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Anionopentaaminecobalt(III) Complexes with Polyamine Ligands. XX. The Synthesis and Reaction Kinetics of Some Isomeric $CoCl(AA)(dien)^{2+}$ (AA = phen, bipy) Complexes

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Two isomeric forms (red and orange) for each of $CoCl(AA)(dien)^{2+}$ (AA = phen, bipy) have been synthesised. From the C-13 nmr spectra the red and orange forms have been assigned to the unsym-fac-cis- *and* mer-*geometric arrangements, respectively. Spectrophotometrically determined kinetic parameters [k_{Hg} (M^{-1} s^{-1}), E_a (kJ mol^{-1}), $\Delta S^{\#}$ (J K^{-1} mol^{-1})] for the Hg^{2+}-assisted chloride release from these complexes in HNO_3 media ($\mu = 1.0$ M) at 298.2 K are* unsym-fac-cis *(phen): 1.65×10^{-2}, 66, −66;* unsym-fac-cis-*(bipy): 1.62×10^{-2}, 73, −44;* mer-*(phen): 1.74×10^{-4}, 93, −15; mer-(bipy): 6.87×10^{-4}, 99, +16. Base hydrolysis kinetics for the* unsym-fac-cis-*complexes were determined using a pH-stat and at 298.2 K ($\mu = 0.1$ M NaCl) activation parameters k_{OH} (M^{-1} s^{-1}), E_a, $\Delta S^{\#}$ are (phen): 1920, 92, +120; (bipy): 1740, 90, +111. These data are compared with those obtained for analogous $CoCl(AA)(dien)^{2+}$ complexes.*

Introduction

For some time, we have been interested in the structure–reactivity patterns of isomeric $CoCl(N_5)^{2+}$ systems where (N_5) is a bidentate–tridentate or bis(monodentate)–tridentate polyamine ligand combination [1–18]. In previous work we have used both symmetrical (dien, dpt) and unsymmetrical (2,3-tri) [17] tridentate ligands with a variety of aliphatic bis(mono) [13–16] and diamine ligands.

The introduction of a pyridine-type ligand into the Co(III) coordination sphere, *e.g.* *cis*-$CoCl(py)(en)_2^{2+}$ or *unsym-fac-cis*-$CoCl(py)_2(dien)^{2+}$ results in some

TABLE I. Analytical Data.

		Calculated				Found			
		C%	H%	Co%	Halide%	C%	H%	Co%	Halide%
$[CoCl(bipy)(dien)]ZnCl_4$	red	29.98	3.77	10.51	31.60	29.80	3.85	10.41	31.44
$[CoCl(bipy)(dien)]ZnCl_4 \cdot H_2O$	orange	29.05	4.00	10.18	30.62	29.06	4.12	10.10	30.68
$[CoCl(bipy)(dien)](ClO_4)_2$	red	30.43	3.83	10.66	19.25	30.62	3.91	10.61	19.33
$[CoBr(bipy)(dien)]ZnBr_4$ [a]		21.47	2.70	7.52	51.01	21.73	2.89	7.42	50.67
$[CoNO_2(bipy)(dien)]ZnCl_4$ [a]		29.42	3.70	10.31	24.82	29.21	3.91	10.21	24.61
$[CoCl(phen)(dien)]ZnCl_4 \cdot 0.5H_2O$	red	32.36	3.73	9.92	29.84	32.26	3.84	9.85	29.77
$[CoCl(phen)(dien)]ZnCl_4$	orange	32.85	3.62	10.07	30.30	32.73	3.69	10.03	30.44
$[CoCl(phen)(dien)](ClO_4)_2$	red	33.33	3.67	10.22	18.44	33.41	3.72	10.25	18.67
$[CoCl(phen)(dien)](ClO_4)_2 \cdot H_2O$	orange	32.32	3.90	9.91	17.89	32.15	4.02	9.98	18.04
$[CoBr(phen)(dien)]ZnBr_4 \cdot H_2O$ [a]		23.29	2.81	7.14	48.42	23.44	2.95	7.24	48.19
$[CoNO_2(phen)(dien)]ZnCl_4$ [a]		32.27	3.55	9.90	23.81	31.92	3.48	9.80	24.07

[a] Derived from the red chloro complex.

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unusual physical properties when compared to the aliphatic analogues in that base hydrolysis rates are greater [19, 20], chiroptical parameters are considerably different [21, 22] and the pattern of stereochemical change observed during base hydrolysis is altered [23].

In this investigation, we have prepared some $CoCl(AA)(ABA)^{2+}$ complexes using 1,10-phenanthroline and 2,2′-bipyridyl as bidentate ligands and diethylenetriamine as the constant tridentate. Thus we can compare the properties of these complexes which contain ligands with extensive π-conjugation with those of previous $CoCl(AA)(dien)^{2+}$ systems, where this feature is absent.*

Experimental

The commercially available amines (J. T. Baker, Fluka, AG) were used without further purification. All other chemicals were of the best reagent grade quality available. *mer*-$Co(NO_2)_3(dien)$ [24] and *mer*-$CoCl_3(dien)$ [25] were prepared using previous methods [15]. Unless otherwise stated, the products isolated in this work were washed with ethanol and then acetone and air dried. Analytical data are listed in Table I. Aqua ions were generated from the $[CoCl(AA)(dien)]ZnCl_4$ isomers by dissolving the solids in 0.76 *M* $HClO_4$ containing 93.4 m*M* $Hg(NO_3)_2$. The visible absorption spectral parameters (Table II) were recorded after 24 hours at room temperature. I.r. spectra of the pure (by C-13 n.m.r., Table III) isomers ($ZnCl_4^{2-}$ salts, KBr disc) are shown in Fig. 1.

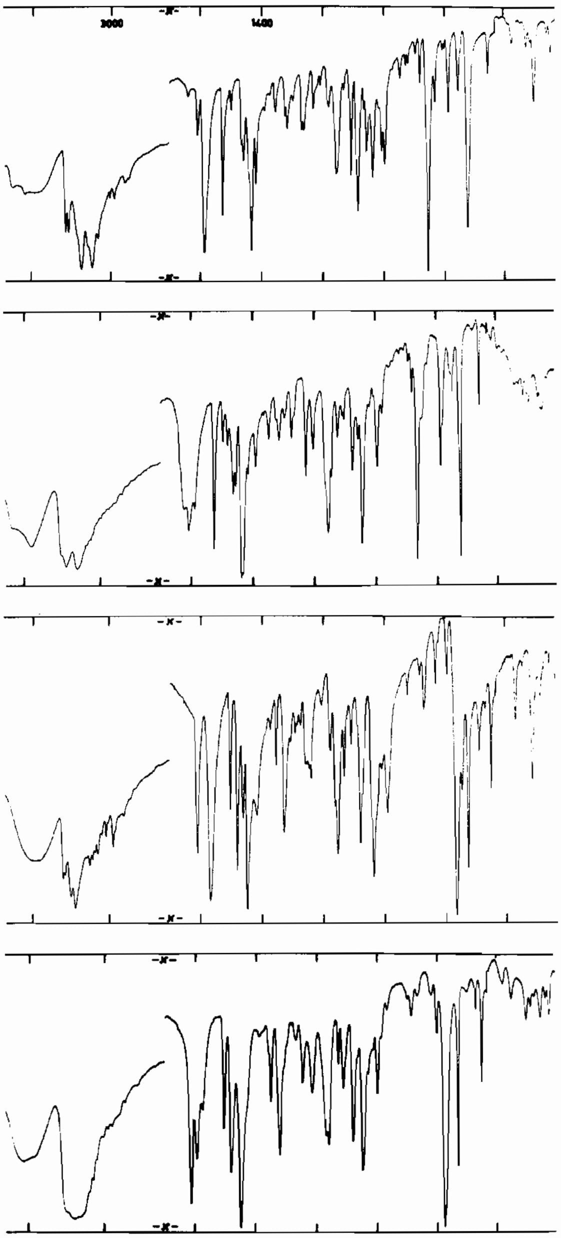

Fig. 1. I.r. spectra ($ZnCl_4^{2-}$ salts, KBr disc) in the 4000–400 cm^{-1} range, of orange-(H↓)-*mer*-$CoCl(phen)(dien)^{2+}$, red-*unsym-fac-cis*-$CoCl(phen)(dien)^{2+}$, orange-(H↓)-*mer*-$CoCl(bipy)(dien)^{2+}$ and red-*unsym-fac-cis*-$CoCl(bipy)(dien)^{2+}$ in descending order.

CAUTION. Although we have experienced no difficulties with the perchlorate salts listed in Table I, these complexes should be treated as potentially explosive and handled accordingly.

Red and Orange Isomers of Chloro(diamine)(dien)-cobalt(III) Tetrachlorozincate(II) Salts

[CoCl(bipy)(dien)]ZnCl₄. Method A

Bipy (5 g) was added to a suspension of *mer*-$CoCl_3(dien)$ 8.5 g, NO_2^- free by i.r.) in ethanol (240 mL) and water (60 mL). The mixture was refluxed for 2 hr, during which time most of the trichloride dissolved. The hot, filtered solution (orange-red) was poured into 75 mL of 12 *M* HCl containing $ZnCl_2$ (25 g) and the (mainly) red isomer crystallised from the cooled solution. Successive crops of the more soluble orange isomer were obtained from the mother liquor after 24 hr at room temperature and on subsequent slow evaporation.

Each crop was recrystallised from 0.1 *M* HCl by the addition of 12 *M* HCl containing $ZnCl_2$. The combined yield of both isomers was 14.2 g. I.r. spectra were used to monitor the isomeric purity of the recrystallised material.

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*Abbreviations used: en = $NH_2(CH_2)_2NH_2$, tn = $NH_2(CH_2)_3NH_2$, dien = $NH_2(CH_2)_2NH(CH_2)_2NH_2$, dpt = $NH_2(CH_2)_3NH(CH_2)_3NH_2$, 2,3-tri = $NH_2(CH_2)_2NH(CH_2)_3NH_2$, phen = 1,10-phenanthroline, bipy = 2,2′-bipyridyl, py = pyridine, DMSO = dimethyl sulphoxide, d_6-DMSO-hexadeutero dimethyl sulphoxide.

TABLE II. Visible Absorption Spectral Parameters for Isomeric CoX(AA)(dien)$^{n+}$ Complexes.[a,b]

Isomer	X	AA	λ_{sh} (nm)	λ_{max} (nm)	λ_{min} (nm)
red *unsym-fac-cis*	Cl	phen		519 (96.3)	419 (28.6)
orange (H↓)-*mer*	Cl	phen	533 (51.2)	465 (81.9)	427 (68.1)
red *unsym-fac-cis*	Cl	bipy		519 (90.2)	416 (24.6)
orange (H↓)-*mer*	Cl	bipy	533 (54.3)	465 (87.8)	420 (60.9)
unsym-fac-cis	OH_2	phen		487 (89.1)	404 (18.9)
(H↓)-*mer*	OH_2	phen		461 (96)	410 (48.8)
unsym-fac-cis	OH_2	bipy		486 (84.4)	401 (15.2)
(H↓)-*mer*	OH_2	bipy		461 (101)	410 (51.1)

[a] For X = Cl, the solvent is 0.1 *M* HCl and for X = OH_2, the solvent is 0.76 *M* $HClO_4$ containing 9.34×10^{-2} $Hg(NO_3)_2$. All spectra were measured at room temperature in duplicate. Reproducibility in ϵ is of the order of 1%. [b] Values in parenthesis are the molar extinction coefficients (ϵ, M^{-1}, cm^{-1}).

[CoCl(phen)(dien)]ZnCl$_4$. Method A

An entirely analogous procedure using 6.9 g of *mer*-$CoCl_3$(dien) and 5 g of phen·H_2O gave a combined yield of 12.7 g for both isomers, with the red form again being the less soluble.

Red-[CoCl(bipy)(dien)]ZnCl$_4$. Method B

Bipy (2.5 g) was added to a suspension of *mer*-$CoCl_3$(dien) (4.2 g, 0.016 mol) in DMSO (25 mL) containing $AgClO_4$ (6.6 g, 0.032 mol). Some glass balls were added and the solution gently warmed (with swirling) for 0.5 hr at 60 °C. 6 *M* HCl (100 mL) was then added and the solution was filtered to remove traces of unreacted trichloride, and the filtrate poured into 12 *M* HCl (30 mL) containing $ZnCl_2$ (30 g). The red isomer that deposited immediately was collected and recrystallised as above to give 6.4 g of isomerically pure material.

Red-[CoCl(phen)(dien)]ZnCl$_4$. Method C

Phen·H_2O (5 g) was added to a suspension of *mer*-$Co(NO_2)_3$dien (10 g) in ethanol (12 mL) and water (38 mL). The mixture was refluxed for 2 hr and then filtered to remove 2.7 g of unreacted trinitro. The filtrate was added to 12 *M* HCl (100 mL) and boiled for 0.5 hr. On cooling, *cis*(?)-[$CoCl_2(phen)_2$]Cl [26] (3.7 g) deposited and was removed by filtration. $ZnCl_2$ (25 g) was added to the warm filtrate and the $ZnCl_4^{2-}$ salt of the red isomer deposited on cooling. A yield of 1.9 g of the isomerically pure product was obtained on recrystallisation.

Perchlorate Salts

The isomerically pure $ZnCl_4^{2-}$ salts (0.5 g) were dissolved in the minimum volume of 40 °C 3 *M* $HClO_4$ and excess $NaClO_4 \cdot H_2O$ was added. The products that crystallised from the ice-cooled solutions were collected, washed with 2-propanol, and then ether and air dried. The yields were: red-[CoCl(bipy)(dien)]$(ClO_4)_2$, 0.38 g; red-[CoCl(phen)(dien)]$(ClO_4)_2$, 0.44 g; orange-[CoCl(phen)(dien)]$(ClO_4)_2 \cdot H_2O$, 0.37 g.

TABLE III. C-13 NMR Data.[a]

		phen						dien			
CoCl(phen)(dien)$^{2+}$	red	154.31	147.36	140.00	130.32	127.71	126.83	55.73	54.19	44.01	41.71
		154.14	147.10	139.73	130.05	127.57	126.17				
	orange	155.56	148.21[b]	140.15	130.82	127.64	126.08		51.59	46.78	
		154.06		139.89	129.83	127.30	126.00				
		bipy						dien			
CoCl(bipy)(dien)$^{2+}$	red	157.31	153.30[b]	141.44	128.16	124.34		55.28	53.56	43.97	41.15
		156.81		141.15	127.49	124.19					
	orange	158.10	154.63	141.46[b]	127.53	124.92			51.49	46.90	
		158.01	152.28		127.17	123.67					
		bipy									
Co(bipy)$_3^{3+}$	(yellow)	156.62	151.65	144.82	132.00	128.00					

[a] 50–100 mg of the $ZnCl_4^{2-}$ salts in d_6-DMSO which also acts as internal standard. [b] These resonances are twice the intensity of the others.

Bromo(diamine)(dien)cobalt(III) Tetrabromozincate(II) Salts; [CoBr(AA)(dien)]ZnBr$_4$

The isomerically pure chloro tetrachlorozincate(II) salts (0.25 g) were refluxed in 24% HBr (40 mL) for 2 hr. The resulting purple-red solutions were cooled and a solution of HBr (24%, 10 mL) containing $ZnBr_2$ (2 g) was added. The platlet crystals that deposited were collected by filtration. The yield from the starting chloro isomers were red-bipy, 0.29 g; red-phen, 0.24 g and orange-phen, 0.24 g respectively. The i.r. spectra indicated that the product from the red-bipy had the same configuration as the starting material, whereas the products from red- and orange-phen were identical and appear to contain approximately 90% red-phen and 10% orange-phen configuration. Separation of these bromo isomers was not attempted.

Nitro(diamine)(dien)cobalt(III) Tetrachlorozincate(II) Salts, [Co(NO$_2$)(AA)(dien)]ZnCl$_4$

The isomerically pure red chloro tetrachlorozincate(II) salts (0.25 g) were dissolved in water (10 mL) and $NaNO_2$ (1 g) was added. After heating for 10 min at 70 °C, the now yellow solution was poured into 1:6 ethanol:acetone (400 mL) and yellow crystals (dipy 0.11 g, phen 0.15 g) slowly deposited. Regeneration (by refluxing in 6 *M* HCl) of the chloro complexes from these nitro derivatives indicated (i.r.) that there was no detectable isomerism of the red-bipy configuration, whereas for the red-phen system, about 10% conversion to the orange form had occurred.

Base Hydrolysis and Reanation

Any isomeric mixture (or the isomerically pure compounds) gives essentially the same result. [CoCl(AA)(dien)]ZnCl$_4$ (1 g) was dissolved in 2 *M* NaOH (25 mL) and the orange-red solutions allowed to stand at room temperature for 30 min. HCl (12 *M*, 25 mL) was then added and the solutions evaporated to near dryness on a steam bath. The residues were dissolved in water (40 mL) followed by 6 *M* HCl (30 mL) containing $ZnCl_2$ (10 g). The crystalline complexes that deposited were collected and the i.r. spectra were recorded to determine the isomeric composition. For AA = bipy, 0.95 g of the pure red isomer was obtained but for AA = phen 0.74 g of red and 0.22 g of the orange form (96% recovery) was produced.

Instrumentation

Infrared spectra were determined in KBr discs using a Perkin Elmer 580 i.r. spectrophotometer. Visible absorption spectra and the rates of Hg^{2+}-assisted chloride release were obtained using a Varian Superscan recording spectrophotometer. In the kinetic work, constant temperature (±0.05 °C) was maintained using water jacketted sample and reference cell holders. Rates of base hydrolysis were measured using a Radiometer pH-stat and C-13 n.m.r. spectra (Table III) were run in d_6-DMSO using a Varian FT-80A NMR spectrometer operating at 20 MHz.

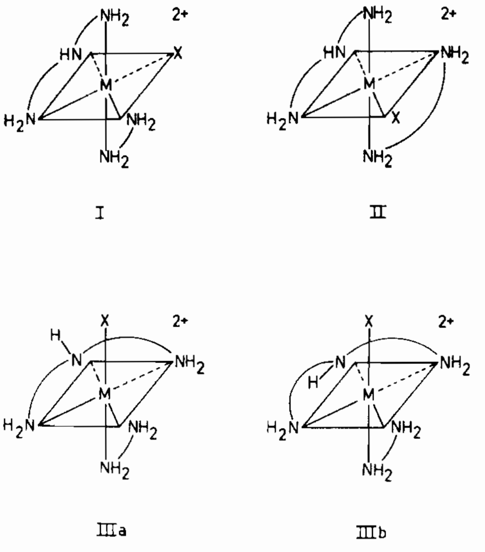
Kinetics

The procedures used in obtaining rate constants for the Hg^{2+}-assisted chloride release and base hydrolysis reactions have been described previously [15, 19]. $ZnCl_4^{2-}$ salts were used for the Hg^{2+}-assisted chloride release reactions and ClO_4^- salts for the base hydrolysis studies. We note, in this regard, that $ZnCl_4^{2-}$ salts can be used for base hydrolysis rate studies using pH-stat techniques, provided the set pH is less than 8.0.

Results and Discussion

Synthesis and Structure

Two isomers each for [CoCl(AA)(dien)]ZnCl$_4$ (AA = phen, bipy) have been isolated from the reaction of *mer*-CoCl$_3$(dien) and the diamines in aqueous ethanol. The less soluble red forms show a clear 4-resonance pattern for the dien C-atoms in the C-13 n.m.r. spectra and are thus assigned to the *unsym-fac-cis-* configuration [15, 27, 28]. The more soluble orange forms have two dien C-atom resonances at ~51.5 and ~46.8 ppm and are assigned to one of the two possible *mer*-dien configurations (Fig. 2). Although the *sym-fac-cis-* configuration also shows two dien C-atom resonances, these occur at ~55 and ~44 ppm, that is, with much greater separation than is observed for the *mer*-isomers.



I II IIIa IIIb

Fig. 2. Possible geometric configurations for a CoCl(AA)(dien)$^{2+}$ complex. I = *unsym-fac-cis-*, II = *sym-fac-cis-*, IIIa = (H↑)-*mer-* and IIIb = (H↓)-*mer-*.

No method, apart from single crystal X-ray analysis, has yet been devised to distinguish between the two possible *mer*-configurations when only one isomeric form has been isolated [17]. Nevertheless, for all *mer*-$CoX(AA)(dien)^{n+}$ complexes where single crystal X-ray data are available [6, 11, 14, 29, 30], the sec-NH proton is directed away from the coordinated aniono ligand. Thus we suggest that these orange forms also have the (H↓)-*mer*-$CoCl(AA)(dien)^{2+}$ configuration (Fig. 2, IIIb) [31].

The isomeric ratio of the complexes produced in the synthetic procedure with phen, bipy and aliphatic monoamines [15] appears to be related to the extend and rate of the (H↓)-*mer* ⇄ *unsym-fac-cis* equilibrium. We suggest that in the reaction mixture, the (H↓)-*mer* is the first formed product and this subsequently isomerises in the basic medium to give the *unsym-fac-cis-* form. Such an isomerism is known to occur for (H↓)-*mer*-$Co(AA)(dien)(OH_2)^{3+}$ ions (AA = $(NH_3)_2$, en, tn) [13] and our base hydrolysis–anation observations for the phen/bipy systems seem to support this hypothesis.

Kinetics

Kinetic data for the rates of Hg^{2+}-assisted chloride release for these isomeric $CoCl(AA)(dien)^{2+}$ complexes in 1.0 *M* NO_3^- media are reported in Table IV and the derived kinetic parameters for these and related systems are listed in Table V. It is known that the medium used for Hg^{2+}-assisted chloride release studies has a considerable influence on the rate of reaction and rate constants determined in 1.0 *M* ClO_4^- are about 0.65 times slower than those determined in 1.0 *M* NO_3^- [32]. Nevertheless, the rates of Hg^{2+}-assisted chloride release from the orange (H↓)-*mer*-$CoCl(AA)(dien)^{2+}$ (AA = phen, bipy) complexes are an order of magnitude slower than those observed for analogous systems with aliphatic diamines and are among the slowest rates reported for $CoCl(N_5)^{2+}$ systems in general [33]. This suggests some *trans* stabilisation of the Co–Cl bond by the heterocyclic diamine, especially as the *unsym-fac-cis* isomers, where this structural feature is absent, react with 'normal' rates (Table V). Unfortunately (H↓)-*mer*-$CoCl(py)_2(dien)^{2+}$ is unavailable for comparative purposes. Indeed, there are very few known Co(III) complexes with a *trans*- Cl-Co-heterocyclic amine structural feature [34] but recent work in this laboratory [35] using $CoCl(en)_2(adenine)^{n+}$ and $CoCl(en)_2(2\text{-amino-pyrimidine})^{n+}$ where a *trans* configuration is suspected, again indicates a slow Hg^{2+}-assisted chloride release reaction.

Base hydrolysis rate data (μ = 0.1 *M*, NaCl) for the *unsym-fac-cis-* isomers are presented in Table VI and relevant kinetic parameters in Table VII. While there is the expected rate increase for these phen/bipy complexes relative to their aliphatic diamine analogues (the rate increases by about a factor of ten, phen:tn) the analogous *unsym-fac-cis*-$CoCl(py)_2(dien)^{2+}$ base hydrolyses 15 times faster again [36]. The only

TABLE IV. Observed and Calculated Rate Constants for the Hg^{2+}-assisted Aquation of Some $CoCl(AA)(dien)^{2+}$ Complexes (μ = 1.0 *M*, HNO_3).[a]

T (°C)	[K]	$[H^+]$ (*M*)	$[Hg^{2+}]_i$[b] m*M*	$10^3 k_{obs}$[c] (s^{-1})	$10^3 k_{Hg}$[d] ($M^{-1}\ s^{-1}$)	$10^3 k_{Hg}(calc)$[e] ($M^{-1}\ s^{-1}$)
unsym-fac-cis-$CoCl(phen)(dien)^{2+}$						
38.4	[311.6]	0.88	35.5	1.87 ± 0.08	5.27 ± 0.22	51.7
				1.90 ± 0.04	5.35 ± 0.11	
36.0	[309.2]	0.88	35.5	1.50 ± 0.02	42.4 ± 0.6	42.4
				1.56 ± 0.04	43.9 ± 1.1	
34.8	[308.0]	0.88	35.5	1.34 ± 0.03	37.7 ± 0.8	38.4
				1.23 ± 0.05	34.6 ± 1.4	
		0.82	57.4	2.03 ± 0.05	35.4 ± 0.9	
				2.10 ± 0.07	36.6 ± 1.2	
32.5	[305.7]	0.88	35.5	1.14 ± 0.03	32.1 ± 0.8	31.6
				1.14 ± 0.02	32.1 ± 0.8	
		0.82	57.4	1.87 ± 0.09	32.6 ± 1.6	
				1.89 ± 0.03	32.9 ± 0.5	
		0.78	67.5	2.11 ± 0.02	31.2 ± 0.2	
				2.18 ± 0.08	32.3 ± 1.0	
		0.88[f]	35.5[f]	1.10 ± 0.02	30.9 ± 0.6	
30.8	[304.0]	0.88	35.5	0.993 ± 0.004	27.9 ± 0.1	27.3
				0.972 ± 0.02	27.4 ± 0.6	
				1.01 ± 0.02	28.5 ± 0.6	
		0.76	77.7	2.18 ± 0.05	28.0 ± 0.6	

(Continued overleaf)

TABLE IV. *(Continued)*

29.9	[303.1]	0.88	35.5	0.921 ± 0.02	25.9 ± 0.6	25.3
		0.82	57.4	1.47 ± 0.07	25.6 ± 1.2	
27.2	[300.4]	0.82	57.4	1.07 ± 0.02	18.6 ± 0.4	20.0
				1.14 ± 0.03	19.9 ± 0.5	
		0.78	67.5	1.35 ± 0.03	20.0 ± 0.5	
				1.36 ± 0.02	20.1 ± 0.3	
25.0	[298.2]					16.5
unsym-fac-cis-CoCl(bipy)(dien)$^{2+}$						
38.4	[311.6]	0.88	35.5	2.23 ± 0.03	62.8 ± 0.8	57.3
36.0	[309.2]	0.88	35.5	1.72 ± 0.03	48.4 ± 0.8	46.0
				1.76 ± 0.04	49.6 ± 1.1	
34.8	[308.0]	0.82	57.4	2.04 ± 0.1	35.5 ± 1.7	41.2
32.5	[305.7]	0.76	77.7	2.40 ± 0.1	30.9 ± 1.3	33.3
		0.88	35.5	1.08 ± 0.01	30.4 ± 0.3	
				1.10 ± 0.03	30.9 ± 0.8	
30.8	[304.0]	0.76	77.7	2.22 ± 0.05	28.5 ± 0.6	28.4
				2.17 ± 0.03	27.9 ± 0.4	
				2.24 ± 0.03	28.8 ± 0.4	
		0.88	35.5	1.03 ± 0.01	29.0 ± 0.3	
				1.02 ± 0.01	28.7 ± 0.3	
29.9	[303.1]	0.82	57.4	1.47 ± 0.1	26.8 ± 2.0	26.1
		0.88	35.5	0.97 ± 0.02	27.3 ± 0.6	
27.2	[300.4]	0.82	57.4	1.24 ± 0.05	21.6 ± 0.9	20.1
25.0	[298.2]					16.2
unsym-fac-cis-CoCl(en)(dien)$^{2+}$						
34.8	[308.0]	0.82	57.4	3.40 ± 0.04	59.2 ± 0.7	61.3
				3.57 ± 0.11	62.2 ± 1.9	
		0.88	35.5	2.25 ± 0.02	63.6 ± 0.6	
30.0	[303.2]	0.88	35.5	1.48 ± 0.03	41.7 ± 0.8	43.5
27.2	[300.4]	0.82	57.4	2.01 ± 0.03	35.0 ± 0.5	35.5
				2.12 ± 0.1	36.9 ± 1.7	
25.0	[298.2]					30.1
mer-CoCl(phen)(dien)$^{2+}$						
62.4	[335.6]	0.76	77.7	0.870 ± 0.04	11.2 ± 0.5	11.1
59.3	[332.5]	0.76	77.7	0.669 ± 0.012	8.16 ± 0.14	8.15
54.2	[327.4]	0.76	77.7	0.366 ± 0.002	4.17 ± 0.03	4.84
49.8	[323.0]	0.76	77.7	0.241 ± 0.009	3.10 ± 0.11	3.05
25.0	[298.2]					0.174
mer-CoCl(bipy)(dien)$^{2+}$						
62.4	[335.6]	0.88	35.5	2.02 ± 0.01	56.9 ± 0.3	57.5
59.3	[332.5]	0.88	35.5	1.48 ± 0.07	41.6 ± 2.0	41.4
54.2	[327.4]	0.76	77.7	1.85 ± 0.08	23.8 ± 1.0	23.8
		0.88	35.5	0.855 ± 0.008	24.1 ± 0.2	
49.2	[322.4]	0.76	77.7	1.04 ± 0.011	13.4 ± 0.1	13.6
25.0	[298.2]					0.687

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[a] As $ZnCl_4^{2-}$ salts in HNO_3 plus $Hg(NO_3)_2$ solution. [b] Initial $[Hg^{2+}]$. [c] Observed pseudo first-order rate constant. Rate constants obtained from fixed wavelength scans at 490 (phen) or 550 nm (en, bipy). [d] $k_{Hg} = k_{obs}[Hg^{2+}]_i^{-1}$. [e] Calculated from the activation parameters cited in Table II. [f] As ClO_4^- salt.

TABLE V. Kinetic Parameters for the Hg^{2+}-assisted Aquation of Some $CoCl(AA)(dien)^{2+}$ Complexes at 298.2 °K (μ = 1.0 *M*).

AA	$10^2 k_{Hg}$ (M^{-1} s^{-1})	E_a kJ mol^{-1}	log PZ	$\Delta S^{\#}$ J K^{-1} mol^{-1}	Ref.
unsym-fac-cis- isomers					
en[a]	1.49	48.1 ± 2	8.38	−93.2 ± 4	c
en[b]	3.01	55.4 ± 3	8.186	−96.5 ± 6	d
$(NH_3)_2$[a]	7.76	65.3 ± 4.5	10.333	−55 ± 9	e
$(MeNH_2)_2$[a]	8.98	61.7 ± 3.0	9.760	−66 ± 6	e
tn[a]	10.0				e
$(py)_2$[a]	0.166	93.1 ± 3.3	13.525	−5.7 ± 6	e
phen[b]	1.65	65.9 ± 2.0	9.767	−66.2 ± 4	d
bipy[b]	1.62	72.6 ± 5.0	10.928	−44 ± 10	d
(H↓)-*mer-* isomers					
en[a]	0.521	81.5		−23	c
$(NH_3)_2$[a]	2.14				e
$(EtNH_2)_2$[a]	16.9				e
tn[a]	25.0				f
phen[b]	0.0174	92.5 ± 2	12.437	−15.1 ± 4	d
bipy[b]	0.0687	98.5 ± 1	14.088	+16.4 ± 2	d

[a] μ = 1.0 *M* $HClO_4$. [b] μ = 1.0 *M* HNO_3. [c] Ref. 8. [d] This research. [e] Ref. 16. [f] Ref. 17.

TABLE VI. Observed and Calculated Rate Constants for the Base Hydrolysis of *unsym-fac-cis*-$[CoCl(AA)(dien)](ClO_4)_2$ (μ = 0.1 *M*, NaCl).

T (°C)	pH	$10^7[OH^-]$[a] (*M*)	$t_{1/2}$[b] (min)	$10^3 k_{obs}$ (s^{-1})	$10^{-3} k_{OH}$[c] (M^{-1} s^{-1})	$10^{-3} k_{OH}$(calc)[d] (M^{-1} s^{-1})
AA = bipy						
10.1	9.00	59.3	7.55	1.53	0.258	0.270
			7.41	1.56	0.263	
	8.50	19.2	22.5	0.513	0.267	
15.3	8.50	29.9	7.0	1.65	0.550	0.547
			6.8	1.70	0.567	
25.0	7.70	10.6	4.5	2.57	2.42	1.92
	7.50	6.70	8.3	1.39	2.07	
			7.0	1.65	2.46	
			7.5	1.54	2.16	
	7.30	3.72	11.4	1.01	2.72	
			12.0	0.963	2.59	
			12.0	0.963	2.59	
30.5	7.00	3.15	10.1	1.14	3.62	3.77
			10.0	1.15	3.65	
	7.10	3.96	8.1	1.43	3.61	
	7.20	4.99	6.4	1.80	3.61	
AA = phen						
10.1	9.00	59.3	7.80	1.48	0.249	0.257
			7.75	1.49	0.251	
15.3	8.50	29.9	7.3	1.58	0.528	0.500
			7.7	1.50	0.502	
25.0	7.5	6.70	9.4	1.23	1.83	1.74
			10.4	1.11	1.65	
	7.3	3.72	16.4	0.704	1.89	

(Continued overleaf)

TABLE VI. *(Continued)*

30.5	7.2	4.99	7.0 7.0 7.1	1.65 1.65 1.63	3.31 3.31 3.27	3.37

[a] $-\log[OH^-] = pK_{wc} - \log \gamma_\pm - pH$: see A. J. Cunningham, D. A. House and H. K. J. Powell, *J. Inorg. Nucl. Chem., 33,* 572 (1971). pH meter calibrated with 0.01 *M* borax buffer pH = 9.18 at 25.0 °C. [b] For 20–30 mg complex in 50 ml 0.1 *M* NaCl (previously adjusted to set pH) using 0.100 *M* NaOH as titrant. V_∞ based on wt. of complex used. [c] $k_{OH} = k_{obs}[OH^-]^{-1}$. [d] Calculated from the activation parameters cited in Table IV.

TABLE VII. Kinetic Parameters for the Base Hydrolysis of Isomeric $CoCl(AA)(dien)^{2+}$ Complexes (μ = 0.1 *M*, NaCl) at 298.2 °K.

AA	k_{OH} (M^{-1} s^{-1})	E_a (kJ mol^{-1})	$\Delta S^{\#}$ (J K^{-1} mol^{-1})	Ref.
unsym-fac-cis- configuration				
$(NH_3)_2$	8.0×10^1			a
$(MeNH_2)_2$	2.52×10^2			a
(en)	2.66×10^1			b
(tn)	1.38×10^2	91.4	+94	c
$(py)_2$	2.77×10^4			a
(bipy)	1.92×10^3	92.4 ± 1.5	+120 ± 3	d
(phen)	1.74×10^3	90.1 ± 1.4	+111 ± 3	d
sym-fac-cis- configuration				
$(NH_3)_2$	6.95×10^{-1}	84.3	+26.5	e
(en)	4.71	93.2	+72	e
(tn)	1.06×10^1	123	+179	c
(H↓)-*mer-* configuration				
(en)	3.0×10^4			b
(tn)	5.02×10^5	83.3	+135	c
(phen)	$\sim 3 \times 10^6$			d

[a] D. A. House, unpublished research. [b] R. W. Hay and K. B. Nolan, *J. Inorg. Nucl. Chem., 38,* 2118 (1976). [c] Ref. 9. [d] This research. [e] Ref. 16.

analogous system where activation parameters have been established is *unsym-fac-cis*-$CoCl(tn)(dien)^{2+}$ [9] and when compared with the phen/bipy systems, it is a more favourable activation entropy for the latter which determines the rate increase.

We were unable to measure the base hydrolysis rate of the orange-$CoCl(AA)(dien)^{2+}$ (AA = phen, bipy) isomers using the pH-stat because at pH = 4–5, where the rate of reaction is measurable, there is prohibitive interference in OH^- uptake from the equilibrium: $Co(OH)(N_5)^{2+} + H_2O \rightleftarrows Co(N_5)(OH_2)^{3+} + OH^-$.

Nevertheless, using an estimated half-life of 10 min (AA = phen, pH = 4.5, NaAc/HAc buffer, μ = 0.1 *M*) measured spectrophotometrically at room temperature we calculate $k_{OH}(298) \sim 3 \times 10^6$ M^{-1} s^{-1}.

Conclusion

The incorporation of conjugated heterocyclic ligands (phen, bipy) to form $CoCl(N_5)^{2+}$ systems has not been well documented, although $CoCl(en)(AA)(NH_3)^{2+}$ (AA = phen, bipy), of unknown stereochemistry, have been reported [37]. These complexes have thermal aquation rates of $k_H(298) \sim 5 \times 10^{-6}$ s^{-1} and we compute [32] an Hg^{2+}-assisted chloride release rate of $k_{Hg}(298) \sim 1.9 \times 10^{-1}$ M^{-1} s^{-1} which is of the same order as $k_{Hg}(298)$ (1.2×10^{-1} M^{-1} s^{-1}) for $CoCl(NH_3)_5^{2+}$ [33]. We would thus suggest that these complexes have the leaving group *trans-* to an aliphatic NH_2 group and probably a *cis*-bis(diamine) configuration.

In the *unsym-fac-cis*-CoCl(AA)(dien)$^{2+}$ configuration, the change from an aliphatic diamine to an heterocyclic diamine appears to have little influence (apart from k_{OH}) on the physical properties measured, but in the *mer*- configuration, where the coordinated anion is *trans*- to the heterocyclic N donor, some Co—Cl bond strengthening seems to occur.

For CoCl(N$_5$)$^{2+}$ systems containing a unidentate amine (*e.g. cis*-CoCl(en)$_2$(N)$^{2+}$ [39] the change from an aliphatic to aromatic heterocyclic ligands (*e.g.* N = MeNH$_2$ to N = py) results in an increase of k_{OH} by a factor of about 30. The comparable factor in the *unsym-fac-cis*-CoCl(AA)(dien)$^{2+}$ reported here is about 70 (bipy:en) but the incorporation of two unlinked unidentate aromatic heterocyclic ligands causes an increase in k_{OH} of about 350 [(py)$_2$:(NH$_3$)$_2$].

However, for the (H↓)-*mer*-CoCl(AA)(dien)$^{2+}$ (AA = phen, bipy) there are two rate accelerating influences contributing to k_{OH} (a) the increased acidity of the sec-NH proton in the 'planar' $-(CH_2)_2-NH-(CH_2)_2-$ polyamine configuration [9, 38, 39], and (b) the 'heterocyclic amine effect', with a factor of ~100 (phen:en) attributed to the latter.

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