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Acidopentaminecobalt(III) Complexes with Polyamine Ligands. V. The Isomers of the $Co(en)(ABA)Cl^{2+}$ Ions

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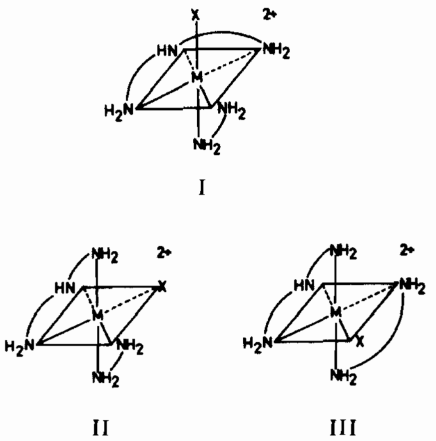
The alleged γ–[Co(en)(dpt)Cl]ZnCl₄ and ε–[Co(en)(dien)Cl]ZnCl₄ isomers are shown to be approximately 73-27% mixtures of the $ZnCl_4^{2-}$ salts of the α-chloro plus α-nitro and π-chloro plus π-nitro isomers, respectively.

Introduction

In previous parts[2-5] of this series, we reported the synthesis, properties and structure of three $[Co(en)(dpt)Cl]ZnCl_4$ (α, β, γ)[2,6] and four $[Co(en)(dien)Cl]ZnCl_4$ (π, ε, ω, ϰ) isomers. These isomers were distinguished on the basis of infrared and visible absorption spectral measurements.

There are potentially three distinct geometrical configurations for these cations (Figure 1). In addition, there exists the possibility of conformational isomerism for isomer I. This arises from the kinetically inert proton (in acid solution) on the secondary nitrogen of the peripheral tridentate ligand (dien or dpt). This type of conformational isomerism is not possible for isomers II and III (Figure 1) with dien in a facial arrangement, but for the more flexible dpt ligand, both normal (as for dien) and inverted configurations of the NH proton are possible.[7] Unfortunately, no dpt complexes in the facial configuration have yet been characterised, and the most favourable conformation has not been established.



I

II

III

Figure 1. The three possible geometric forms of the $Co(en)(ABA)X^{n+}$ cation. Conformational isomers are not distinguished in these diagrams.

Single crystal X-ray analysis of $α–[Co(en)(dpt)Cl]I_2 \cdot H_2O$,[5] $β–[Co(en)(dpt)Cl]ZnCl_4$,[4] ϰ– and $π–[Co(en)(dien)Cl]ZnCl_4$,[8] and $ω–[Co(en)(dien)Cl]Cl_2 \cdot ½H_2O$[9] show that the α– and $β–Co(en)(dpt)Cl^{2+}$ isomeric cations are of type I (Figure 1) and related by inversion at the secondary nitrogen center of the peripheral dpt ligand.[4,5] The π– and $ω–Co(en)(dien)Cl^{2+}$ isomeric cations are of type II and III (Figure 1) respectively, while the $ϰ–Co(en)(dien)Cl^{2+}$ cation is of type I with the NH proton remote from the Cl ligand.

We had noticed previously[2,3] that the infrared spectra and X-ray powder diffraction patterns of the pairs γ– and $α–[Co(en)(dpt)Cl]ZnCl_4$ and ε– and $π–[Co(en)(dien)Cl]ZnCl_4$ were very similar, but there were considerable differences in the visible absorption spectrum. Preliminary single crystal X-ray studies on these compounds showed that the γ:α (both as the chloride and tetrachlorozincate salts) and ε:π pairs had identical space groups and cell dimensions and were crystallographically indistinguishable (Table I).

An appraisal of the synthetic methods used to prepare the γ and ε forms revealed that in both cases nitro complexes were used as intermediates and it was apparent from an examination of the visible absorption spectrum that these forms were mixtures of the known α–chloro plus α–nitro[10] and π–chloro plus π–nitro complexes respectively (Figures 2 and 3). Analysis of the spectral parameters of «$γ–[Co(en)(dpt)Cl]ZnCl_4$» and «$ε–[Co(en)(dien)Cl]ZnCl_4$» indicate that these are the $α–[Co(en)(dpt)Cl]ZnCl_4$ and $π–[Co(en)(dien)Cl]ZnCl_4$ isomers containing about 27% of the corresponding nitro isomers, respectively (Figures 2 and 3).

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[1] Author to whom correspondence should be addressed.

[2] Part I, A. R. Gainsford and D. A. House, *Inorg. Chim. Acta*, *3*, 33 (1969).

[3] Part II, A. R. Gainsford and D. A. House, *Inorg. Chim. Acta*, *3*, 437 (1969).

[4] Part III, P. R. Ireland, D. A. House and W. T. Robinson, *Inorg. Chim. Acta*, *4*, 137 (1970).

(5) Part IV, D. A. House, P. R. Ireland, I. E. Maxwell and W. T. Robinson, *Inorg. Chim. Acta*, *5*, 397 (1971).

(6) Abbreviations used: en = $NH_2(CH_2)_2NH_2$, dien = $NH_2(CH_2)_2NH(CH_2)_2NH_2$, dpt = $NH_2(CH_2)_3NH(CH_2)_3NH_2$.

(7) This point is not clear in reference 5

(8) A.R. Gainsford, D.A. House, and W.T. Robinson, *Inorg. Chim. Acta*, *5* 595 (1971).

(9) J. Johnston, M.Sc. Thesis, Victoria University of Wellington, New Zealand, 1969; *Z. Krist.*, *131*, 155 (1970).

(10) This complex was previously assigned as γ-nitro in reference 2.

Table I. Crystallographic Data for Some [Co(en)(ABA) X]$ZnCl_4$ Isomers.[a].

ABA	Isomer[b]	X	Crystal System,	Space Group	Z	a(Å)	b(Å)	c(Å)	β	Reference
dpt	α	NO_2	Orthorhombic,	Pma2 or $Pma2_1$	2	8.73	6.74	15.35	—	This work
dpt	α	Cl	Hexagonal,	$P6_3$	6	14.60	14.60	14.83	—	This work
dpt	γ	Cl	Hexagonal,	$P6_3$	6	14.60	14.60	14.83	—	This work
dpt	α[c]	Cl	Orthorhombic,	Pma2 or $Pma2_1$	4	12.52	7.26	14.84	—	This work
dpt	γ[c]	Cl	Orthorhombic,	Pma2 or $Pma2_1$	4	12.52	7.24	14.76	—	This work
dpt	α[d]	Cl	Orthorhombic,	$Pna2_1$	4	14.49(1)	9.123(6)	13.27(1)	—	5
dpt	β	Cl	Monoclinic,	$P2_1/c$	4	7.875(3)	15.824(11)	14.748(8)	94.69(5)°	4
dien	π	NO_2	Monoclinic,	$P2_1/n$	4	10.91	18.10	8.42	75° 10′	This work
dien	π	Cl	Monoclinic,	$P2_1/n$	4	13.745(3)	8.202(2)	15.117(6)	98.557(14)°	8
dien	ε	Cl	Monoclinic,	$P2_1/n$	4	13.73	8.25	15.05	98° 35′	This work
dien	ϰ	Cl	Monoclinic,	Cc	4	9.676(1)	12.790(2)	13.888(3)	93.629(14)°	8
dien	ω	Cl	Orthorhombic,	$Pna2_1$	4	14.86	7.85	14.32	—	9
dien	ω[e]	Cl	Monoclinic,	Cc	4	14.44	7.87	12.30	100.1°	9
dien	ω[d]	I	Monoclinic,	C2	4	14.80	8.53	13.06	99.4°	9

[a] Errors in the unrefined cell dimensions are of the order of 0.25% (H.T. Evans, *Rev. Sci. Instr., 20,* 751 (1940)). Numbers in parentheses are estimated standard deviations in the least significant digits quoted and are derived from the inverse matrix in non-linear least-squares refined calculations. [b] Greek letters assigned as in References 2 and 3. [c] As the chloride salt. [d] As the iodide monohydrate salt. [e] As the chloride hemihydrate salt.

The differences in the infrared spectrum of the γ:α and ε:π pairs are consistent with nitro complex impurity in the α and π isomers (see Reference 2, Figure 3 and Reference 3 Figure 2). The γ and ε forms have also been synthesised from α–chloro/α–nitro[10] and π–chloro/π–nitro mixtures (3 parts chloro to 1 parts nitro on a weight basis). After the first recrystallisations, the visible absorption spectral parameters remained essentially constant over five subsequent recrystallisations, indicating constant composition mixtures were crystallising. After five recrystallisations, slight loss of the nitro component was detected, in both cases.

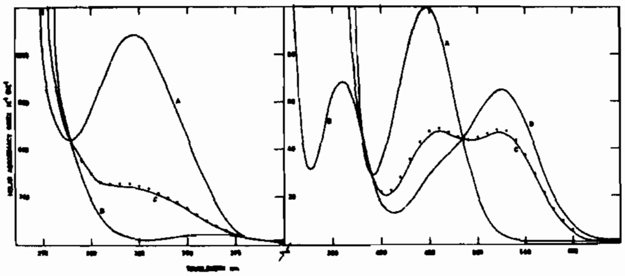

Figure 2. The absorption spectrum of π-Co(en)(dien)NO_2^{2+} (A), π-Co(en)(dien)Cl^{2+} (B) and « ε-Co(en)(dien)Cl^{2+} » (C) (after three recrystallisations) in 0.1 F HCl, in the 275-650 nm range. The curve, x x x x, is a theoretical spectrum of (C), generated using the equation $a_M(C) = 0.73a_M(B) + 0.27a_M(A)$.

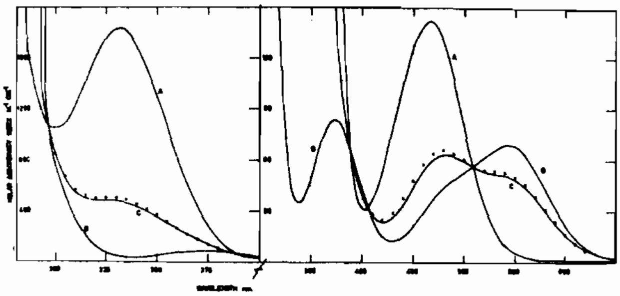

Figure 3. The absorption spectrum of α-Co(en)(dpt)NO_2^{2+} (A), α-Co(en)(dpt)Cl^{2+} (B) and « γ-Co(en)(dpt)Cl^{2+} » (C) (after three recrystallisations) in 0.1 F HCl, in the 275-650 nm range. The curve, x x x x, is a theoretical spectrum of (C), generated using the equation $a_M(C) = 0.74a_M(B) + 0.26a_M(A)$.

The NMR spectra of π–[Co(en)(dien)X]$ZnCl_4$ (X = Cl, NO_2 (A and C respectively in Figure 4) and «ε–[Co(en)(dien)Cl]$ZnCl_4$» (B in Figure 4) in d_6–DMSO, also indicate that the ε isomer is a mixture of the first two components. The ε isomer (spectrum B) having bands due to NH protons characteristic of both π–chloro (spectrum A) and π–nitro (spectrum C) and in the ratio of ca. 2:1. Similarly, the NMR spectrum of «γ–Co(en)(dpt)Cl^{2+}» is made up of contributions from α–Co(en)(dpt)X^{2+} (X = Cl, NO_2) although the bands are less clearly resolved.

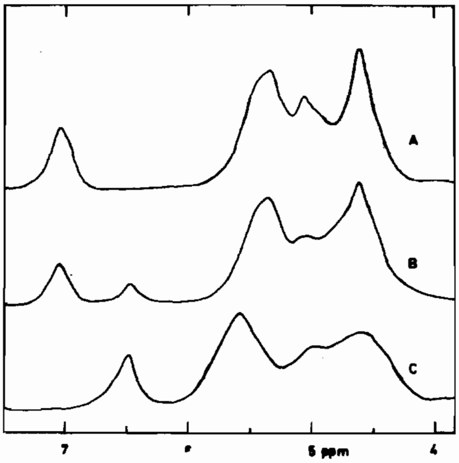

Figure 4. The room temperature NMR spectrum of π-Co(en)(dien)NO_2^{2+}(C), π-Co(en)(dien)Cl^{2+} (A) and « ε-Co(en)(dien)Cl^{2+} » (B) (as the $ZnCl_4^{2-}$ salts) in d_6-DMSO. Only resonances due to the NH protons are shown.

It is perhaps surprising that the chloro and nitro complexes should co-crystallise from aqueous solution, as the tetrachlorozincate(II) salts are not isomorphous in either the dpt or dien systems (Table I).

Consequently, it has been unusually difficult to differentiate such mixtures from pure compounds, in these systems where geometric isomers are common and expected.

From our previously published work,[2] it appears that the α–Co(en)(dpt)NO_2^{2+} cation can co-crystallise with the bromo, iodo and thiocyanato complexes in addition to the chloro, and with a variety of anions (*e.g.* Cl^-, ClO_4^-, $ZnCl_4^{2-}$). However, π–Co(en)(dien)-NO_2^{2+} co-crystallises only with the chloro and azido complexes.

Thus only two (α and β) of the four possible Co(en)(dpt)Cl^{2+} isomeric cations have been characterised,[2,4,5,11] both with a peripheral dpt ligand. In view of the enhanced stabilisation of *trans* or peripheral configurations by ligands with six-membered rings,[12] we believe the formation of Co(en)(dpt)X^{n+} isomers with the facial configuration (types II and III, Figure 1), to be unlikely.

Similarly, only three (π, ϰ, and ω) of the four possible Co(en)(dien)X^{n+} isomers have been isolated. However, attempts to produce a Co(en)(dien)X^{n+} isomer of type I (Figure 1) with the NH proton adjacent to the coordinated acido ligand are now being made.

Experimental Section

Preparation of Compounds. α–[Co(en)(dpt)Cl]$ZnCl_4$,[2] γ–[Co(en)(dpt)Cl]$ZnCl_4$,[2] α–[Co(en)(dpt)NO_2]$ZnCl_4$,[2,10] π–[Co(en)(dien)Cl]$ZnCl_4$,[3] and ε–[Co(en)(dien)Cl]$ZnCl_4$[3] were prepared as described previously.

π–Nitro(ethylenediamine)(diethylenetriamine)cobalt(III) Tetrachlorozincate(II): One gramme of π–[Co(en)(dien)Cl]$ZnCl_4$ was dissolved in 25 ml of 0.2 *F* HCl, 3 g of $NaNO_2$ was added, and the solution was heated for 1 hr at 80°. The hot solution was slowly poured into 100 ml of 50:50 acetone:2-propanol solution containing 5 g of dissolved $ZnCl_2$ and 1 ml of 12 *F* HCl. The yellow crystals that deposited on cooling (79%) were washed with acetone and ether and air dried.

Anal. Calcd for [Co(en)(dien)NO_2]$ZnCl_4$: Co, 12.40; Cl, 29.83%. Found: Co, 12.35; Cl, 29.79%.

α–Chloro(ethylenediamine)(dipropylenetriamine)cobalt(III) Tetrachlorozincate(II)/α–Nitro(ethylenediamine)(dipropylenetriamine)cobalt(III) Tetrachlorozincate(II) Mixture - «γ–[Co(en)(dpt)Cl]ZnCl₄»: 0.75 g of α–[Co(en)(dpt)Cl]$ZnCl_4$ and 0.25 g of α–[Co(en)(dpt)NO_2]$ZnCl_4$ were dissolved together in 25 ml of 0.2 *F* CH_3CO_2H at 40° 15 ml of 12 *F* HCl and 2.5 g of $ZnCl_2$ were then added. The product that deposited was collected, washed with 2-propanol and dried with ether. The yield was 77%. This material was recrystallised five times from 25 ml of 0.2 *F* CH_3CO_2H at 40° by the addition of 12 *F* HCl (15 ml) and $ZnCl_2$ (2.5 g) and cooling. Small samples for absorption spectral measurements were retained after each recrystallisation.

π–Chloro(ethylenediamine)(diethylenetriamine)cobalt(III) Tetrachlorozincate(II)/π–Nitro(ethylenediamine)(diethylenetriamine)cobalt(III) Tetrachlorozincate(II) Mixture - «ε–[Co(en)(dien)Cl]ZnCl₄»: A similar method to the above was employed using 0.75 g of π–[Co(en)(dien)Cl]$ZnCl_4$ and 0.25 g of π–[Co(en)(dien)NO_2]$ZnCl_4$. The yield was 83%.

Single Crystal X-ray Studies: Crystals of α and γ–[Co(en)(dpt)Cl]Cl_2 and π, ε, and ϰ–[Co(en)(dien)Cl]$ZnCl_4$, suitable for X-ray studies, were grown from dilute aqueous HCl solutions of the $ZnCl_4^{2-}$ salts. Crystals of α and γ–[Co(en)(dpt)Cl]$ZnCl_4$ were grown from aqueous HCl containing 10% $ZnCl_2$. Unit cell dimensions were calculated from precession photographs collected at ambient temperature and the data are listed in Table I.

Spectral Data. Visible and near ultraviolet absorption spectral data were obtained in 0.1 *F* HCl using a Shimadzu MPS-50L recording spectrophotometer and the infrared spectra were run in KBr discs using a Shimadzu IR-27G spectrometer. Room temperature NMR spectra were run in d_6–DMSO with external TMS standard using a Varian A-60 Analytical NMR Spectrometer.

Acknowledgment. We thank Dr. Ward T. Robinson for his interest and criticism.

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(11) A.R. Gainsford and D.A. House, *Inorg. Nucl. Chem. Letters*, *4*, 621 (1968).

(12) M.C. Couldwell and D.A. House, *J. Inorg. Nucl. Chem.*, 33, 2583 (1971).