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Isomers of the *trans*-Dichlorobis(2-methyl-1,2-diaminopropane) Cobalt(III) Cation

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Abstract

Two isomers of *trans*-$CoCl_2(ibn)_2^+$ have been isolated from the reaction of dioxygen with methanolic solutions of $CoCl_2 \cdot 6H_2O$ and the diamine. The most abundant is assigned the *trans-gem*-dimethyl configuration and the least abundant has been characterised as the *cis-gem*-dimethyl form by single crystal X-ray analysis of the $ZnCl_4^{2-}$ (monohydrate) salt. *Cis-gem*-dimethyl-*trans*-$[CoCl_2(ibn)_2]_2ZnCl_4 \cdot H_2O$ crystallizes in the monoclinic space group $P2_1/c$, with a = 15.02(1), b = 11.100(2), c = 21.68(2), β = 105.64(7) and four formula units per unit cell. Each $ZnCl_4^{2-}$ anion is associated with two independent cations. Both cations have the δ,λ chelate ring conformation, but differ by 3° in the Cl–Co–Cl bond angle. The rates of loss of the first chloro ligand from *trans-trans*- and *cis-trans*-$CoCl_2(ibn)_2^+$ were measured spectrophotometrically in 1.0 M HCl over a 15 K temperature range. At 25 °C, the first order rate constants and kinetic parameters are 10^3 k (sec^{-1}) = 0.994, 3.07, E_a (kJ mol^{-1}) = 106, 93.6, log [PZ (sec^{-1})] = 15.552, 13.894 and $\Delta S^{\ddagger}_{298}$ J K^{-1} mol^{-1}) = +44.5, +12.8 respectively.

Introduction

Unsymmetrical bidentate ligands are of interest because of the possibility of end-for-end isomerism in bis complexes of inert transition metal ions [1].

As part of a programme to investigate Co(III) complexes containing ligands with axial methyl groups that may be capable of oxidation [2], we have prepared *trans*-$CoCl_2(ibn)_2^+$ where ibn (Fig. 1) is an unsymmetrical achiral diamine ligand. This complex was first described by Basolo [3] and synthesised by H_2O_2 oxidation of Co(II) plus ibn in aqueous solution giving a 19% yield. Although no isomeric assignments were made [3], the isolated complex had a half-life for the loss of the first chloro ligand of about 5 min in acidic aqueous solution at 25 °C [4].

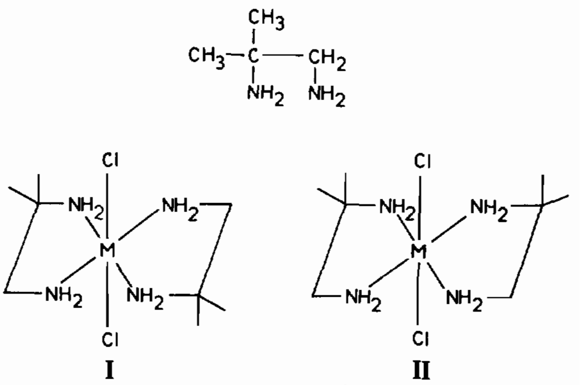

Fig. 1. Isomers of *trans*-$CoCl_2(ibn)_2^+$.

This paper describes the isolation of two isomeric forms of *trans*-$CoCl_2(ibn)_2^+$ and the least abundant isomer (the *cis-gem*-dimethyl) has been characterised by a single crystal X-ray structure analysis.

Experimental

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

2-Methyl-1,2-diaminopropane was purchased from Aldrich Chemical Company and used as supplied. All other chemicals were of the best Reagent Grade available.

trans-trans- and cis-trans-Dichloro(2-methyl-1,2-diaminopropane)cobalt(III) Perchlorate, t,t- and c,t-$[CoCl_2(ibn)_2]ClO_4$

Dioxygen was bubbled through a solution of $CoCl_2 \cdot 6H_2O$ (4 g) and ibn (2.95 g) in methanol (100 ml) at room temperature for two hours. To the brown oxidised solution was added HCl (15 ml, 12 M) and the volume reduced to about one half, on a steam bath. Addition of $HClO_4$ (5 ml, 60%) to the

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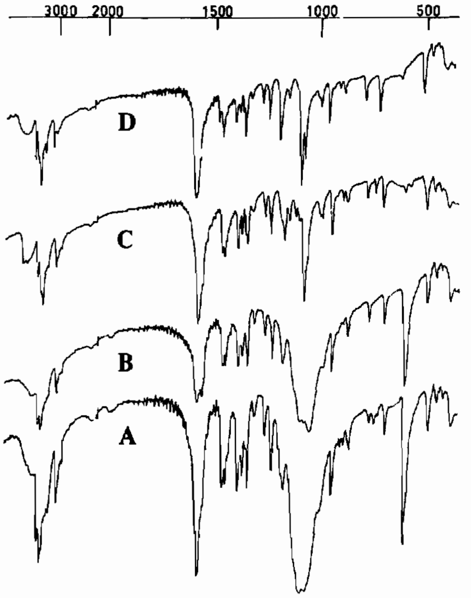


Fig. 2. IR spectra of *t,t*-(B), *c,t*-$[CoCl_2(ibn)_2]ClO_4$ (A) and *t,t*-(D), *c,t*-$[CoCl_2(ibn)_2]_2ZnCl_4 \cdot H_2O$ (C) in KBr discs.

warm green solution, resulted in the precipitation of *t,t*-$[CoCl_2(ibn)_2]ClO_4$.

After standing at room temperature for 1–2 h, the green product (3.5 g, 51%) was collected by filtration and washed successively with isopropanol and ether, and air dried.

The mother liquor was allowed to stand at room temperature for 2–3 weeks, during which time, darker green crystals of *c,t*-$[CoCl_2(ibn)_2]ClO_4$ slowly deposited. These (~1 g, 15%) were collected, washed and dried as above. The first crop from the mother liquor was occasionally a *c,t*-/*t,t*-mixture.

Both isomers were recrystallized as perchlorate salts from the minimum volume of 60° 0.1 M HCl, by addition of an equal volume of 12 M HCl and $HClO_4$ (5 ml, 60%). The $ZnCl_4^{2-}$ salts were obtained by a similar procedure, but replacing the $HClO_4$ with $ZnCl_2$ (10 g). The IR spectrum of the *t,t*- and *c,t*-ClO_4^- and $ZnCl_4^{2-}$ salts are shown in Fig. 2.

Characterisation

t,t-$[CoCl_2(ibn)_2]ClO_4$: *Anal.* Calcd, for $(CoCl_2(ibn)_2]ClO_4$, $C_8H_{24}N_4O_4Cl_3Co$: C, 23.67; H, 5.92; N, 13.81%. Found: C, 23.61; H, 6.28; N, 13.81%. C-13 NMR (DMF: ppm relative to dioxane at 67.39) 59.49, 56.53, 28.11. Visible absorption spectra (3 M HCl); λ, nm; (ε, M^{-1} cm^{-1}): max 612.5 (36.1), min 530 (24.8), sh 446 (34). *t,t*-$[CoCl_2(ibn)_2]_2ZnCl_4 \cdot H_2O$ *Anal.* Calcd. for $C_{16}H_{50}N_8Co_2ZnO$: C, 22.95; H, 6.02; N, 13.38%. Found: C, 22.97; H, 6.39; N, 13.34%. *c,t*-$[CoCl_2(ibn)_2]ClO_4$; C-13 NMR (DMF, ppm relative to dioxane at 67.39) 59.29, 56.28, 28.21. Visible absorption spectra (3 M HCl); λ, nm; (ε, M^{-1} cm^{-1}) max. 611.6 (34.5), min. 532.5 (24.5), sh 432 (35). *c,t*-$[CoCl_2(ibn)_2]_2ZnCl_4 \cdot H_2O$: see following single crystal X-ray structure. Isomeric Mixtures: The C-13 NMR spectra (DMF) of an obvious (IR) *c,t*-/*t,t*-$[CoCl_2(ibn)_2]ClO_4$ mixture had resonances at 59.49, 59.28; 56.80, 56.55; 28.23 ppm, corresponding well to the positions of the pure components. From the relative intensities of 11:34; 73:18 respectively, we estimate about 28% *t,t*-isomer. There was no obvious splitting of the $C(CH_3)_2$ resonance at 28.23 ppm in this isomeric mixture.

X-ray Structure Analysis

c,t-$[CoCl_2(ibn)]_2ZnCl_4 \cdot H_2O$ forms dark green crystals which are stable to X-rays. An elongated hexagonal shaped crystal with approximate dimensions of 0.64 × 0.36 × 0.12 mm was used.

Crystal unit cell data were established from precession photographs and measured accurately by means of a NICOLET XRD P3 four-circle diffractometer. The space group was determined unambiguously from systematic absences of appropriate reflections. Mo X-radiation ($\lambda MoK\alpha = 0.71069$ Å) from a crystal monochromator and ω-scan techniques were used to collect reflection intensities. The cell parameters were determined by least-squares refinement, the setting angles of 25 accurately centered reflections ($29 < 2\theta < 31$) being used. The boundary faces were indexed and numerical absorption corrections were applied, resulting in maximum and minimum transmission factors of 0.496 and 0.817 respectively.

Crystal Data

$C_{16}H_{50}N_8OCl_8ZnCo_2$: M_r = 837.50, monoclinic, $P2_1/c$, a = 15.02(1), b = 11.100(2), c = 21.68(2) Å, β = 105.64(7)°, V = 3481.41 Å^3, D_m = 1.56, D_{calc} = 1.56 g cm^{-3}, Z = four molecular units, μ ($MoK\alpha$) = 0.87 cm^{-1}.

A total of 3627 independent reflections were collected, with 2741 having $I > 3\sigma(I)$. The structure was solved using the Patterson function to locate the positions of the heavy atoms and then difference Fourier syntheses. Blocked cascade least-squares refinement methods were employed using reflection weights $1/\{\sigma^2(F_o) + g(F_c)^2\}$ ($g = 2.5 \times 10^{-4}$). The function minimised was $\Sigma w(|F_o| - |F_c|)^2$ and anomalous dispersion corrections were made from Cromer and Liberman [5]. All non-hydrogen atoms were assigned anisotropic thermal parameters and all hydrogen atoms except those on the H_2O molecule were included as rigid groups pivoting about their respective C or N atoms. The SHELXTL [6] programme was used for all computations and the final R-factors were R = 0.0487 and R_w = 0.0546. A final Fourier synthesis showed no significant residual electron density and there were no abnormal discrepancies between observed and calculated structure factors.

TABLE I. Atom Coordinates (×10^4), Bond Lengths (Å) and Selected Bond Angles (°) for *Cis-gem*-dimethyl-*trans*-[CoCl$_2$(ibn)$_2$]$_2$-ZnCl$_4$·H$_2$O.

Atom Coordinates

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Zn	2459(1)	6533(1)	5195(1)	Cl(5)	3290	5182	5910
Cl(6)	1619(3)	5615(3)	4295(2)	Cl(7)	3415	7858	4873
Cl(8)	1510(2)	7545(3)	5668(1)	O(1)	655	4703	5726
Cation (1)				Cation (2)			
Co(1)	2721(1)	6533(1)	5195(1)	Co(2)	2570(1)	7045(1)	7743(1)
Cl(1)	1428(2)	1358(3)	4258(1)	Cl(3)	3095(2)	5158(3)	7972(1)
Cl(2)	4061(2)	1813(3)	5827(1)	Cl(4)	2042(2)	8942(3)	7526(1)
N(1)	2047(7)	2483(8)	5562(4)	N(5)	1454(6)	6442(8)	7139(4)
N(2)	2455(7)	216(8)	5473(4)	N(6)	1860(6)	6915(8)	8382(4)
N(3)	3415(7)	901(8)	4506(4)	N(7)	3693(6)	7695(8)	8326(4)
N(4)	2996(6)	3137(7)	4675(4)	N(8)	3228(6)	7216(7)	7095(4)
C(1)	1673(10)	1657(11)	6007(6)	C(9)	667(8)	6176(11)	7442(6)
C(2)	2305(10)	535(10)	6088(6)	C(10)	863(9)	6893(12)	8041(5)
C(3)	1785(11)	2213(13)	6642(6)	C(11)	635(10)	4838(10)	7556(7)
C(4)	686(10)	1355(14)	5687(7)	C(12)	−232(10)	6563(13)	6989(6)
C(5)	4059(8)	1793(9)	4351(5)	C(13)	4228(8)	8380(10)	7952(5)
C(6)	3574(8)	2998(10)	4202(5)	C(14)	4208(8)	7651(9)	7342(5)
C(7)	4267(10)	4000(12)	4287(6)	C(15)	4449(9)	8503(11)	6856(5)
C(8)	2910(9)	3001(10)	3517(5)	C(16)	4870(8)	6584(10)	7483(5)

Bond Lengths (Å)

Zn–Cl(5)	2.273(6)	Zn–Cl(6)	2.260(6)	Zn–Cl(7)	2.292(6)	Zn–Cl(8)	2.266(6)
Cation (1)				Cation (2)			
Co(1)–Cl(1)	2.236(6)	Co(1)–Cl(2)	2.264(6)	Co(2)–Cl(3)	2.245(6)	Co(2)–Cl(4)	2.256(6)
Co(1)–N(1)	1.937(11)	Co(1)–N(2)	1.944(10)	Co(2)–N(5)	1.947(9)	Co(2)–N(6)	1.968(10)
Co(1)–N(3)	1.948(11)	Co(1)–N(4)	1.922(9)	Co(2)–N(7)	1.954(9)	Co(2)–N(8)	1.934(10)
N(1)–C(1)	1.543(18)	C(1)–C(2)	1.547(19)	N(5)–C(9)	1.528(17)	C(9)–C(10)	1.484(17)
C(1)–C(3)	1.476(19)	C(1)–C(4)	1.497(19)	C(9)–C(11)	1.509(17)	C(9)–C(12)	1.502(17)
N(2)–C(2)	1.453(17)	N(3)–C(5)	1.485(16)	N(6)–C(10)	1.481(15)	N(7)–C(13)	1.495(16)
C(5)–C(6)	1.516(16)	C(6)–C(7)	1.501(18)	C(13)–C(14)	1.545(15)	C(14)–C(15)	1.529(17)
C(6)–C(8)	1.549(14)	N(4)–C(6)	1.518(16)	C(14)–C(16)	1.524(16)	N(8)–C(14)	1.505(14)

Selected Bond Angles (°)

Cation (1)		Cation (2)	
Cl(1)–Co(1)–Cl(2)	175.8(2)	Cl(2)–Co(2)–Cl(3)	179.3(2)
Cl(1)–Co(1)–N(1)	91.6(3)	Cl(3)–Co(2)–N(5)	90.9(3)
Cl(2)–Co(1)–N(1)	91.5(3)	Cl(4)–Co(2)–N(5)	89.4(3)
Cl(1)–Co(1)–N(2)	89.7(3)	Cl(3)–Co(2)–N(6)	90.1(3)
Cl(2)–Co(1)–N(2)	87.8(3)	Cl(4)–Co(2)–N(6)	89.3(3)
N(1)–Co(1)–N(2)	84.5(4)	N(5)–Co(2)–N(6)	85.1(4)
Cl(1)–Co(1)–N(3)	88.8(3)	Cl(3)–Co(2)–N(7)	90.6(3)
Cl(2)–Co(1)–N(3)	88.3(3)	Cl(4)–Co(2)–N(7)	89.1(3)
N(1)–Co(1)–N(3)	177.0(4)	N(5)–Co(2)–N(7)	177.9(4)
N(2)–Co(1)–N(3)	98.4(4)	N(6)–Co(2)–N(7)	96.3(4)
Cl(1)–Co(1)–N(4)	92.9(3)	Cl(3)–Co(2)–N(8)	92.0(3)
Cl(2)–Co(1)–N(4)	89.9(3)	Cl(4)–Co(2)–N(8)	88.7(3)
N(1)–Co(1)–N(4)	92.2(4)	N(5)–Co(2)–N(8)	93.6(4)

(continued overleaf)

TABLE I. *(continued)*

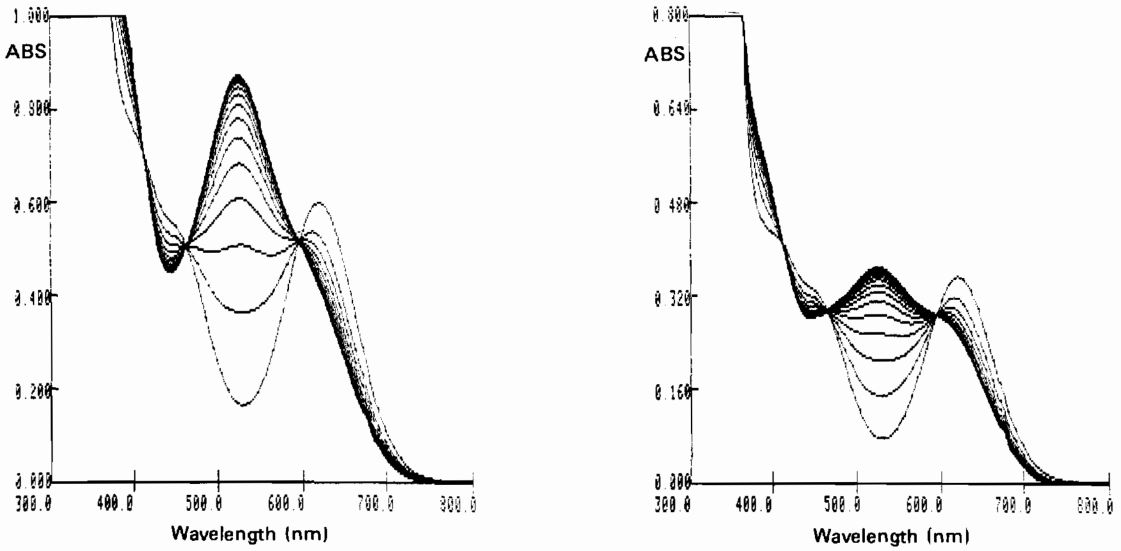
Cation (1)		Cation (2)	
N(2)–Co(1)–N(4)	175.9(4)	N(6)–Co(2)–N(8)	177.6(3)
N(3)–Co(1)–N(4)	84.8(4)	N(7)–Co(2)–N(8)	84.9(4)

Selected Torsion Angles (°)

Cation (1)		Cation (2)	
N(1)–C(1)–C(2)–N(2)	−42.2(1.2)	N(5)–C(9)–C(10)–N(6)	−38.9(1.2)
N(3)–C(5)–C(6)–N(4)	39.2(1.0)	N(7)–C(13)–C(14)–N(8)	43.1(1.0)

Selected Non-Bonded Distances (Å)

Cation (1)				Cation (2)			
Cl(1)–C(4)	3.56	Cl(1)–C(8)	3.58	Cl(6)–C(11)	3.58	Cl(3)–C(12)	3.50
Cl(2)–C(3)	4.28	Cl(2)–C(7)	4.20	Cl(4)–C(11)	4.22	Cl(4)–C(15)	4.28



(a) (b)

Fig. 3. Spectrophotometric changes observed on dissolving *t,t*- (left) or *c,t*- (right) $[CoCl_2(ibn)_2]ClO_4$ in 1 M HCl at room temperature (*ca.* 18 °C) (1.0 nm, 5.0 min, 15 cycles set, 15 cycles complete).

The final refined atom coordinates, bond lengths and selected bond angles are listed in Table I and the structure factor Table and other structural parameter lists are available*.

Kinetic Measurements

The spectrophotometrically determined rate constants for the loss of the first chloro ligand from t,t- and *c,t*-$[CoCl_2(ibn)_2]ClO_4$ were obtained from plots of absorbance *vs.* time at 530 nm using a Varian Superscan Recording Spectrophotometer. Small samples of the complexes were dissolved in *ca.* 2 ml of 1 .0 M HCl (previously equilibrated at the desired temperature) in a 1.00 cm spectrophotometer cell. The absorbance *vs.* time was recorded until no further change in absorbance was observed (6–8 half-lives). Temperature control was maintained by circulating water from a constant temperature (±0.05 °C) water bath. k_{obs} was calculated from the variation of absorbance with time as described previously [7], as were the activation parameters from the variation of k_{obs} with temperature.

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*These have been reviewed by the referees and may be obtained from the authors (DAH) on request.

Results and Discussion

Synthesis

The room temperature oxidation of methanolic solutions of $CoCl_2 \cdot 6H_2O$ containing two mol equivalents of ibn, with dioxygen, results in the isolation (after $HCl/HClO_4$ work up) of green needles of *trans*-$[CoCl_2(ibn)_2]ClO_4$. We assign this form to the *trans-gem*-dimethyl isomer. The mother liquor slowly (weeks) deposits a darker green *trans*-$[CoCl_2(ibn)_2]$-ClO_4 isomer which is assigned to the *cis-gem*-dimethyl configuration on the basis of a single crystal X-ray structure on the $ZnCl_4^{2-}$ (monohydrate) salt.

The perchlorate or $ZnCl_4^{2-}$ salts of the two isomers are easily distinguished by their IR spectra (Fig. 2).

While C-13 NMR can be used to distinguish *c,t*/*t,t*-$[CoCl_2(ibn)_2]ClO_4$ mixtures, there are only minor differences in the positions of the C resonances for the two isomers. Both isomers are quite rapidly hydrolysed in dilute acidic solution with half-lives of 11.6 and 3.76 min at 25.0 °C for the *t,t*- and *c,t*-forms, respectively. The extent of steric change is, however, different for the two isomers and Fig. 3 shows the visible absorption spectral scans with time.

Figure 1 illustrates the configuration of the two possible isomers for a square planar bis(ibn) complex. For both isomers, the puckering of the chelate rings allows the possibility of $\delta\lambda$ and $\lambda\lambda$ (or $\delta\delta$) conformations in the solid state. Similar isomeric forms are possible for square planar bis(pn) (pn = 1,2-diaminopropane) complexes, but here there are additional complications in that the bis complex for the racemic ligand could contain the mixed ligand (R–pn) (S–pn), or the equally paired $(R–pn)_2$/$(S–pn)_2$ ligand combinations [8].

To date only bis(ibn) or bis(pn) complexes with the C-methyl groups in the *trans* configuration (Fig. 1, I) have been characterised by single crystal X-ray structures. Among such complexes are *trans*-$CoCl_2(R\text{-}pn)_2^+$ (λ,λ; both Me eq.) [9], $Pt(R\text{-}pn)_2^+$ (λ,δ; one Me ax.) [10] $Cu(R\text{-}pn)(S\text{-}pn)^{2+}$ (λ,δ; both Me eq.) [11], and $Pd(ibn)_2^{2+}$ (δ,δ) [12].

The present single crystal X-ray structure analysis of the least abundant *trans*-$CoCl_2(ibn)_2^+$ isomer shows that the C-methyl groups are in the *cis*-configuration (Fig. 1, II). A general view of the two independent *cis-gem*-dimethyl-*trans*-$CoCl_2$-$(ibn)_2^+$ cations is shown in Fig. 4. Both have the λ,δ chelate ring conformation, with similar dihedral angles and non-bonded CH_3–Cl distances (Table I). The major difference between the crystallographically distinct cations, is the 4° deviation of the Cl–Co–Cl angle from linearity in cation (1).

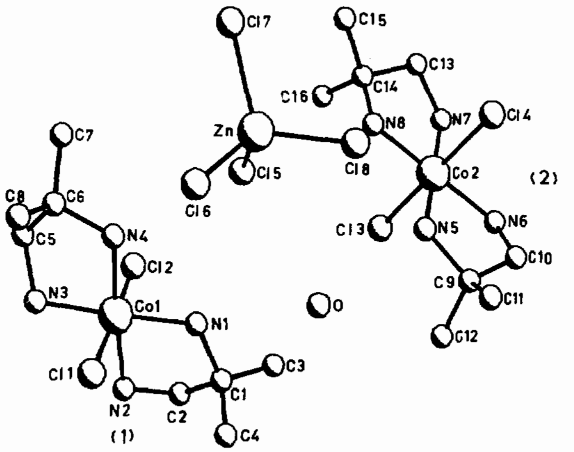

Fig. 4. A general view of one molecular unit of *cis-gem*-dimethyl-*trans*-$[CoCl_2(ibn)_2]_2ZnCl_4 \cdot H_2O$.

Although numerous single crystal X-ray structure analyses for *cis*- and *trans*-$CoX_2(diamine)^+$ salts are reported, the present salt type, [cation]$_2$-[anion], *i.e.* A_2B, is only poorly represented; δ,λ-*trans*-$[CoCl_2(en)_2]_2S_6O_6$ [13] is another obvious example.

Kinetic Data

Preliminary experiments showed that when green *t,t*- or *c,t*-$[CoCl_2(ibn)_2]ClO_4$ are dissolved in 1 M HCl solution, the colour changes from green to purple with excellent isosbestic points at 600, 466, 412 and 597, 466, 412 nm, respectively (Fig. 3). A similar green to pink colour change is observed in 0.1 M HNO_3, but the isosbestic points that were observed in 1 M HCl, slowly shift as the reaction proceeds. The observed colour changes can be interpreted in terms of the following reactions:

$$t\text{-}CoCl_2(ibn)_2^+ \xrightarrow{-Cl^-} c + t\text{-}CoCl(ibn)_2(OH_2)^{2+} \xrightarrow{-Cl^-}$$

$$c + t\text{-}Co(ibn)_2(OH_2)_2^{3+}$$

with the shift in isosbestic points in 0.1 M HNO_3 being due to the slow secondary solvolysis which is suppressed in 1 M HCl.

When HNO_3 containing Hg^{2+} is used as the solvent, there is a rapid reaction (within the time of transference to the spectrophotometer) to give, presumably *t,t*- or *c,t*-$Co(ibn)_2(OH_2)_2^{3+}$. This is followed by a slow isomerisation to give predominantly *cis* diaqua species. It should be noted that there are potentially three *cis* diaqua isomers; the *t,t-cis*-, *c,c-cis*- and *t,c-cis*-. Assuming an edgewise displacement for the isomerisation, the latter is generated uniquely from the *c,t*-precursor. The final *cis*-diaqua species from the *t,t*- or *c,t*-dichloro

TABLE II. Spectrophotometrically Determined First Order Rate Constants for the Loss of the First Chloro Ligand from *t,t*- and *c,t*-[$CoCl_2(ibn)_2$]ClO_4 in 1.0 M HCl.

T °C (K)	*t,t*-isomer		*c,t*-isomer	
	$10^3\,k_{obs}$	$10^3\,k_{calc}$[a]	$10^3\,k_{obs}$	$10^3\,k_{calc}$[a]
14.0	0.203 ± 0.011	0.193	0.714 ± 0.013	0.723
(287.2)				
17.8	0.360 ± 0.015	0.345	1.18 ± 0.05	1.20
(291.0)			1.27 ± 0.02	
25.0	1.12 ± 0.01	0.994	3.05 ± 0.02	3.07
(298.2)	1.10 ± 0.03[b]		2.96 ± 0.10	
27.3	1.35 ± 0.03	1.38	4.13 ± 0.04	4.10
(300.5)	1.38 ± 0.10		4.20 ± 0.10	
35.5	4.24 ± 0.04	4.25		
(308.7)	4.14 ± 0.06			

[a] Calculated from the activation parameters cited in Table III. [b] In 0.1 M HNO_3.

TABLE III. Kinetic Parameters for the Primary Hydrolysis Step of Some *t*-$CoCl_2(N_4)^+$ Complexes in Acidic Solution at 25.0 °C.

N_4	[H^+] (M)	$10^5\,k$ (s^{-1})	Ea (kJ mol^{-1})	$\Delta S^{\ddagger}_{298}$ ($JK^{-1}\ mol^{-1}$)	Ref.
$(NH_3)_4$	0.1	180	98.8	+36	a
$(en)_2$	0.01[b]	3.2	111.8	+44	c
	0.01	3.5	110	+58	d
$(pn)_2$	0.1	6.2	117	+58	f
t,t-$(ibn)_2$	1.0	99.4	106 ± 3	+45 ± 6	g
c,t-$(ibn)_2$	1.0	307	93.6 ± 2	+13 ± 4	g
(en)(tn)	0.3	39.6	101	+21	h
$(tn)_2$	?	5530	89	+29	i
$(N{-}Me{-}en)_2$[e]	0.01[b]	1.59	113	+36	c

[a] Ref. 14. [b] Ionic strength = 0.1 M. [c] Ref. 15. [d] Ref. 16. [e] The methyl groups are presumed to be in the *trans*-orientation. See Refs. 9 and 17. [f] Ref. 4. [g] This research. [h] Ref. 18. [i] Ref. 19.

precursors were similar in both peak positions (λ_{max} = 497, 358 nm) and intensity.

Rate constants for the loss of the first chloro ligand in both 0.1 M HNO_3 and 1.0 M HCl were within experimental error at 25.0 °C, and all rate data (Table II) have been measured in this latter medium. Activation parameters (Table III) were computer calculated from the variation of k_{obs} with temperature.

This *c,t*-isomer hydrolyses approximately three times faster than the *t,t*-analog and with apparently more stereochemical retention in the chloroaqua product, (Fig. 3). Nevertheless, the positive activation entropy observed is entirely consistent with Tobe's postulate [20] that some stereochemical change occurs for both isomers.

From the kinetic data reported here, it would appear that the sample used by Pearson *et al.* [4], for their kinetic studies, was considerably enriched with the *c,t*-isomer.

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