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Anionopentaaminecobalt(III) Complexes with Polyamine Ligands.
22. The Formation of a Novel Tridentate Ligand by Oxidative Deamination of 2-Methyl-1,2-diaminopropane

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Abstract

[CoCl(ibn)(L)]ZnCl$_4$ (ibn = $NH_2CH_2C(CH_3)_2NH_2$, L = $NH_2CH_2C(CH_3)_2N{=}CHC(CH_3)_2NH_2$) has been isolated from the reaction between dioxygen, $CoCl_2 \cdot 6H_2O$ and ibn in refluxing methanol. A single crystal X-ray structure of the dinitrate (trihydrate) salt shows that the tridentate ligand adopts a meridonal arrangement, and, in the remaining three octahedral sites, the unsymmetrical ibn ligand occupies a position such that the $-CH_2NH_2$ end is *trans* to the chloro ligand. Kinetic parameters for the Hg^{2+}, assisted loss of the coordinated chloro ligand from [CoCl(ibn)(L)]ZnCl$_4$($HClO_4$, $\mu = 1.0$ M) are $10^3\ k_{Hg}$ (298) = 1.33 $M^{-1}\ s^{-1}$, $E_a = 73.8$ kJ mol^{-1}, $\Delta S_{298}^{\ddagger} = -60.7$ J $K^{-1}\ mol^{-1}$.

Introduction

As part of a programme to investigate ligands with axial methyl groups that may be capable of oxidation [1], we have prepared several Co(III) complexes of 2-methyl-1,2-diaminopropane(ibn). Both *cis-trans-* and *trans-trans-*[CoCl$_2$(ibn)$_2$]ClO$_4$ can be isolated from the dioxygen oxidation of $CoCl_2 \cdot 6H_2O$ and ibn (1:2 mole ratio) at room temperature [2] and this paper describes the formation of an unexpected chloropentaaminecobalt(III) complex when the above reaction is performed at reflux temperature.

Experimental

2-Methyl-1,2-diaminopropane was purchased from Aldrich Chemical Co., and used as supplied. All other chemicals were the best Reagent Grade available. The complexes described in this section were washed with 2-propanol, then ether, and air dried.

Chloro(2-methyl-1,2-diaminopropane)(2,2,5,5-tetramethyl-1,4,7-triazahept-3-ene)cobalt(III)tetrachlorozinoate(II), [CoCl($NH_2C(CH_3)_2CH_2NH_2$)($NH_2CH_2C(CH_3)_2N{=}CHC(CH_3)_2NH_2$]ZnCl$_4$.

(A) Dioxygen was bubbled through a refluxing methanolic solution (100 ml) of $CoCl_2 \cdot 6H_2O$ (2.88 g) and 2-methyl-1,2-diaminopropane (3.04 g) for four h. Addition of HCl (12 M, 15 ml) and $HClO_4$ (60%, 5 ml) followed by warming and evaporation resulted in the isolation of green *trans-gem*-dimethyl-*trans*-[CoCl$_2$(ibn)$_2$]ClO$_4$ (4 g) [2]. $ZnCl_2$ (2 g) was added to the filtrate (~30 ml) and pink needles of [CoCl($C_{12}H_{31}N_5$)]ZnCl$_4$ deposited (1.5 g).

(B) Dioxygen was bubbled through a solution of 2-methyl-1,2-diaminopropane (3.04 g) in methanol (100 ml) under reflux. After 4 h, $CoCl_2 \cdot 6H_2O$ (2.88 g) in methanol (30 ml) was added and oxygenation and refluxing continued for a further two h. Addition of HCl (12 M, 10 ml) and $ZnCl_2$ (7.5 g) resulted in the precipitation of pink crystals. Two further crops of pink product were collected, with the final crop being contaminated with green *trans*-[CoCl$_2$(ibn)$_2$]$_2$ZnCl$_4 \cdot H_2O$ [2]. The pink products (3.5 g) were combined and recrystallised by dissolving in the minimum volume of 40 °C 0.1 M HCl, followed by the addition of an equal volume of 12 M HCl and solid $ZnCl_2$. *Anal.* Calcd. for [CoCl($C_{12}H_{31}N_5$)]ZnCl$_4$: C, 26.4; H, 5.67; N, 12.84%. Found: C, 27.21; H, 6.15; N, 12.86%. Visible absorption spectra (0.1 M HCl): λ (nm), (ε, $M^{-1}\ cm^{-1}$): max. 488.5 (124.7) min. 414 (40.0), max. 362.8 (107.3), min. 342.2 (82.5).

Nitro(2-methyl-1,2-diaminopropane)(2,2,5,5,-tetramethyl-1,4,7-triaza-3-ene)cobalt(III) tetrachlorozincate(II), [Co(NO_2)($NH_2C(CH_3)_2CH_2NH_2$)($NH_2CH_2C(CH_3)_2N{=}CHC(CH_3)_2NH_2$)]ZnCl$_4$.

Pink [CoCl(ibn)($NH_2CH_2C(CH_3)_2N{=}CHC(CH_3)_2NH_2$)]ZnCl$_4$ (0.5 g) was dissolved in water (10 ml) and $NaNO_2$ (0.5 g) was added. On warming (~60 °C), the solution changed colour from pink to yellow-orange. Addition of HCl (12 M, 1 ml) and $ZnCl_2$ (2 g) resulted in the slow (days) deposition of golden yellow needles (0.4 g). *Anal.* Calcd. for [Co(NO_2)-

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$(C_{12}H_{31}N_5)]ZnCl_4$: C, 25.85; H, 5.57; N, 15.08%. Found: C, 26.07; H, 5.87; N, 14.89%. Visible absorption spectra (0.1 M HCl): max. 451.6 (216.4), min. 396 (68.2).

^{13}C *NMR Spectra*

These were recorded in 0.1 M HCl with dioxane (67.39 p.p.m.) as an internal standard. Data for $[CoX(C_{12}H_{31}N_5)]ZnCl_4$: X = Cl: 184.95, 71.99, 67.99, 58.73, 58.08, 56.79, 27.07, 26.82, 26.49, 26.23, 25.60. X = NO_2: 185.73, 72.50, 58.21, 57.81, 56.61, 27.00, 26.12, 25.98. (5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane-1,8-diene)nickel(II) perchlorate in DMF has a ^{13}C NMR resonance at 183.29 p.p.m. attributed to the $-N{=}\underline{C}<$ carbon.

Kinetic Data

The rates of Hg^{2+} assisted chloride release from $[CoCl(C_{12}H_{31}N_5)]ZnCl_4$ dissolved in $HClO_4/Hg(NO_3)_2$ solution (μ = 1.0 M) were measured spectrophotometrically over a 23 °C temperature range. Preliminary studies showed excellent isosbestic points at 487, 411, 352 and 342 nm were maintained during the course of reaction, and 530 nm was the wavelength chosen to monitor the extent of reaction with time. Second order rate constants (k_{Hg}, M^{-1} s^{-1}) (Table I) and activation parameters were calculated as previously described [3].

X-ray Structural Analysis

$[CoCl(C_{12}H_{31}N_5)]ZnCl_4$ was converted to the nitrate salt by recrystallisation from 0.1 M HCl in the presence of $NaNO_3$. A dark red crystal (0.21 mm × 0.10 mm × 0.30 mm), shown to be $[CoCl(C_{12}H_{31}N_5](NO_3)_2 \cdot 3H_2O$, was used for the data collection. Intensity data were collected at room temperature on a Nicolet R3m four-circle diffractometer using graphite-monochromated MoKα radiation. The cell parameters were determined by least-squares refinement of 18 accurately centered reflections ($29 < 2\theta < 31°$) and found to be triclinic a = 8.789(3), b = 15.484(4), c = 8.853(4) Å, α = 90.03(3), β = 106.31(3), γ = 90.44(2)°. A total of 3514 reflections were collected using ω-scans ($3° < 2\theta < 45°$) and variable scan rates (4.9–29.3° min^{-1}). Crystal stability was monitored by recording 3 standards every 50 reflections and no significant variation was observed. Data reduction gave 3034 unique reflections of which 2264 with $I > 3[\sigma(I)]$ were used for subsequent structural analysis. Intensities were corrected for Lorentz polarisation effects and for absorption. Statistical analysis suggested the centrosymmetric space group $P\bar{1}$.

The Co and Cl atoms were located from Patterson calculations and the remaining non-hydrogen atoms were located from difference Fourier maps. Blocked cascade least-squares refinement with all the atoms anisotropic resulted in a conventional R value of 0.068. Hydrogen atoms were included at calculated positions using a riding model with C–H, N–H = 0.96 Å and the isotropic thermal parameters of the hydrogens fixed at 1.2 U of their carrier atoms. The refinement converged with R = 0.047 R_w = 0.051, the function minimised was $\Sigma w(|F_o| - |F_c|)^2$ where $w = [\sigma^2(F_o) + 0.00136\, F_o^2]^{-1}$. A final difference map showed no features greater than ±0.5 e^- Å^3. All the programmes used for data reduction and structure solution are included in the SHELXTL (Version 4.0) [4] package.

Atomic coordinates are listed in Table II and selected bond lengths and angles in Table III[‡].

[‡] Complete structural listings have been deposited with the Editor and can be obtained from DAH on request.

TABLE I. Observed and Calculated Rate Constants for the Hg^{2+}, Assisted Chloride Release from $[CoCl(C_{12}H_{31}N_5)]ZnCl_4$.

T (°C [K])	$[Hg^{2+}]_i$[a] (mM)	$[H^+]$[b] (M)	$10^3\, k_{obs}$[c] (s^{-1})	$10^3\, k_{Hg}$[d] ($M^{-1}\, s^{-1}$)	$10^3\, k_{Hg}$ calc[e] ($M^{-1}\, s^{-1}$)
25.0 [298.2]					1.33
40.2 [313.4]	64.5	0.82	3.96 ± 0.05	6.14 ± 0.08	5.65
	64.5	0.82	3.61 ± 0.2	5.59 ± 0.3	
	64.5	0.82	3.27 ± 0.06	5.07 ± 0.09	
52.7 [325.9]	64.5	0.82	10.5 ± 0.6	16.3 ± 0.9	16.7
	64.5	0.82	12.3 ± 0.2	19.1 ± 0.3	
	64.5	0.82	10.6 ± 0.3	16.4 ± 0.5	
63.2 [336.4]	64.5	0.82	24.3 ± 0.1	37.7 ± 0.2	39.2
	64.5	0.82	27.9 ± 0.6	43.3 ± 0.9	
	44.7	0.88	18.2 ± 0.5	40.7 ± 1.1	
	44.7	0.88	15.2 ± 0.2	34.0 ± 0.5	

[a] Initial $[Hg^{2+}]$, initial [Co(III)] ~ 1–5 m M. [b] $[HClO_4]$. [c] Observed pseudo-first-order rate constant. [d] $k_{Hg} = k_{obs}\, [Hg^{2+}]_i^{-1}$. [e] Calculated from the activation parameters: E_a = 73.8 ± 2.7 kJ mol^{-1}; $\Delta S_{298}^{\#}$ = −60.7 ± 5.4 J K^{-1} mol^{-1}.

TABLE II. Atom Coordinates (×10^4) for [CoCl($C_{12}H_{31}N_5$)]$(NO_3)_2 \cdot 3H_2O$.

Co	1851(1)	1935(1)	537(1)
Cl	654(2)	1230(1)	2129(2)
N(1)	2776(5)	2459(3)	−1015(4)
N(2)	1142(4)	1021(3)	−1042(4)
N(3)	3854(4)	1349(3)	1581(5)
N(4)	2589(5)	2776(3)	2107(5)
N(5)	−29(5)	2677(3)	−143(5)
C(1)	2894(6)	1808(3)	−2198(6)
C(2)	1449(5)	1220(3)	−2589(5)
C(21)	3(6)	1658(4)	−3656(6)
C(22)	1806(6)	396(3)	−3348(6)
C(3)	4816(6)	1852(4)	2993(6)
C(31)	5113(7)	1309(4)	4479(7)
C(32)	6397(6)	2135(4)	2728(7)
C(4)	3883(7)	2632(4)	3126(6)
C(5)	1543(6)	3527(3)	2138(6)
C(51)	1527(7)	3758(4)	3808(7)
C(52)	2128(7)	4291(4)	1372(7)
C(6)	−118(6)	3219(4)	1195(6)
		NO_3	
N(6)	3108(5)	9007(3)	911(5)
O(61)	3885(5)	9411(3)	180(5)
O(62)	3136(5)	8213(3)	965(6)
O(63)	2298(5)	9436(3)	1575(6)
		NO_3	
N(7)	3065(9)	6149(4)	3820(10)
O(71)	2532(7)	6416(4)	2459(8)
O(72)	2151(7)	6043(4)	4691(6)
O(73)	4471(7)	5937(4)	4286(9)
		H_2O	
O(1)	9124(5)	6085(3)	2607(5)
O(2)	6732(6)	4797(3)	2306(6)
O(3)	4645(5)	6186(3)	526(6)

TABLE III. Selected Bond Lengths (Å) and Bond Angles (°) in the CoCl($C_{12}H_{31}N_5$)$^{2+}$ Cation.

Co–Cl	2.259(2)	Co–N(1)	1.955(4)
Co–N(2)	1.960(4)	Co–N(3)	1.972(4)
Co–N(4)	1.878(4)	Co–N(5)	1.970(4)
N(1)–C(1)	1.478(7)	C(1)–C(2)	1.516(7)
C(2)–C(21)	1.519(7)	C(2)–C(22)	1.518(7)
C(2)–N(2)	1.500(7)	N(3)–C(3)	1.509(6)
C(3)–C(31)	1.523(8)	C(3)–C(32)	1.533(8)
C(3)–C(4)	1.488(8)	C(4)–N(4)	1.259(6)
C(4)–C(5)	1.493(7)	C(5)–C(51)	1.526(8)
C(5)–C(52)	1.520(8)	C(5)–C(6)	1.536(7)
C(6)–N(5)	1.472(7)		
Cl–Co–N(1)	173.9(1)	Cl–Co–N(2)	89.4(1)
N(1)–Co–N(2)	84.7(2)	Cl–Co–N(3)	89.7(1)
N(1)–Co–N(3)	91.7(2)	N(2)–Co–N(3)	93.5(2)
Cl–Co–N(4)	89.7(1)	N(1)–Co–N(4)	96.4(2)
N(2)–Co–N(4)	177.5(2)	N(3)–Co–N(4)	84.2(2)
Cl–Co–N(5)	88.6(1)	N(1)–Co–N(5)	91.2(2)
N(2)–Co–N(5)	97.8(2)	N(3)–Co–N(5)	168.6(2)
N(4)–Co–N(5)	84.5(2)	C(4)–N(4)–C(5)	124.7(4)
Co–N(4)–C(5)	117.9(3)	Co–N(4)–C(4)	117.2(4)
C(3)–C(4)–N(4)	120.1(5)		
Selected torsion angles			
N(1)–C(1)–C(2)–N(2)	−42.6(5)		
N(3)–C(3)–C(4)–N(4)	−3.3(7)		
N(4)–C(5)–C(6)–N(5)	−37.2(5)		

Results and Discussion

The formation of Co(III) amine complexes by aerial or dioxygen oxygenation of Co(II) solutions containing the amine is a well established preparative method. To succeed, it is assumed that the nitrogen ligand will not be affected by the reaction conditions.

The isolation of a red-pink tetrachlorozincate salt from the HCl/$ZnCl_2$ work up of an oxidised (O_2) solution of $CoCl_2 \cdot 6H_2O$ and 2-methyl-1,2-diaminopropane in refluxing methanol was quite unexpected. The visible absorption spectral changes observed on dissolving the complex in $HClO_4$ containing Hg^{2+} were fully consistent with the complex containing the $CoCl(N_5)^{2+}$ chromophore, as was the replacement of the chloro ligand by NO_2^- to give [$CoNO_2(N_5)$]$ZnCl_4$.

Both the chloro and nitro complexes have analytical data corresponding to [CoX($C_{12}H_{31}N_5$)]$ZnCl_4$, and the IR, ^{1}H and ^{13}C spectra indicate the presence of a –HC=N– group (IR stretch at 1660 cm^{-1}, ^{1}H resonance (D_2O) at 8.1 p.p.m., ^{13}C resonance (0.1 M HCl) at 185 p.p.m.). The formulation of the complexes as either [CoX(ibn)($NH_2C(CH_3)_2CH_2N{=}CHC(CH_3)_2$)]$ZnCl_4$ or [CoX(ibn)($NH_2CH_2C(CH_3)_2N{=}CHC(CH_3)_2NH_2$]$ZnCl_4$ is fully consistent with the spectroscopic and analytical data.

The formation of the tridentate ligand can be represented by the reaction scheme [5]

$$\begin{tikzcd} \mathrm{NH_2C(CH_3)_2CH_2NH_2} \arrow[r, "{[O]}"] & \mathrm{NH_2C(CH_3)_2CH{=}NH} \arrow[d, "\mathrm{H_2O}"] \\ & \mathrm{NH_2C(CH_3)_2CH{=}O + NH_3} \end{tikzcd}$$

followed by condensation of the resultant aminoaldehyde with a further ibn molecule, at either the NH_2–$C(CH_3)_2$–(unsymmetrical) or NH_2–CH_2–(symmetrical) end.

To establish which tridentate is formed, and which of the three possible topological forms for an octahedral complex with a mixed bidentate–tridental ligand combination [6] is adopted, a single crystal

X-ray structure of $[CoCl(C_{12}H_{31}N_5)](NO_3)_2 \cdot 3H_2O$ was performed.

The structure is shown in Fig. 1 with the tridentate ligand having the unsymmetrical condensation arrangement and the meridional topology. In this topology, there are end-for-end alternatives for the binding of the isolated ibn residue. The structure adopted is the one with the $-CH_2NH_2$ end *trans* to the coordinated chloro ligand.

Kinetic data for the rate of Hg^{2+}, assisted chloride release from $[CoCl(C_{12}H_{31}N_5)]ZnCl_4$ in $Hg^{2+}/HClO_4$ ($\mu = 1.0$ M) are presented in Table I. Using the cited activation parameters, we calculate 10^3 k_{Hg} (298) = 1.33 M^{-1} s^{-1}, very much slower than that reporded [7] for the complex shown in Fig. 2 (10^3 k_{Hg}(298) = 528 M^{-1} s^{-1}, $\mu \sim 2$ M).

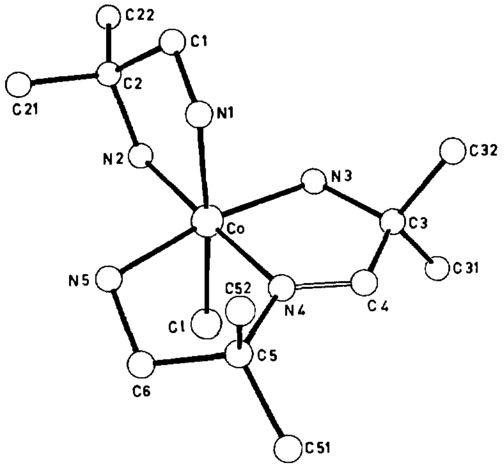

Fig. 1. A general view of the $CoCl(C_{12}H_{31}N_5)^{2+}$ cation, *mer*-chloro (2-methyl-1,2-diaminopropane)(2,2,5,5-tretramethyl-1,4,7-triazahept-3-ene)cobalt(III).

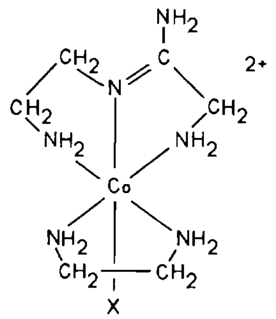

Fig. 2. The structure of the $CoX(C_6H_{20}N_5)^{2+}$ (X = Cl) cation, *sym-fac*-chloro (1,2-diaminoethane) (3-amino-1,4,7-triazahept-3-ene)cobalt(III) [8].

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