2$-group. e.g. NH$_2$–C(6)–C(5)–C(4)–C(3)–C(2)–C(1). [f] Aromatic C-atom numbering is according to conventional organic nomenclature. [g] Background to noise very high.

TABLE IV. Chiroptical Parameters for some *unsym-fac-cis*-CoCl(dien)$(A_2)^{2+}$ Ions.[a]

A	Spectra	Wavelength (rotation)[b]							
nPentNH$_2$[c]	CD	560 (+0.243)	518 (0)	470 (−0.258)	400sh (−0.042)	380 (0)	352 (+0.171)	315 (0)	
nPentNH$_2$[c]	ORD	600 (+384)	570 (0)	520 (−720)	477 (0)	440 (+504)	416 (+396)	380 (+696)	350 (0)
nPentNH$_2$[d]	CD	560 (−0.162)	518 (0)	470 (+0.209)	400sh (+0.051)	380 (0)	352 (−0.127)	315 (0)	
py[e]	CD	548 (+1.92)	505 (0)	470 (−1.82)	400sh (−0.142)	360 (−0.095)			
py[f]	CD	548 (−1.30)	505 (0)	470 (+1.22)	400sh (+0.103)	360 (+0.086)			

[a] In 0.1 *M* HCl at room temperature. [b] Units of rotation for CD are $\Delta\epsilon$ in M^{-1} cm^{-1} and for ORD are [M] in deg M^{-1} m^{-1}. [c] As $ZnCl_4^{2-}$ salt from the less-soluble (+)-AsOT$^-$ salt. [d] As $ZnCl_4^{2-}$ salt from mother liquors after removal of the less soluble (+)-AsOT$^-$ salt. [e] As the less soluble (+)-AsOT$^-$ salt. [f] Large crystals (hand sorted) of the more soluble (+)-AsOT$^-$ salt.

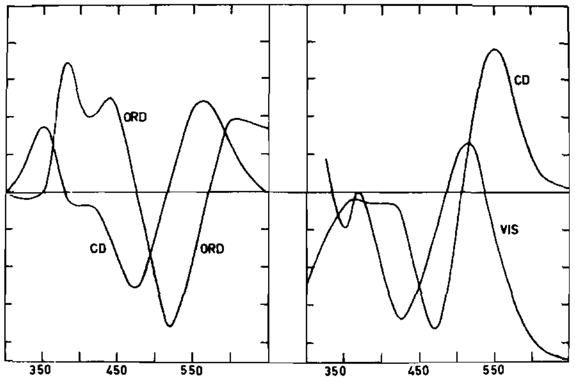


Fig. 3. ORD, CD and visible absorption spectra for Δ-*unsym-fac-cis*-CoCl(dien)$(A)_2^{2+}$ in 0.1 *M* HCl. Abcissia in nm. Each ordinate corresponds to $\Delta\epsilon = \pm 0.1$ M^{-1} cm^{-1} or [M] = ±200 deg M^{-1} m^{-1} for Δ-CoCl(dien)$(pentNH_2)_2^{2+}$ (left hand diagram) and $\Delta\epsilon = \pm 0.5$ M^{-1} cm^{-1} for Δ-CoCl(dien)$(py)_2^{2+}$ (right hand diagram). Zero for the extinction coefficient in the visible absorption spectrum of CoCl(dien)$(py)_2^{2+}$ is at the bottom of the diagram with the ordinate markings corresponding to ϵ = 10, 30, 50 *etc.* M^{-1} cm^{-1}.

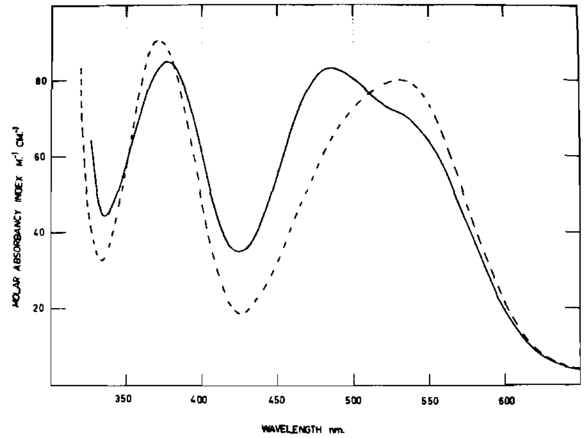


Fig. 4. Visible absorption spectra of *mer-cis*- (———) and *unsym-fac-cis*-CoCl(dien)$(EtNH_2)_2^{2+}$ (- - - -) in 0.1 *M* HCl.

The monochloro complexes were isolated as $ZnCl_4^{2-}$ salts and the dichloro's as perchlorates. The general order of solubility of the monochloro $ZnCl_4^{2-}$ salts was *mer-cis*- < *unsym-fac-cis*- but where fractional crystallisation failed to give an efficient separation, the dithionate salts were used, as these showed the reverse solubility order.

The C-13 NMR spectra of the *mer-cis*- and *unsym-fac-cis* [CoCl(dien)$(A)_2$]$ZnCl_4$ salts are clearly distinguishable (Table III, Figure 1) and the relative amounts of the two isomers obtained in the initial product (Table II) was estimated from the intensities of the resonances due to the individual species. During the latter stages of isomer separation, C-13 NMR spectra were used as an index of purity. I.r. spectra (Figure 2) were also used to monitor isomeric purity and the results obtained were in agreement with the C-13 NMR data.

The successful resolution (Figure 3, Table IV) of CoCl(dien)$(A)_2^{2+}$ using the method of racemic modification [18] with Na[(+)AsOT] (A = py, nPentylNH$_2$) establishes the geometry as *unsym-fac-cis*- and this configuration is consistent with the C-13, i.r. and visible absorption spectral data (Figure 4, Table V). In particular, only this configuration (Figure 5) would be expected to show all four diethylenetriamine carbon atoms as individual resonances (Table III).

Preliminary investigations of the aquation kinetics of *unsym-fac-cis*-CoCl(dien)$(MeNH_2)_2^{2+}$ (1.0 *M* $HClO_4$, T = 343 K) using visible absorption spectral scans, show that the chloride release is quite rapidly followed by a subsequent reaction and the final spectrum does not corresond to *unsym-fac-cis*-Co(dien)$(MeNH_2)_2(OH_2)^{3+}$ (generated from the chloro by Hg^{2+} assisted aquation).

TABLE V. Visible Absorption Spectral Parameters.[a,b]

Configuration[d]	A	$CoCl(dien)(A)_2^{2+}$ [c]			
		λ_{max}	λ_{min}	λ_{max}	λ_{min}
fac-cis-	$MeNH_2$[e]	529 (78.2)	425 (18.3)	370 (86.9)	322 (34.4)
mer-cis-	$MeNH_2$	493[f] (76.6)	424 (30.4)	374 (84.4)	335 (41.8)
fac-cis-	$EtNH_2$	529 (79.4)	425 (18.3)	371 (89.0)	333 (32.6)
mer-cis-	$EtNH_2$	485[f] (82.6)	424 (34.6)	377 (83.8)	337 (44.3)
fac-cis-	$nPrNH_2$	528 (83.4)	426 (20.9)	371 (95.3)	334 (39.7)
fac-cis-	$nBuNH_2$	527 (82.0)	425 (20.9)	369 (97.7)	334 (55.6)
mer-cis-	$nBuNH_2$	484[f] (91.1)	425 (41.0)	349 (109)	
fac-cis-	$iBuNH_2$	527 (84.9)	427 (19.1)	371 (96.5)	333 (41.4)
fac-cis-	$nPentNH_2$	527 (83.7)	426 (20.6)	371 (98.0)	333 (43.7)
fac-cis-	$nHexNH_2$	528 (83.1)	427 (21.0)	372 (97.9)	334 (43.7)
fac-cis-	$BzNH_2$	530 (86.0)	430 (21.9)	372 (112)	357 (105)
fac-cis-	$cyclohexCH_2NH_2$	525 (86.2)	428 (25.5)	374 (105)	338 (50.5)
fac-cis-	py	522 (116)	425 (22.7)	373 (89.7)	350 (71.2)
fac-cis-	4-nPrpy	520 (121)	426 (22.9)	373 (97.3)	352 (78.9)
fac-cis-	4-Bzpy	518 (124)	425 (26.2)	371 (103)	352 (89.7)
fac-cis-	$3,5-Me_2py$	522 (119)	426 (23.7)	370sh (112)	
fac-cis-	3-Et,4-Mepy	521 (121)	426 (25.9)	370 (105)	360 (103)

		$CoCl_2(dien)(A)^+$ [g]					
		λ_{max}	λ_{min}	λ_{max}	λ_{min}	λ_{max}	λ_{min}
mer-trans-	$MeNH_2$	623 (36.9)	555 (17.8)	465 (87.7)		430sh (82.0)	403 (71.8)
mer-trans-	$EtNH_2$	622 (37.4)	557 (18.7)	461 (93.9)	450 (93.0)	430 (86.9)	405 (77.3)
mer-trans-	$nPrNH_2$	625 (43.1)	550 (13.9)	461 (93.7)	446 (93.2)	435 (93.5)	374 (54.2)
mer-trans-	$nBuNH_2$	622 (38.1)	553 (18.5)	461 (84.7)	450 (84.1)	430 (85.5)	373 (53.8)
mer-trans-	$BzNH_2$[h]	625 (43.9)	552 (20.2)	465sh (97.4)		430 (101)	378 (51.0)
mer-trans-	$cyclohexNH_2$[h,i]	628 (43.6)	557 (19.1)	466 (108)	455 (108)	433 (111)	397 (87.3)
mer-trans-	$cyclohexCH_2NH_2$[h,i]	621 (39.5)	565 (28.9)	467 (102)	446 (98.9)	430 (97.8)	407 (92.2)
mer-trans	py[h]	622 (41.7)	550 (15.2)	462 (92.0)	450 (91.4)	430 (93.1)	378 (50.0)

(continued on facing page)

TABLE V. *(continued)*

		$CoCl_2(dien)(A)^{+g}$					
		λ_{max}	λ_{min}	λ_{max}	λ_{min}	λ_{max}	λ_{min}
mer-trans	3,5-Me$_2$py^h	622 (41.5)	552 (15.8)	465 (96.0)	448 (95.2)	435 (95.4)	395 (70.7)

[a] Mean of three determinations. [b] Numbers in parenthesis at the extinction coefficients (ϵ) in M^{-1} cm^{-1}. [c] As $ZnCl_4^{2-}$ salts in 0.1 *M* HCl. [d] *fac-cis-* is the *unsym-fac-cis-* configuration. [e] In 1.0 *M* $HClO_4$. [f] These spectra show a pronounced shoulder at about 540 nm (see Figure 4). [g] As ClO_4^- salts in 3 *M* HCl. [h] Data from reference 19. [i] Differences in ϵ from those cited in reference 19 probably due to partial hydrolysis of the dichloro complexes, in the earlier work.

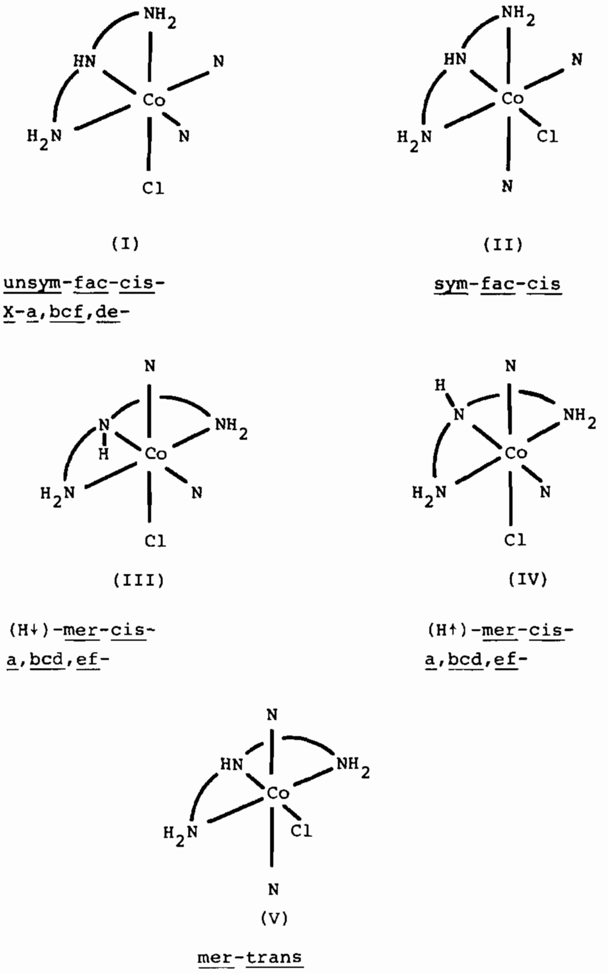


Fig. 5. Potential geometric isomers of CoCl(dien)(N)$_2^{2+}$.

The green dichloro salts [19–20] are assigned the *trans*-$CoCl_2$(dien)(A)$^+$ configuration on the basis of their visible absorption (Table V) and 13-C NMR spectra (Table III).

Discussion

There are potentially five isomers for the CoCl(dien)(A)$_2^{2+}$ system (Figure 5) with only the *unsym-fac-cis-* form (I) being possibly chiral. The *mer-trans-* (V) and *sym-fac-cis-* (II) isomers have the coordinated aniono ligand *trans* to the secNH group of the diethylenetriamine and are unlikely to be formed under the conditions of synthesis used here, as the ligand *trans* to the secNH is thought to be the most labile [1, 21].

The isolation of several *trans*-dichloro-$CoCl_2$(dien)A$^+$ complexes from the reaction products suggests the pathway shown in Figure 6 which would exclude the *mer-trans- and sym-fac-cis* (monoamine) isomers. Indeed, one *mer-cis-* and the *unsym-fac-cis-* (I) isomers are observed in several cases, but we have no evidence for isomers with configurations II and V being formed.

We have shown previously [22] that with A = NH_3, the *mer-cis*-isomer has the H(↑)–(IV) configuration and we will assume this assignment for all the *mer-cis-* isomers described here.

The analogous $CoCl_2$(dien)(NH_3)$^+$ can also be prepared using this route or, with more control, via *trans*-Co(NO_2)$_2$Cl(dien) [19, 24].

Circular dichroism spectra (Figure 3) of (–)$_{500}$-*unsym-fac-cis*-CoCl(dien)(A)$_2^{2+}$ (A = nPentNH$_2$, py) (isolated as the less-soluble (+)AsOT$^-$ salts) are very

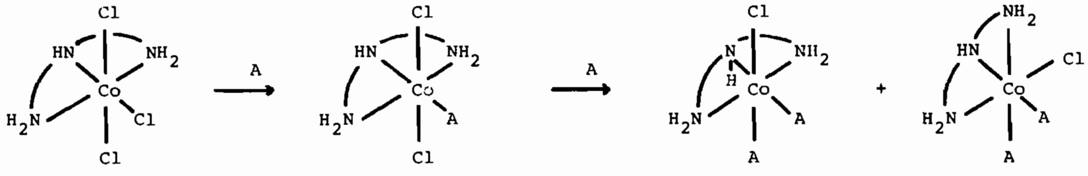
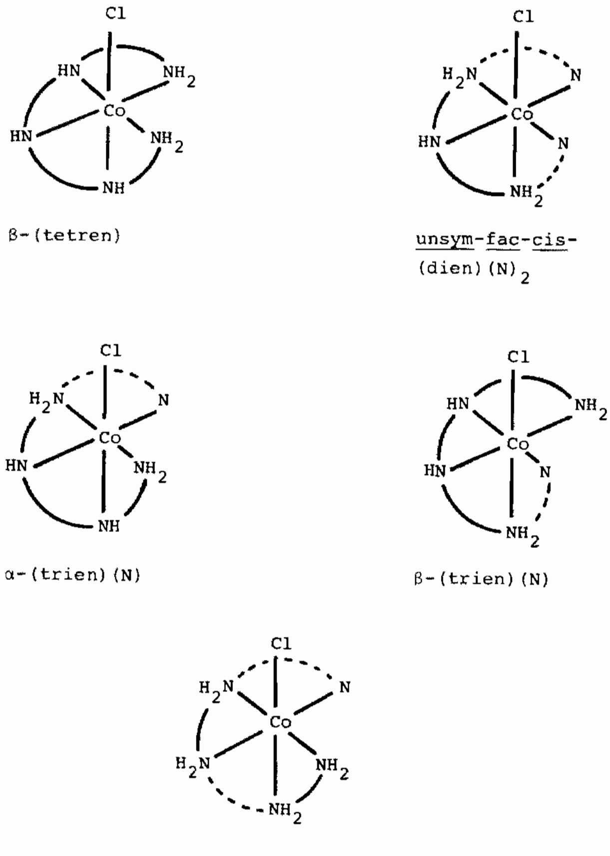


Fig. 6. Possible reaction path for the formation of *trans-mer*$CoCl_2$(dien)(A)$^+$, (H↓)-*mer-cis*-CoCl(dien)(A)$_2^{2+}$ and *unsym-fac-cis*-CoCl(dien)(A)$_2^{2+}$.



β-(tetren)

unsym-fac-cis-(dien)(N)$_2$

α-(trien)(N)

β-(trien)(N)

cis-(en)$_2$(N)

Figure 7. Relationships between some $CoCl(N_5)^{2+}$ complexes in the Δ-configuration.

similar to that of Δ-(−)$_{500}$-αβ(S)-$CoCl(tetren)^{2+}$ [25, 26] and are assigned to the Δ configuration (structure II in Figure 7) on this basis. Figure 7 shows the relationships for the Δ-configuration of $CoCl(tetren)^{2+}$, $CoCl(dien)(A)_2^{2+}$, $CoCl(trien)(A)^{2+}$ and $CoCl(en)_2(A)^{2+}$. CD spectra have now been reported for $CoCl(tetren)^{2+}$ [11], $CoCl(dien)(A)_2^{2+}$ and $CoCl(en)_2(A)^{2+}$ [17] and the Δ configuration is characterised by a negative Cotton effect at about 470 nm. The sign of the Cotton effect at 550 nm, for this configuration, is apparently related to the nature of the coordinated monoamine and while positive for $CoCl(tetren)^{2+}$, $CoCl(dien)(NH_2CH_2R)_2^{2+}$, $CoCl(dien)(py)_2^{2+}$ and $CoCl(en)_2(py)^{2+}$, it is negative for $CoCl(en)_2(NH_2CH_2R)^{2+}$ [17]. Resolution of other *unsym-fac-cis-* complexes described here is currently under investigation.

Although C-13 NMR spectra have been used primarily for the configurational assignment of the diethylenetriamine ligand, other observations can be made. In both the *mer-cis-* and *unsym-fac-cis-* configurations, the monoamines are in non-equivalent positions. This non-equivalence is reflected in two resonances being seen for the α and β carbon atoms in the aliphatic chain, beyond these, the C-atoms become equivalent. For the bis(pyridine type) ligands, six ring C-atom resonances are observed but side-chain C-atoms are not always distinguished.

In the *mer-cis-* isomer, one monoamine is in a unique position, being *trans* to a chloro ligand (all others are *trans* to NH or NH_2 groups). This is the probable cause of the three resonances observed for the CH_3NH_2 carbons in the isomeric mixture of $CoCl(dien)(MeNH_2)_2^{2+}$ (Figure 1) but would not be a remarkable effect if such an isomeric mixture had not been formed.

The C-13 NMR spectra have now been recorded for some of these monoamines coordinated to several different polyaminecobalt(III) centers *e.g.* *cis*-$CoCl(en)_2(BzNH_2)^{2+}$ [27] *cis*-$CoCl(tmd)_2(BzNH_2)^{2+}$ [28] *cis*-$Co(NH_3)(en)_2(BzNH_2)^{3+}$ [27] *trans-mer*-$CoCl_2(dien)(BzNH_2)^{+}$ and *unsym-fac-cis*-$CoCl(dien)(BzNH_2)_2^{2+}$. Despite differences in solvent, the benzylamine CH_2 carbon resonances in these examples differ by less than 1 ppm. However, shifts of up to 2 ppm are observed for the linear alkyl amines when the coordination sphere is changed from *cis*-$CoCl(tmd)_2(NH_2CH_2R)^{2+}$ [28] to *unsym-fac-cis*-$CoCl(dien)(NH_2CH_2R)_2^{2+}$, with the differences becoming smaller as the Co–C distance is progressively increased.

Infrared spectra have previously been used to distinguish between *mer-* and *fac*-$MCl_3(dien)$ [14, 29, 30] with these forms having 4 and 3 bands, respectively in the 800–950 cm^{-1} region. In the present series of complexes, additional $-CH_2-$ bands are observed in this region (especially about 870 cm^{-1}), nevertheless, a band at 920 cm^{-1} seems characteristic of the meridional diethylenetriamine geometry (Figure 2), especially for the n-alkylamine complexes.

The visible absorption spectra are characteristic of $CoCl(N)_5^{2+}$ systems with the *unsym-fac-cis-* isomers having two maxima at about 530 and 370 nm. For the alkylamine complexes, the intensity of the 530 nm band is less than that of the 370 nm band and is often characterised by some asymmetry on the low wavelength side (Figure 4). The order of band intensities is reversed for complexes containing pyridine-type ligands (Figure 3).

In the *mer-cis-* complexes the high wavelength band is shifted to about 490 nm with a pronounced shoulder on the high wavelength side (Figure 4). This type of absorption spectra has been found for other *mer-cis*-$CoCl(dien)(A)_2^{2+}$ complexes *e.g.* for A = en [31], pn [32], tmd [33], and Metmd [34] and gives rise to an orange or orange-pink colour for the solid.

Acknowledgements

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2 Abbreviations used: $MeNH_2 = CH_3NH_2$, $EtNH_2 = CH_3CH_2NH_2$, $nPrNH_2 = CH_3(CH_2)_2NH_2$, $nBuNH_2 = CH_3(CH_2)_3NH_2$, $iBuNH_2 = (CH_3)_2CHCH_2NH_2$, $nPentNH_2 = CH_3(CH_2)_4NH_2$, $nHexNH_2 = CH_3(CH_2)_5NH_2$, $BzNH_2$ = benzylamine, $cyclohexNH_2$ = cyclohexylamine, $cyclohexCH_2NH_2$ = cyclohexylmethylamine, py = pyridine, 4-nPrpy = 4-npropylpyridine, 4-Bzpy = 4-benzylpyridine, 3,5-Me_2py = 3,5-dimethyl pyridine, 3-Et, 4-Mepy = 3-ethyl-4-methylpyridine, en = $NH_2(CH_2)_2NH_2$, tmd = $NH_2(CH_2)_3NH_2$, pn = $NH_2CH(CH_3)CH_2NH_2$, Metmd = $CH_3NH(CH_2)_3NH_2$, dien = $NH_2(CH_2)_2NH(CH_2)_2NH_2$, trien = $NH_2(CH_2)_2NH(CH_2)_2NH(CH_2)NH_2$, tetren = $NH_2(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2$, Na[(+)AsOT] = sodium arsenyl-(+)-tartrate, DMF = dimethylformamide.

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