195. Aniono-pentaaminecobalt(III) Complexes with Polyamine Ligands

Part 23[1])

A Chloropentaamine By-product from the Preparation of the *trans*-$CoCl_2(en)_2^+$ Cation

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Dedicated to Prof. Dr. *Silvio Fallab* on the occasion of his 60th birthday

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The isolation and characterisation of $[CoCl(en)(L)]ZnCl_4$, L = $NH_2CH_2CH{=}NCH_2CH_2NH_2$ (1,4,7-triaza-hept-3-ene), as a by-product (~ 8% yield) from the H_2O_2 synthesis of *trans*-$CoCl_2(en)_2^+$, is described.

Introduction. – The $CoCl_2(en)_2^+$ cation[3]) has played an important role in establishing the octahedron as the major structural entity for Co(III) complexes. With such a ligand combination, in octahedral stereochemistry, both *cis*- and *trans*-isomers should exist, and routes for their synthesis were designed by *Werner* [2]. Essentially, Co(II) and the diamine in dilute aqueous solution were oxidised by air, and green *trans*-$[CoCl_2(en)_2]Cl \cdot HCl \cdot 2H_2O$ [2] was isolated after addition of HCl and concentrating to a small volume. Concentration of acid-free solutions of $CoCl_2(en)_2^+$ led to the isolation of violet *cis*-$[CoCl_2(en)_2]Cl$.

The preparation of those isomers is now regularly performed in many undergraduate laboratories [3], and more recently, H_2O_2 has been the preferred oxidising agent, as the preparation time is considerably shortened [4]. A yield of ~ 65% can be obtained for *trans*-$CoCl_2(en)_2^+$ using this procedure, and some $Co(en)_3^{3+}$ is also formed [4].

High yields can only be expected, if it is assumed that the ligand remains inert to the oxidising agent used. Recently, we have had cause to question this assumption [1], as the dioxygen oxidation of Co(II) and ibn[3]) in MeOH leads to considerable quantities of *mer*-$CoCl(ibn)(T)^{2+}$, where T is a tridentate *Schiff*'s base ligand, $NH_2CH_2C(CH_3)_2N{=}CHC(CH_3)_2NH_2$. This ligand is believed to be formed by oxidative deamination of 1 mol of diamine, followed by condensation of the resultant amino-aldehyde with a further mole of diamine [1].

We describe here the isolation of a similar complex $CoCl(en)(L)^{2+}$, L = $NH_2CH_2CH{=}NCH_2CH_2NH_2$, as a by-product from the H_2O_2 method [4] for the synthesis of *trans*-$CoCl_2(en)_2^+$.

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[3]) Abbreviations: en = $NH_2(CH_2)_2NH_2$, ibn = $NH_2CH_2C(CH_3)_2NH_2$, 2,2-Me_2tn = $NH_2CH_2C(CH_3)_2CH_2NH_2$, dien = $NH_2(CH_2)_2NH(CH_2)_2NH_2$.

Experimental. – The method of *Krishnamurthy* [4] was followed on a ½ scale, with $NH_2CH_2CH_2NH_2$ and H_2O_2 successively added dropwise to the ice-cooled Co(II) soln. After addition of HCl, the soln. was maintained at 60–70° for 10 min and $HClO_4$ (15 ml, 70%) was added. Green crystals of *trans*-$[CoCl_2(en)_2]ClO_4$ rapidly deposited from the hot soln. and the mixture was cooled in an ice bath for 30 min. The green solid was removed by filtration (*Caution:* perchlorate salts are potentially explosive) and the mother liquor was retained. After washing with i-PrOH and air drying, the yield of *trans*-$[CoCl_2(en)_2]ClO_4$ was 9.3 g (64%, based on the amount of en used). The orange-pink mother liquor was heated to 50° and 10 g of $ZnCl_2$ stirred in. On cooling in ice, 1.1 g (8%, based on the en used) of brick-red crystals were collected by filtration and washed with acetone.

The crude product was recrystallised by dissolving it in 0.1M HCl (25 ml/1 g) at 50–60° and adding 12M HCl (½ the volume of 0.1M HCl) and $ZnCl_2$ (2 g/1 g). Brick-red crystals deposited from the hot soln., and, after cooling the sol. in ice, these were collected, washed with acetone and air dried. The recovery was 85–90%. UV/VIS (λ(nm), (ε, [$M^{-1}cm^{-1}$]); 0.1M HNO_3): ~ 520 sh (~ 79), 470 max. (102.7), 402 min. (39.1), 358 max. (94.5), 327 min. (61.6). ^{13}C-NMR (H_2O, ppm relative to dioxane at 67.39 ppm): 181.84, 57.24, 47.29, 46.30, 45.86. Anal. calc. for $[CoCl(C_6H_{19}N_5)]ZnCl_4$: C 15.57, H 4.14, N 15.13; found: C 15.50, H 4.12, N 15.02.

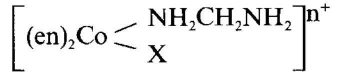
The $Co(C_6H_{19}N_5)(OH_2)^{3+}$ cation was generated in soln. by Hg^{2+}-assisted chloride release. Weighed amounts of $[CoCl(C_6H_{19}N_5)]ZnCl_4$ were dissolved in a soln. containing 3.00×10^{-2}M $Hg(Ac)_2$ and 0.9M HNO_3 ($\mu = 1.0$M). The colour slowly changed from orange-pink to yellow and final visible absorption spectral parameters were recorded after 4 h at r.t.: 458 max. (122.0), 390 min. (33.8), 345 max. (90.6). During the course of this reaction, excellent isosbestic points were maintained at 488, 400, and 345 nm, and 460 nm was chosen as the wavelength to monitor the reaction rate.

Repeating the synthesis on a 2× *Krishnamurthy* scale produced 35 g of *trans*-$[CoCl_2(en)_2]ClO_4$ (60%) and 3.4 g (7.3%) of crude $[CoCl(C_6H_{19}N_5)]ZnCl_4$ giving 3.0 g of the pure product on recrystallisation.

Results and Discussion. – The first indication that a chloropentaamine by-product could be obtained from the conventional H_2O_2 synthesis [4] of *trans*-$CoCl_2(en)_2^+$, was the observation of a brick-red contaminant, when the green cation was isolated as the $ZnCl_4^{2-}$ salt, rather than the normal $[Cl \cdot HCl \cdot 2H_2O]^-$ or ClO_4^- salts [6]. The *trans*-$[CoCl_2(en)_2]_2ZnCl_4$ was 'washed out' with 3M HCl and the remaining brick-red solid recrystallised from 0.1M HCl by addition of HCl and $ZnCl_2$. Subsequent modification (*Experimental*) by removal of the *trans*-$CoCl_2(en)_2^+$ cation as the perchlorate salt, before addition of $ZnCl_2$, allowed a higher yield to be obtained.

The brick-red salt has the elemental composition $[CoCl(C_6H_{19}N_5)]$ $ZnCl_4$. The IR spectrum shows a strong band at 1680 cm^{-1} and the ^{13}C-NMR spectrum (6 C atoms) has a resonance at 181.84 ppm, both indicating a >C=N– functional group. Thus, by analogy with the related ibn complex, whose crystal structure has been determined [1], we are confident that the complex can be formulated as $[CoCl(en)(NH_2CH_2CH{=}NCH_2CH_2NH_2)]ZnCl_4$.

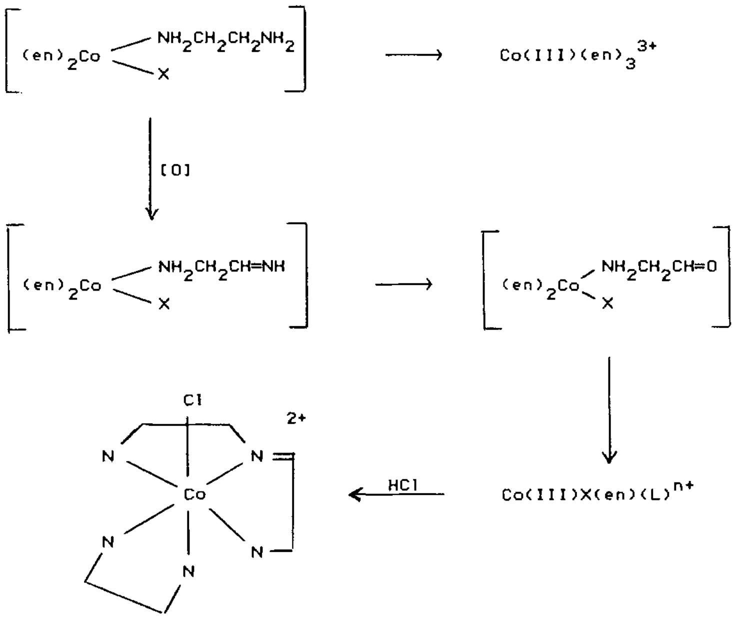
The mechanism for the formation of the tridentate *Schiff*'s base ligand by oxidative deamination is more speculative. We would not expect the free tridentate ligand to have more than a transitory existence in aqueous alkaline solution, as such aliphatic *Schiff*'s bases are known to be rapidly hydrolysed [7]. However, *Gainsford* and *Sargeson* [8] have shown that coordinated amino-aldehydes will condense with adjacent NH_2 groups under such conditions and the following *Scheme* could account for the formation of the various by-products. The key intermediate [9] is



$$\left[(en)_2Co \begin{matrix} \diagup NH_2CH_2NH_2 \\ \diagdown X \qquad\qquad \end{matrix}\right]^{n+}$$

(n = 2 if $X = OH^-$) which can either cyclise to give $Co(en)_3^{3+}$, be oxidised to give the coordinated amino-aldehyde, or condense with an additional $Co(en)_2X_2^{m+}$ unit to form $(en)_2CoCl(en)CoCl(en)_2^{4+}$ [5].

Scheme



$X = OH^-$ or OH_2, $L = NH_2CH_2CH{=}NCH_2CH_2NH_2$. The oxidation state of Co in the intermediates (square brackets) is uncertain.

In all cases where the configuration has been established [8], the final condensation of the coordinated amino-aldehyde has resulted in a *meridional* configuration at the imine N atom. We thus propose a *meridional* configuration for the tridentate *Schiff*'s base ligand in $[CoCl(en)(L)]ZnCl_4$.

One intriguing aspect of this work is the question as to why this particular product has not been detected earlier. Obviously, the key to the isolation has been the use of an appropriate anion, and we have found previously that the tetrachlorozincate(II) ion is eminently suitable for divalent cations.

Table. *Kinetic Data for the Rate of Hg^{2+}-Assisted Chloride Release from Some CoCl(diamine)(triamine)$^{2+}$ Complexes* (25°, μ = 1.0 M)

Diamine	Triamine	Configuration	$10^3 \times k_{Hg}$ [$M^{-1}s^{-1}$]	Ref.
en	$NH_2CH_2CH{=}NCH_2CH_2NH_2$	*mer*	24.3	a)
ibn	$NH_2CH_2C(CH_3)_2N{=}CHC(CH_3)_2NH_2$	*mer*	1.33	[1]
en	$NH_2CH_2CH_2N{=}C(NH_2)CH_2NH_2$	*sym-fac*	528b)	[12]
2,2-Me$_2$-tn	$NH_2CH_2C(CH_3)_2CH{=}NCH_2C(CH_3)_2CH_2NH_2$	*mer*	c)	[10]
en	$NH_2CH_2CH_2N{=}C(CH_3)CH_2C(CH_3)_2NH_2$	*mer?*	366	[10]
en	dien	*mer*	5.21	[12]
tn	$NH_2CH_2CH_2CH{=}NCH_2CH_2CH_2NH_2$	*mer*	c)	[10]

a) This work.
b) $\mu \approx 2$M.
c) Not yet measured.

The trapping of tridentate *Schiff*'s base ligands by Co(III) after oxidative deamination of a diamine, during the synthesis of *trans*-$CoCl_2(diamine)_2^+$ complexes, appears to be rather general. We have previously obtained CoCl(diamine)(tridentate *Schiff*'s base)$^{2+}$ complexes where the diamine is $NH_2CH_2C(CH_3)_2NH_2$ [1], $NH_2CH_2C(CH_3)_2CH_2NH_2$ [10], $NH_2(CH_2)_3NH_2$ [10] [11], and now $NH_2(CH_2)_2NH_2$. For the first three ligands, dioxygen can be used as the oxidising agent, but for en, H_2O_2 is required. Second-order rate constants (k_{Hg}, $M^{-1}s^{-1}$) for the rate of Hg^{2+}-assisted chloride release from several *mer*-CoCl(bidentate)(tridentate)$^{2+}$ polyamine complexes are presented in the *Table*. The introduction of a >C=N– group in the tridentate skeleton appears to cause a rate increase of approximately 5 ($NH_2CH_2CH_2NHCH_2CH_2NH_2$ relative to $NH_2CH_2CH{=}NCH_2CH_2NH_2$), but we do not have sufficient data to see if this is a general trend.

Note Added in Proof. – Recently M. Yashiro, A. Shimada, T. Usui, S. Yano, K. Kobayashi, T. Sakurai and S. Yoshikawa (*J. Am. Chem. Soc.* **1985**, *107*, 4351) have described a system where a C–N bond is formed by attack of an imine on a deprotonated Co–N group. Direct imine attack in the above *Scheme* is also possible.

I thank Prof. *S. Fallab* for research facilities and the *New Zealand University Grants Committee* for the award of a *Claude McCarthy Fellowship*. It is perhaps appropriate that the by-product described in this paper was first isolated in Switzerland, the home of *Alfred Werner*, who worked extensively with *trans*-$CoCl_2(en)_2^+$ [2].

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