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Anionopentaaminecobalt(III) Complexes with Polyamine Ligands. 15. Some Properties of CoCl(323-tet)(amine)$^{2+}$ Complexes

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Some trans-*(RR,SS)-[CoCl(323-tet)(amine)]* $ZnCl_4$ *salts (amine =* NH_3, $MeNH_2$ *and imidazole) have been prepared and characterised by C-13 NMR spectroscopy. The ammine complex has been resolved into the (SS) and (RR) (not isolated) forms using arsenyl tartrate. Mercury(II)-assisted aquation rates for these complexes have been measured spectrophotometrically and values of* 10^4 k_{Hg} *(298 K) (*μ *= 1.0 M) are 5.75, 98.4 and 37* M^{-1} s^{-1}, *in the above order. Base hydrolysis rates have been measured using a pH-stat for amine =* NH_3, $MeNH_2$ *and values of* 10^{-4} k_{OH} *(298 K) (*μ *= 0.1 M) are 3.48 and 76.4* M^{-1} s^{-1} *respectively. These rate data are interpreted in terms of previously established structure–reactivity patterns.*

Introduction

A general method for the synthesis of *cis*-$CoCl(N_4)(amine)^{2+}$ complexes is to react *trans*-$CoCl_2(N_4)^+$ with the amine in a suitable solvent [1–5]. However, the specific factors which can be used to predict if a particular monoamine will coordinate are not fully understood [3, 4, 6]. Thus, α-substituted aliphatic monoamines and 2-substituted pyridines do not usually react with *trans*-$CoCl_2(en)_2^+$ to give the desired product.

The stereochemical change that accompanies the reaction is also of interest, and *trans*-$CoCl(N_4)(amine)^{2+}$ systems are rather uncommon. For example, *trans*-$CoCl_2(en)_2^+$ [5], *trans*-$CoCl_2(tn)_2^+$ [7], and *trans-mer*-$CoCl_3(dien)$ [8] all react to give *cis*-products. In fact, the *trans*-$Co(NO_2)(NH_3)_4(py)^{2+}$ [9] and *trans*-$CoCl(en)_2(NH_3)^{2+}$ [10] systems both require specific synthetic procedures.

The propensity for the tetramine ligand, 323-tet [14], to form *trans*-$CoXY(N_4)^{n+}$ systems [11, 12] led us to investigate the reaction of *trans*-(RR,SS)-$CoCl_2(323\text{-tet})^+$ with monoamines in the hope that further *trans*-$CoCl(N_4)(amine)^{2+}$ complexes could be isolated. To this end, we have been partially successful, and *trans*-chloro amine complexes with amine = ammonia, methylamine and imidazole have been prepared and characterised.

Experimental

The 1,2-bis(3-aminopropylamino)ethane, 323-tet, was obtained from Fluka and used as supplied. *Trans*-(RR,SS)-$[CoCl_2(323\text{-tet})]Cl\cdot H_2O$ and the perchlorate salt were prepared by the method of Bosnich *et al.* [12]. Found λ (nm), (ε) (M^{-1} cm^{-1}) (MeOH solution of the perchlorate salt); max 635 (34.5), max 470 (35), max 395 (53). Literature [12, 13] (estimated from Figure); max 630 (35), max 470 (35), max 395 (52).

Trans-*(RR,SS)-[CoCl(323-tet)(NH$_3$)]* $ZnCl_4$

Trans-(RR,SS)-$[CoCl_2(323\text{-tet})](ClO_4)$ (5 g) was heated at 80–90 °C for 10–15 min with water (15 ml) and concentrated aqueous ammonia (20 ml, ρ = 0.880) to form an orange red solution. Concentrated HCl (25 ml, 12 *M*) and zinc chloride (10 g) were then added and the solution was again heated to 80–90 °C. Red-violet crystals (5 g) deposited from the hot solution, which was filtered while still warm. The pale yellow-brown mother liquor was discarded. The crude product (contaminated with a little of the starting material) was dissolved in *ca.* 100 ml of 80 °C 0.1 *M* HCl, filtered, and reheated with an equal volume of 12 *M* HCl containing 10 g of $ZnCl_2$. The red-violet crystals that deposited (4 g) were collected from the cooled solution, washed with 2-propanol and then ether and air dried. Calcd. for $[CoCl(323\text{-tet})(NH_3)]ZnCl_4$ (F.W. = 492.90): C, 19.49; H, 5.11; N, 14.21. Found: C, 19.71; H, 4.82; N, 14.39. λ (nm), (ε) (M^{-1} cm^{-1}) in 0.1 *M* HCl: max 548 (48.6), min 510 (43.6), max 480 (46.8), min 425 (21.8), max 370 (71.1), min 340 (42.6).

Trans-*(SS)-CoCl(323-tet)(NH$_3$)*$^{2+}$

The (RR,SS)-$ZnCl_4^{2-}$ salt (2 g) was dissolved in 40 ml of warm water containing 1 g of (+)-tartaric acid and sodium arsenyl (+)-tartrate (2 g) was added.

Violet-pink needles (*ca.* 1 g, contaminated with some zinc tartrate) deposited from the warm solution. This product was not characterised further, but was used to determine the chiroptical parameters of the optically active cation. CD λ (nm), ($\Delta\epsilon$) (M^{-1} cm^{-1}) in 0.1 *M* HCl: max 570 (+0.20), sh 500 (+0.12), min 432 (+0.018), sh 390 (+0.17), max 360 (+0.21). ORD λ (nm), [*M*] (deg M^{-1} m^{-1}) in 0.1 *M* HCl: max 610 (+460), 589 (+381), 550(0), min 535 (−29), max 512 (−10), min 472 (−127), 445(0), max 405 (+274), 370(0).

The *trans*-configuration of the racemic cation was established by C-13 NMR and the (SS)-configuration of the less soluble diastereoisomeride by conversion to *trans*-(SS)-$CoCl_2$(323-tet)$^+$. A small amount of the less soluble arsenyl tartrate salt was refluxed for 1.5 hr in 3 *M* HCl. A green solution was slowly formed and the CD of this was similar to that of the *trans*-(SS)-$CoCl_3$(323-tet)$^+$ form [13]. The *trans*-(SS)-$CoCl_2$(323-tet)$^+$ so produced was precipitated as the perchlorate salt, and the CD of this complex in 3 *M* HCl was of similar intensity to that of an equivalent solution of optically pure *trans*-(SS)-$ClCl_2$(323-tet)$^+$ in methanol [12, 13].

Trans-*(RR,SS)-[CoCl(323-tet)(MeNH$_2$)]ZnCl$_4$*

Trans-[$CoCl_2$(323-tet)]Cl·H_2O (5 g) was slurried in 30 ml of dimethylacetamide and methylamine (5 ml, 40% aqueous solution) was added. A rapid green to red colour change took place and orange-red crystals (3.5 g) deposited within 2 min, leaving a pale orange mother liquor. The filtered product was dissolved in 50 ml of warm 0.1 *M* HCl and HCl (50 ml, 12 *M*) and $ZnCl_2$ (10 g) were added. Red-violet crystals (3.5 g) deposited from the hot solution. The crude product was recrystallised as for the ammine analogue. (Yield = 3.0 g). Calcd. for [CoCl(323-tet)-($MeNH_2$)]$ZnCl_4$ (F.W. = 506.93): C, 21.32; H, 5.37; N, 13.82%. Found: C, 21.32; H, 5.15; N, 14.10%. λ (nm), (ϵ) (M^{-1} cm^{-1}) in 0.1 *M* HCl: max 552 (50.4), min 515 (43.7), max 485 (46.9), min 430 (22.2), max 372 (70.7), min 344 (45.2).

Trans-*(RR,SS)-[CoCl(323-tet)(imid)]ZnCl$_4$*

This complex was prepared in a similar manner to the corresponding ammine, but with a rather lower yield. Calcd. for [CoCl(323-tet)(imidazole)]$ZnCl_4$ (F.W. = 543.95): C, 24.29; H, 4.82; N, 15.45%. Found: C, 24.72; H, 4.83; N, 15.24%. λ (nm), (ϵ) (M^{-1} cm^{-1}) in 0.1 *M* HCl: max 550 (41.3), min 528 (40.5), max 480 (51.7), min 430 (27.5), sh 365 (93).

Trans-*Co(323-tet)(amine)(OH$_2$)$^{3+}$ Ions*

The spectral parameters for the aqua ions were obtained by dissolving weighed amounts of the *trans*-(RR,SS)-[CoCl(323-tet)(amine)]$ZnCl_4$ salts (or the less soluble arsenyl tartrate salt, amine = NH_3) in a solution that was 0.8 *M* in $HClO_4$ and 65.6 m*M* in $Hg(NO_3)_2$. Visible absorption or CD spectra were recorded after 48 hr at room temperature. *Trans*-(RR,SS)-Co(323-tet)(NH_3)(OH_2)$^{3+}$: λ (nm), (ϵ) (M^{-1} cm^{-1}); sh 530(45), max 475(61.4), min 412(23.0), max 352(73.4). *trans*-(SS)-Co(323-tet)(NH_3)(OH_2)$^{3+}$ CD: λ (nm), ($\Delta\epsilon$) (M^{-1} cm^{-1}); min 575 (−0.02), 557(0), max 492 (+0.27), min 418 (+0.018), max 350 (+0.17). ORD: λ (nm), (*M*) (deg M^{-1} m^{-1}); max 532 (+528), 589 (+239), 490(0), min 460 (−352), 410(0), max 390 (+76), 372(0). *trans*-(RR,SS)-Co(323-tet)($MeNH_2$)(OH_2)$^{3+}$: λ (nm), (ϵ) (M^{-1} cm^{-1}); sh 540 (42.9), max 480 (61.3), min 417 (23.5), max 352 (76.7), min 327 (50.8).

Isosbestic points for the chloro to aqua conversion are predicted (and found) to be as follows. A = NH_3: 530 (532), 417 (419), 365 (366) nm. A = $MeNH_2$: 533 (533), 420 (420), 367 (368), 333 (335) nm.

Reactions with Other Monoamines

Attempts to prepare other CoCl(323-tet)(amine)$^{2+}$ complexes via methods similar to those above were unsuccessful with $EtNH_2$ (slight trace of violet product, after acidification, using DMA method), nPrNH_2, nBuNH_2, nHexNH_2 and pyridine. One reaction did produce *cis*-β-(RR,SS)-CoCl(323-tet)-(py)$^{2+}$ but we have been unable to repeat the synthesis. *cis*-β-(RR,SS)[Co(CO_3)(323-tet)]ClO_4 was slurried with $HClO_4$ at room temperature until effervescence ceased and pyridine was added dropwise. On cooling the slightly warmed solution, a red-pink precipitate deposited, which formed red-violet *cis*-β-(RR,SS)-[CoCl(323-tet)(py)]$ZnCl_4$ on heating with HCl containing $ZnCl_2$. A perchlorate salt was obtained by metathesis. Five attempts to repeat this preparation gave only violet *trans*-(RR,SS)-[Co(OH)(323-tet)(OH_2)](ClO_4)$_2$.
Calcd. for [CoCl(323-tet)(py)]$ZnCl_4$ (F.W. = 554.97): C, 28.14; H, 4.90; N, 12.6%. Found: C, 27.83; H, 4.88; N, 12.74%. Calcd. for [CoCl(323-tet)(py)](ClO_4)$_2$ (F.W. = 546.81): C, 28.56; H, 4.98; N, 12.81%. Found: C, 28.50; H, 4.84; N, 12.76%.

Kinetic Studies and Instrumentation

Procedures used to determine the rates of Hg^{2+}-assisted aquation (μ = 1.0 *M*) of *trans*-(RR,SS)CoCl(323-tet)(A)$^{2+}$ were similar to those previously described [15]. Base hydrolysis rates were determined using a Metrohm pH-stat [16].

Results and Discussion

Reaction of ammonia, methylamine or imidazole with *trans*-(RR,SS)-$CoCl_2$(323-tet)$^+$, in aqueous (NH_3, imid) or DMA ($MeNH_2$) solution, followed by treatment with HCl/$ZnCl_2$, forms salts analysing as

TABLE I. Kinetic Data for the Base Hydrolysis of Some *trans*-CoCl(323-tet)X^{n+} Complexes at 298.2 K (μ = 0.1 *M*).

X	pH (10^8 [OH^-], *M*)	10^3 k_{obs} s^{-1}	k_{OH} M^{-1} s^{-1}
Cl[a]	6.00 (1.30)	1.32 ± 0.02	1.01×10^5
		1.30 ± 0.04	1.00
		1.37 ± 0.02	1.05
			Mean (1.02 ± 0.03) × 10^5
NH_3[b]	6.70 (6.54)	2.15 ± 0.04	3.28×10^4
		2.17 ± 0.07	3.32
	6.60 (5.19)	2.05 ± 0.04	3.94
	6.50 (4.13)	1.55 ± 0.03	3.75
		1.49 ± 0.02	3.61
			Mean (3.58 ± 0.3) × 10^4
$MeNH_2$[b]	5.48 (0.395)	2.98 ± 0.06	7.54×10^5
	5.35 (0.292)	2.22 ± 0.06	7.60
		2.27 ± 0.02	7.77
			Mean (7.64 ± 0.1) × 10^5

[a] μ = 0.1 *M* (NaCl), loss of first chloride. [b] μ = 0.1 *M* ($NaClO_4$).

TABLE II. C-13 NMR Data for Some 323-tet Co(III) Complexes.[a]

Complex	Solvent	Shielding Value[b]			
trans-(RR,SS)-[$CoCl_2$(323-tet)]Cl·H_2O	H_2O	53.31	49.46	39.87	27.76
trans-(RR,SS)-[CoCl(323-tet)(NH_3)]$ZnCl_4$	H_2O	53.21	49.28	39.56	27.19
		53.15	48.93	39.44	27.10
		53.73	48.89		
trans-(RR,SS)-[CoCl(323-tet)($MeNH_2$)]$ZnCl_4$	H_2O	53.25	49.37	39.75	27.73
		52.95	48.85	39.35	27.41
					27.01
		CH_3NH_2	48.40		
trans-(RR,SS)-[CoCl(323-tet)($MeNH_2$)]$(ClO_4)_2$	DMF	53.14	49.48	39.45	27.31
		53.04		39.26	26.94
		52.89			
		52.81			
		CH_3NH_2	48.36		
trans-(RR,SS)-Co(323-tet)($MeNH_2$)$(OH_2)^{3+}$	HNO_3/Hg^{2+}	53.71	50.29	39.99	27.13
		53.54	49.70	39.39	27.05
		CH_3NH_2	48.54		
trans-(RR,SS)-[CoCl(323-tet)(imid)]$ZnCl_4$	H_2O	53.82	50.35	39.85	27.35
		52.69	49.66	39.73	27.20
		imid	140.19	128.52	122.15
cis-β-(RR,SS)-[Co(323-tet)CO_3]ClO_4	H_2O	54.55	50.71	48.77	46.83
		40.42	40.01	27.08	22.24
cis-β-(RR,SS)-[CoCl(323-tet)(py)]$ZnCl_4$	H_2O	57.88	52.13	50.28	48.49
		39.48	39.23	26.59	22.54
		py	154.57	142.04	128.32

[a] See refs. 8, 17 for the technique used. [b] P.p.m. relative to dioxane at 67.39 p.p.m.

[CoCl(323-tet)(amine)]$ZnCl_4$. The reaction appears to proceed via an aqua intermediate, as the chloro complexes are not isolated directly, but only after anation with chloride ion. This contrasts with the bis(ethylenediamine) systems and may reflect the much greater rate of base hydrolysis observed for the *trans*-dichloro(323-tet) complex (Table I).

A *trans*-configuration has been assigned to the isolated chloropentaamines on the basis of C-13 NMR spectroscopy (Table II). From model com-

TABLE III. Spectrophotometrically Determined Rate Constants for the Hg^{2+}-assisted Chloride Release from *trans*-(RR,SS)-CoCl(323-tet)(A)$^{2+}$ Complexes (μ = 1.0 *M*).

A	T, °C [K]	$[H^+]$, *M*	$[Hg^{2+}]_i$[a] m*M*	$10^4 k_{obs}$[b] s^{-1}	$10^2 k_{Hg}$ (obs), M^{-1} s^{-1}	$10^2 k_{Hg}$ (mean), M^{-1} s^{-1}	$10^2 k_{Hg}$ (calc), M^{-1} s^{-1}
NH_3	60.1 [333.3]	0.80	65.6[h]	22.1 ± 0.5	3.36 ± 0.08	3.33 ± 0.1	3.29[c]
		0.76	86.8[h]	29.1 ± 1.1	3.42 ± 0.13		
		0.76	86.8[h]	28.0 ± 1.1	3.23 ± 0.13		
	55.0 [328.2]	0.76	86.8[h]	15.8 ± 0.7	1.82 ± 0.08	1.86 ± 0.05	1.93[c]
		0.76	86.8[g]	16.5 ± 1.2	1.90 ± 0.14		
	49.7 [322.9]	0.76	86.8[g]	9.57 ± 0.34	1.10 ± 0.04	1.10 ± 0.02	1.08[c]
		0.76	86.8[h]	9.46 ± 0.15	1.09 ± 0.02		
		0.76	86.8[h]	9.57 ± 0.2	1.10 ± 0.02		
	48.2 [321.4]	0.77	82.3[h]	7.89 ± 0.4	0.958 ± 0.05	0.958 ± 0.05	0.922[c]
	47.4 [320.6]	0.77	82.3[h]	6.76 ± 0.3	0.821 ± 0.04	0.821 ± 0.04	0.843[c]
	25.0 [298.2]	0.76	86.8[d]	~0.4		~0.05	0.0575[c]
$MeNH_2$	36.35[309.6]	0.80	65.6[e]	19.4 ± 0.9	2.96 ± 0.14	2.95 ± 0.02	2.89[i]
		0.80	65.6[f]	19.2 ± 0.2	2.93 ± 0.03		
	32.3 [305.5]	0.80	65.6[g]	13.1 ± 0.5	2.00 ± 0.07	2.01 ± 0.02	1.99[i]
		0.80	65.6[f]	13.3 ± 0.2	2.02 ± 0.03		
	30.25[303.5]	0.80	65.6[e]	10.2 ± 0.4	1.55 ± 0.06	1.58 ± 0.06	1.63[i]
		0.80	65.6[f]	10.0 ± 0.3	1.53 ± 0.05		
		0.80	65.6[g]	10.6 ± 0.2	1.61 ± 0.03		
		0.76	86.8[f]	14.2 ± 0.3	1.63 ± 0.03		
	27.05[300.3]	0.76	86.8[h]	10.6 ± 0.1	1.22 ± 0.01	1.22 ± 0.01	1.19[i]
		0.76	86.8[h]	10.5 ± 0.2	1.21 ± 0.02		
	25.4 [298.6]	0.76	86.8[h]	9.13 ± 0.08	1.05 ± 0.01	1.04 ± 0.01	1.02[i]
		0.76	86.8[h]	9.06 ± 0.1	1.04 ± 0.01		
	25.0 [298.2]						0.984[i]
imid	25.0 [298.2]	0.76	86.8[e]	3.40 ± 0.1	0.391 ± 0.01	0.37 ± 0.03	
		0.76	86.8[h]	3.00 ± 0.1	0.346 ± 0.01		

[a]Initial Hg^{2+} in $HClO_4$. [b]$k_{Hg} = k_{obs}[Hg^{2+}]i^{-1}$. [c]Calculated using the activation parameters E_a = 95.3 ± 2 kJ mol^{-1}, log PZ = 13.454, $\Delta S^{\#}_{298}$ = +4 ± 4 J K^{-1} mol^{-1}. [d]Estimated from the change in CD with time for $(+)_{589}$-(SS)-CoCl(323-tet)$(NH_3)^{2+}$ at room temperature, see Fig.1. [e]Spectral scan. Data analysed at 480 nm. [f]Fixed wavelength at 480 nm. [g]Spectral scan. Data analysed at 570 nm. [h]Fixed wavelength at 570 nm. [i]Calculated using the activation parameters E_a = 73.0 ± 2 kJ mol^{-1}, log PZ = 10.780, $\Delta S^{\#}_{298}$ = −47 ± 4 J K^{-1} mol^{-1}.

pounds, the *trans*-323-tet configuration shows four resonances, while in the *cis*-β-323-tet configuration, all eight polyamine C-atom resonances are distinguished. Despite some splitting of the C-atom resonances in the spectrum of the CoCl(323-tet)(amine)$^{2+}$ complexes (possibly due to non-equivalent axial ligands), the four-band pattern is maintained. In addition, the methyl carbon in CoCl(323-tet)$(MeNH_2)^{2+}$ is more deshielded (48.4 p.p.m.) than in complexes where the methylamine is *trans* to an NH or NH_2 group (~29 p.p.m.) [8]. In contrast, the CoCl(323-tet)$(py)^{2+}$ complex shows an eight-band polyamine C-atom resonance pattern characteristic of the *cis*-β configuration.

Resolution of the *trans*-(RR,SS)-CoCl(323-tet)-$(NH_3)^{2+}$ cation has been achieved using sodium arsenyl tartrate and the less soluble (+)-diastereoisomeride can be converted into *trans*-(SS)-$CoCl_2$-(323-tet)$^+$ by refluxing HCl. Although chemical interconversion methods are not always reliable, we believe that inversion would be unlikely under the acidic reaction conditions, and that the *trans*-$(+)_{589}$-CoCl(323-tet)$(NH_3)^{2+}$ isomer can confidently be assigned to the (SS)-form.

Preliminary investigations showed that the thermal aquation of coordinated chloride in acid solution was slow and, like some *trans*-CoCl(macrocycle)-$(NH_3)^{2+}$ complexes, complicated by loss of monoamine [18]. However, the Hg^{2+}-assisted aquation reactions proceeded smoothly with good isobestic or isorotatory (Fig. 1) points. The *trans*-configuration of the resulting aqua ion (amine = $MeNH_2$) was established from the C-13 NMR spectrum of a concentrated aquated solution (Table II). The rates of Hg^{2+}-assisted aquation are amongst the slowest recorded for $CoCl(N_5)^{2+}$ systems (Tables III, IV) and *trans*-CoCl(323-tet)$(NH_3)^{2+}$ reacts with Hg^{2+} about 200 times more slowly than *cis*-CoCl-

TABLE IV. Second-Order Rate Constants (k_{Hg}, M^{-1} s^{-1}) for the Mercury(II)-assisted Aquation of Some $CoClN_5^{2+}$ Complexes at 298.2 K and μ = 1.0 *M*.

N_5	A = NH_3	A = $MeNH_2$
cis-$(en)_2$(A)	1.45×10^{-2} [a]	3×10^{-2} [b]
cis-$(tn)_2$(A)	1.22×10^{-1} [c]	1.7[c]
sym-fac-cis-(dien)$(A)_2$	2.88×20^{-2} [d]	–
unsym-fac-cis-(dien)$(A)_2$	7.76×10^{-2} [d]	8.98×10^{-2} [d]
trans-$(en)_2$ (A)	4.64×10^{-2} [a]	–
trans-(RR,SS)-(323-tet)(A)	5.75×10^{-4} [e]	9.84×10^{-3} [e]

[a]C. Bifano and R. G. Link, *Inorg. Chem.*, 7, 908 (1968). [b]S. C. Chan and S. F. Chan, *J. Chem. Soc.*, 202 (1969), rate constants at μ = 0.2 *M* multiplied by 2. [c]Ref. 7. [d]Ref. 15. [e]This work.

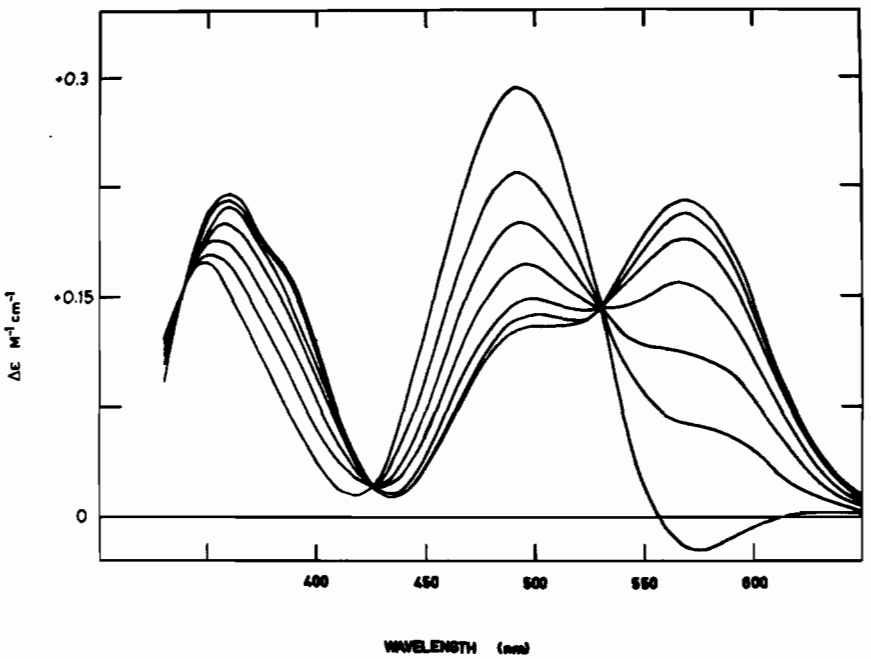

Fig. 1. Changes in the CD spectrum with time for {+}-*trans*-(SS)CoCl(323-tet)$(NH_3)^{2+}$ in 0.76 *M* $HClO_4$, 86.8 m*M* $Hg(NO_3)_2$ (μ = 1.0 *M*), at room temperature. Spectra recorded at arbitrary time intervals over 48 hours, $\Delta\epsilon$ decreases with time at 570 nm.

$(tn)_2(NH_3)^{2+}$ and 25 times more slowly than *cis*-$CoCl(en)_2(NH_3)^{2+}$. The corresponding $MeNH_2$ complex reacts about 10 times more rapidly than the ammine and thus the effect of the non-replaced ligand on the order of reactivity of the coordinated chloride is $NH_3 < MeNH_2$, as observed for many other systems [15].

However, in terms of our previous theories [15, 19], we believe that the relative inertness of these *trans*-CoCl(323-tet)$(A)^{2+}$ complexes is not related to the ground state geometry, but to the hypothesis that the *trans*-323-tet configuration does not readily distort towards a suitable 5-coordinate trigonal bipyramid transition state.

On the other hand, base hydrolysis of the coordinated chloride is extremely rapid (k_{OH} = 3.6 × 10^4 M^{-1} s^{-1} at 298.2 K, μ = 0.1 *M* for A = NH_3) when compared to *cis*-$CoCl(en)_2(NH_3)^{2+}$ (k_{OH} = 8.1 M^{-1} s^{-1} under the same conditions) and the A = $MeNH_2$ analogue hydrolyses about 20 times faster than the ammine complex (k_{OH} = 7.6 × 10^5 M^{-1} s^{-1}). This situation, is however, not unusual, and many anionocobalt(III) polyamine complexes containing a secondary amine NH proton in a meridional configuration exhibit base hydrolysis rates some 10^3–10^4 times greater than systems without this structural arrangement [19, 20].

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14 Abbreviations used: en = 1,2-diaminoethane, tn = 1,3-diaminopropane, dien = bis-(2-aminoethyl)-amine, py = pyridine, 323-tet = 1,2-bis-(3-aminopropylamino)-ethane, $MeNH_2$ = methylamine, imid = imidazole, DMA = dimethyl acetamide, sodium arsenyl(+)-tartrate = sodium (+)-tartrate(−2)arsenic(III) oxide.
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