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Anionopentaaminecobalt(III) Complexes with Polyamine Ligands.
24. The Isolation and Structure of *mer*-[CoCl(tn)(1,5,9-triazanon-4-ene)]$ZnCl_4$

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Abstract

The title complex is obtained as a by-product from the synthesis of *trans*-$CoCl_2(tn)_2^+$ by dioxygen oxidation of Co(II) and the diamine in water at room temperature. A single crystal X-ray structure analysis shows that the tridentate Schiff's Base ligand adopts a meridional configuration and the remaining three octahedral sites are occupied by one bidentate tn ligand and one chloro ligand.

Introduction

In 1978 we reported that an uncharacterised red crystalline product could be isolated from the mother liquors of our procedure for the synthesis of *trans*-$CoCl_2(tn)_2^+$ [1]*. This material had all the characteristics of a chloro pentaamminecobalt(III) complex and could be crystallised as either the perchlorate [1] or tetrachlorozincate(II) salts [2].

More recently, we have found that the oxidation of Co(II) and various diamines (1:2 mole ratio) results in the formation of chloropentaamines with general composition *mer*-CoCl(diamine) $(\text{triamine})^{2+}$, as well as the expected *trans*-$CoCl_2(\text{diamine})_2^+$. The triamine is a tridentate aliphatic Schiff's Base ligand, and is thought to be formed by oxidative deamination of 1 mol of diamine, followed by condensation of the resultant amino aldehyde, either *in situ* or by using the metal ion as a template, with a 2nd mol of diamine.

Thus we have prepared *mer*-$CoCl(ibn)(NH_2CH_2C(CH_3)_2N{=}CHC(CH_3)_2NH_2)^{2+}$ [3], *mer*-$CoCl(2,2\text{-}Me_2tn)(NH_2CH_2C(CH_3)_2CH_2N{=}CHC(CH_3)_2CH_2NH_2)^{2+}$ [2] and *mer*-$CoCl(en)NH_2CH_2CH_2N{=}CHCH_2NH_2)^{2+}$ [4]. The complexes exhibit an IR band at about 1660 cm^{-1} and a ^{13}C resonance at ~184 ppm, both characteristic of the >C=N– functional group.

This paper shows that the red chloropentaamine complex isolated when the diamine used is tn, is quite analogous and can be formulated as *mer*-$[CoCl(tn)(NH_2CH_2CH_2CH_2N{=}CHCH_2CH_2NH_2)]^{2+}$.

Experimental

mer-chloro(1,3-diaminopropane)(1,5,9-triazanon-4-ene)cobalt(III) Tetrachlorozincate(II)

We previously isolated the perchlorate salt of this complex by slow evaporation of the mother liquors from the synthesis of *trans*-$[CoCl_2(tn)_2]ClO_4$ [1]. This same complex is more easily obtained as the less soluble $ZnCl_4^{2-}$ salt, by adding $ZnCl_2$ to the warm (60 °C) mother liquor, after removal of the *trans*-$[CoCl_2(tn)_2]ClO_4$. One or two recrystallisations from HCl, by the addition of $ZnCl_2$ are sufficient to remove any contaminating green *trans*-$[CoCl_2(tn)_2]_2ZnCl_4$ that sometimes deposits with the chloropentaamine. The following single crystal X-ray structural analysis shows the $ZnCl_4^{2-}$ salt to have the elemental composition $[CoCl(C_9H_{25}N_5)]ZnCl_4$ and to be *mer*-$[CoCl(NH_2(CH_2)_3NH_2)(NH_2(CH_2)_3N{=}CH(CH_2)_2NH_2)]ZnCl_4$.

The ^{13}C NMR spectrum of the $ZnCl_4^{2-}$ salt in water is complicated by hydrolysis of the chloro ligand during the data collection (poor solubility prevented the use of aqueous HCl or DMF as solvents). Nevertheless, a nine carbon spectrum is quite apparent and the >C=N– carbon has a resonance at 183.2 ppm relative to dioxane at 67.4 ppm. Visible absorption spectra (0.1 M HCl) λ (nm); (ϵ, M^{-1} cm^{-1}): 550 max (54.5), ~500sh (~52), 422 min (14.3), 370 max (73.4), 340 min (46.8).

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*Abbreviations used: en = $NH_2(CH_2)_2NH_2$, tn = $NH_2(CH_2)_3NH_2$, ibn = $NH_2C(CH_3)_2CH_2NH_2$, 2,2-Me₂tn = $NH_2CH_2C(CH_3)_2CH_2NH_2$, dien = $NH_2(CH_2)_2NH(CH_2)_2NH_2$, dpt = $NH_2(CH_2)_3NH(CH_2)_3NH_2$.

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X-ray Structural Analysis

Table I summarises the crystal data and details of the data collection and structure refinement procedures. SHELX-76 [5] was used for all calculations and complex neutral-atom scattering factors were taken from ref. 6.

Final positional parameters are given in Table II and selected bond distances and angles in Table III (see also 'Supplementary Material').

TABLE I. Summary of Crystal Data, Intensity Collection, Structure, Solution and Refinement for [$\mathrm{CoCl(C_9H_{25}N_5)}$]$\mathrm{ZnCl_4}$

Formula	$\mathrm{C_9H_{25}N_5CoCl_5Zn}$
M_r (Dalton)	504.90
Space group	*Pn*
a (Å)	9.270(3)
b (Å)	9.196(1)
c (Å)	11.086(2)
α (°)	90.0
β (°)	102.84(3)
γ (°)	90.0
Z	2
V (Å^3)	921.5
D_c (g cm^{-3})	1.820
F(000)	484
Instrument	Enraf-Nonius CAD4
Radiation (Å)	Mo Kα, 0.7107
μ (Mo Kα) (cm^{-1})	11.46
Scan type	θ–2θ
Reflections measured	±*h*,*k*,*l*
θ max (°)	24
Unique total data	1554
Data in refinement [$F_o > 2\theta > (F_o)$]	1381
Atoms/asymmetric unit	21
Number of variables	190
Phasing technique	Patterson
R	0.051
R_w	0.0615

TABLE II. Atom Coordinates for [$\mathrm{CoCl(C_9H_{25}N_5)}$] $\mathrm{ZnCl_4}$

Atom	*x*/*a*	*y*/*b*	*z*/*c*
Co	−0.0608(2)	0.6173(2)	−0.2757(2)
Cl(1)	0.0651(4)	0.5056(4)	−0.1001(3)
N(1)	−0.1573(13)	0.4313(13)	−0.3338(11)
N(2)	0.1112(12)	0.5754(13)	−0.3526(10)
N(3)	0.0196(13)	0.8053(15)	−0.2070(11)
N(4)	−0.2201(13)	0.6494(13)	−0.1868(10)
N(5)	−0.1629(13)	0.7119(13)	−0.4312(10)
C(1)	−0.0934(17)	0.3374(16)	−0.4211(14)
C(2)	0.0669(16)	0.3147(17)	−0.3691(14)
C(3)	0.1530(15)	0.4492(18)	−0.3755(13)
C(4)	0.2060(15)	0.6904(17)	−0.3827(13)
C(5)	0.2485(18)	0.8084(20)	−0.2824(17)
C(6)	0.1194(17)	0.8964(18)	−0.2604(14)
C(7)	−0.3318(17)	0.7632(17)	−0.2193(14)
C(8)	−0.3929(15)	0.7695(18)	−0.3591(13)
C(9)	−0.2809(15)	0.8208(17)	−0.4301(13)
Zn	0.0574(2)	0.8137(2)	0.2766(2)
Cl(2)	0.0112(5)	0.5771(4)	0.3175(4)
Cl(3)	0.3083(5)	0.8574(5)	0.3196(4)
Cl(4)	−0.0375(4)	0.9564(4)	0.4041(3)
Cl(5)	−0.0479(6)	0.8502(6)	0.0742(4)

(continued)

TABLE II *(continued)*

TABLE III. Selected Bond Lengths, Bond Angles and Torsion Angles for [$\mathrm{CoCl(C_9H_{25}N_5)}$]$\mathrm{ZnCl_4}$

Bond lengths (Å)

Co–Cl(1)	2.280(4)	N(5)–C(9)	1.485(19)
Co–N(1)	1.971(12)	C(1)–C(2)	1.484(21)
Co–N(2)	2.006(12)	C(2)–C(3)	1.482(22)
Co–N(3)	1.967(13)	C(4)–C(5)	1.541(23)
Co–N(4)	1.971(13)	C(5)–C(6)	1.508(25)
Co–N(5)	1.975(11)	C(7)–C(8)	1.528(20)
N(1)–C(1)	1.513(21)	C(8)–C(9)	1.511(22)
N(2)–C(3)	1.267(20)	Zn–Cl(2)	2.282(4)
N(2)–C(4)	1.460(20)	Zn–Cl(3)	2.304(4)
N(1)–C(1)	1.513(21)	Zn–Cl(4)	2.246(4)
N(3)–C(6)	1.467(22)	Zn–Cl(5)	2.264(4)
N(4)–C(7)	1.460(17)		

Bond angles (°) about Co, N(2) and Zn

N(1)–Co–Cl(1)	89.9(3)	N(3)–Co–N(4)	86.4(5)
N(2)–Co–Cl(1)	88.4(3)	N(3)–Co–N(5)	91.0(5)
N(3)–Co–Cl(1)	89.3(4)	N(4)–Co–N(5)	96.0(5)
N(4)–Co–Cl(1)	86.5(3)	Co–N(2)–C(4)	122.2(1.0)
N(5)–Co–Cl(1)	177.5(4)	Co–N(2)–C(3)	124.6(1.1)
N(1)–Co–N(2)	92.3(5)	C(3)–N(2)–C(4)	113.1(1.3)
N(1)–Co–N(3)	173.9(6)	Cl(3)–Zn–Cl(2)	110.5(2)
N(1)–Co–N(4)	87.6(5)	Cl(4)–Zn–Cl(2)	108.4(2)
N(1)–Co–N(5)	90.1(5)	Cl(4)–Zn–Cl(3)	106.7(2)
N(2)–Co–N(3)	93.7(5)	Cl(5)–Zn–Cl(2)	106.2(2)
N(2)–Co–N(4)	174.9(4)	Cl(5)–Zn–Cl(3)	111.8(2)
N(2)–Co–N(5)	89.1(5)	Cl(5)–Zn–Cl(4)	113.2(2)

Selected torsion angles (°) and ring assignment[a]

Co–N(1)–C(1)–C(2)	51.6	A
Co–N(3)–C(6)–C(5)	−50.9	B
Co–N(4)–C(7)–C(8)	44.9	C
Co–N(5)–C(9)–C(8)	−48.0	C
Co–N(2)–C(4)–C(5)	42.9	B
Co–N(2)–C(3)–C(2)	10.9	A
N(4)–C(7)–C(8)–C(9)	−67.9	C
C(7)–C(8)–C(9)–N(5)	70.8	C
C(4)–C(5)–C(6)–N(3)	66.6	B
N(1)–C(1)–C(2)–C(3)	−71.6	A
N(2)–C(4)–C(5)–C(6)	−64.4	B
C(1)–C(2)–C(3)–N(2)	40.8	A

[a] Ring A = fused six-membered ring with the double bond; ring B = fused six-membered ring without the double bond; ring C = isolated six-membered ring.

Results and Discussion

The single crystal X-ray structural analysis of the red by-product from the *trans*-$CoCl_2(tn)_2^+$ synthesis shows that it is indeed analogous to similar chloropentaaminecobalt(III) complexes believed to be formed by the oxidative deamination of a bidentate diamine ligand [3, 4].

The structure consists of discrete $CoCl(C_9H_{25}N_5)^{2+}$ cations and $ZnCl_4^{2-}$ anions. Within the cation, three N atoms are linked to form the tridentate 1,5,9-triazanon-4-ene Schiff's base which is coordinated in the meridional topology. The remaining three sites of the octahedron are occupied by a bidentate 1,3-diaminopropane and a chloro ligand (Fig. 1). Within the tridentate ligand, the >C=N– distance is 1.24 Å and the N–Co distance at this site (Co–N(2) = 2.01 Å) is slightly larger than the mean of the other four N-donor atoms (1.97 Å). Corresponding bond lengths in the related ibn complex [3] are 1.26, 1.88 and 1.96 Å, where the Co–N(imine) distance is considerably shorter than the mean Co–N(amine) distance.

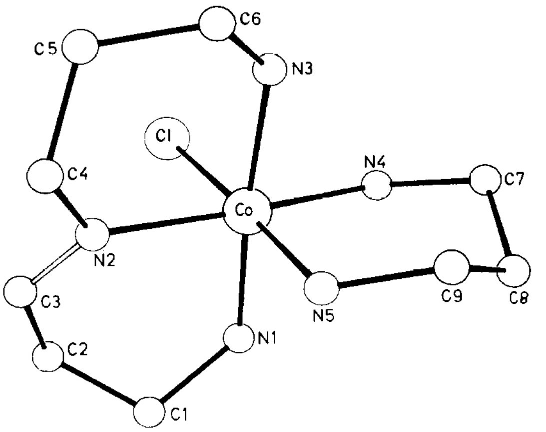

Fig. 1. Structure of the $[CoCl(C_9H_{25}N_5)]^{2+}$ cation, hydrogen atoms are excluded for clarity.

The isolated six-membered 1,3-diaminopropane ring and the fused six-membered ring not involved in Schiff's base formation both adopt slightly distorted chair conformations, but the fused six-membered ring containing the imine function is considerably twisted. This is reflected in the Co–N(2)=C(3)–C(2) torsion angle of 10.9° when compared with the Co–N(2)–C(4)–C(5) torsion angle of 42.9°. Even so, there is quite close similarity to the ring conformations found here for the tridentate Schiff's base, and those adopted by fully saturated dpt ligand in the *mer* configuration [7, 15]. The $ZnCl_4^{2-}$ shows no unusual structural properties [7–14].

In aqueous acidic solution (0.1 M HNO_3) the $CoCl(C_9H_{25}N_5)^{2+}$ cation slowly aquates to form the $Co(C_9H_{25}N_5)(OH_2)^{3+}$ cation ($k_H = 10.4 \times 10^{-5}$ s^{-1} at 25 °C) with isosbestic points at 510, 415 and 363 nm. The same final product is generated more rapidly in the presence of Hg^{2+}. The thermal aquation rate constant can be compared with that obtained for *mer*-$CoCl(tn)(dpt)^{2+}$ ($k_H = 1.74 \times 10^{-5}$ s^{-1} at 25 °C) [15], a complex of similar topology, but without the Schiff's base functional group. Thus the >C=N– group appears to have a minor labilising effect on the coordinated chloro ligand, a point noted previously [4].

Supplementary Material

Tables of final observed and calculated structure factors, anisotropic thermal parameters, etc. have been deposited with the Editor-in-Chief and are available from author M.Z. on request.

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