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Chiral Metal Complexes.
Part 22[*]. Stereoisomers of the Dichloro[3,6-diaza-2*S*,7*S*-di(2-pyridyl)octane]-cobalt(III) Ion and Related Species

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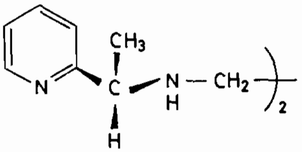
Abstract

The reaction of 3,6-diaza-2*S*,7*S*-di(2-pyridyl)-octane, *S*,*S*-peaen, with Co(II) and O_2 in aqueous solution yields a mixture, from which may be isolated three chelate diastereomers after the addition of HCl and $HClO_4$. These are Δ-α-[Co(*S*,*S*-peaen)Cl_2]ClO_4 and its Λ-α and Δ-β analogues. Previous workers had reported that a second β-diastereoisomer could be obtained but it has been shown that this is in fact an isomeric mixture of both Δ-α- and Λ-α-[Co(*S*,*S*-peaen)Cl_2]ClO_4. All three isomers react with oxalate anions to form an apparently unique product Λ-α-[Co(*S*,*S*-peaen)ox]$^+$ in aqueous solution and which can be crystallized as its perchlorate salt. Two of the reactions reported represent unusual examples of octahedral inversions.

Introduction

Over the last few years we have been investigating the degree of stereoselectivity in the coordination of several linear nitrogenous tetradentates because of their potential use in systems capable of catalysing stereospecific reactions in the remaining octahedral binding sites of Co(III) complexes and related species [1]. In addition we have been interested in exploring those sources of chiral discrimination which are important in this class of complexes [2], particularly those based upon the ligand picen[†]. Our attention was thus drawn naturally to the work of Suzuki *et al.*, [3], who synthesised the related tetradentate *S*,*S*-peaen (1) and studied its coordination behaviour in several complexes of Co(III). They concluded that three isomeric complexes of the type [Co(*S*,*S*-peaen)Cl_2]$^+$ could be formed, one having the Δ-α-configuration and two others each having the Δ-β-configuration. Those workers suggested that the difference between the latter two isomers was the absolute configuration of the in-plane amine nitrogen atom of the tetradentate. We found this suggestion to be somewhat surprising in view of our earlier work on related complexes [2]. Furthermore, reaction of Δ-α-[Co(*S*,*S*-peaen)Cl_2]$^+$ with oxalate anion gave as the sole product Λ-α-[Co(*S*,*S*-peaen)ox]$^+$; this represents, although it was not realised at the time, a second example of an octahedral inversion in which the α topology is retained [4]. Thus we thought it worthwhile to reexamine some of the coordination chemistry of *S*,*S*-peaen with trivalent cobalt. The results of the study are reported below.



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Experimental

The preparation of 1-(2-pyridyl)ethylamine, (pea) from 2-pyridyl-methylketoxime was carried out following methods given in the literature [5, 6]. The product was resolved [5] by the fractional crystallization of the *R*,*R*-hydrogen tartrate salts. The least soluble diastereoisomer containing *S*-pea was recrystallized to constant rotation with $[\alpha]_D^{25}$ = +4.5° (C = 4, H_2O); Lit.: +4.8° (C = 4, H_2O) [5], +5.4° (C = 4, H_2O) [7], +5.1° (C = 4, H_2O) [8]. *S*,*S*-peaen was prepared in 55% yield by the published method [3] employing 1,2-dibromoethane as a coupling reagent.

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[*] Part 21: M. A. Anderson, J. P. G. Richards, A. G. Stark, F. S. Stephens, R. S. Vagg and P. A. Williams, *Inorg. Chem.*, in press.

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[†] Picen = 2,5-diaza-1,6-di(2-pyridyl)hexane; peaen = 3,6-diaza-2,7-di(2-pyridyl)octane; trien = 1,4,7,10-tetraazadecane; 3*S*,8*S*-dimetrien = 1,4,7,10-tetraaza-3*S*,8*S*-dimethyldecane.

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TABLE I. Spectral Data for the Complexes

Complex	λ (nm)	ε (dm^2 mol^{-1})	Δε (dm^2 mol^{-1})
Δ-α-[Co(*S*,*S*-peaen)Cl_2]ClO_4[a]	550	1140	
	604		+16.6
	526		−23.8
	418		−5.2
	340		+30.8
Δ,Λ-α-[Co(*S*,*S*-peaen)Cl_2]ClO_4[a]	544	1090	
	613		+1.8
	534		−2.8
	396[c]		+1.7
Λ-α-[Co(*S*,*S*-peaen)ox]ClO_4[b]	490	1280	
	360	1630	
	496		+30.9
	378		+3.6

[a] Measured in conc. HCl. [b] Measured in H_2O. [c] Shoulder.

Δ-α-[Co(S,S-peaen)Cl$_2$]ClO$_4$

This complex was prepared by following the method of Suzuki *et al.*, [3]. In water (50 ml) was dissolved *S*,*S*-peaen·4HCl (2.08 g, 5.05 mmol), LiOH (0.65 g, 15.6 mmol) and $CoCl_2·6H_2O$ (1.20 g, 5.06 mmol). A stream of air was passed through the solution for three hours and then conc. HCl (8 ml) followed by conc. $HClO_4$ (2.4 ml) were added slowly with stirring to the dark yellow–brown solution. After a few minutes the mixture became a deep red colour and it was filtered and transferred to an evaporating basin. The volume of the solution was reduced on a steam bath until crystals began to form. The mixture was then cooled to room temperature, and the violet crystals collected at the pump, washed with cold water, then acetone, and sucked dry. Yield: 3%. *Anal.* Calc. for $C_{16}H_{22}N_4O_4Cl_3Co$: C, 38.5; H, 4.4; N, 11.3. Found: C, 38.6; H, 4.5; N, 11.2%.

Δ,Λ-α-[Co(S,S-peaen)Cl$_2$]ClO$_4$

The filtrate from the above preparation was evaporated further to about half its original volume, then cooled to room temperature. The violet crystals which had formed were collected and dried as above. Yield: 15%. *Anal.* Found: C, 38.5; H, 4.6; N, 11.1%.

Δ-β-[Co(S,S-peaen)Cl$_2$]ClO$_4$

Subsequent evaporation of the filtrate from the above preparation to a small volume on the steam bath gave a further crop of purple crystals. This Δ-β-complex was isolated as described earlier. Yield: 16%. *Anal.* Found: C, 38.4; H, 4,4; N, 11.3%. Further evaporation of the filtrate resulted in the formation of a viscous green oil from which no solid could be isolated.

Λ-α-[Co(S,S-peaen)ox]ClO$_4$

A suspension of Δ,Λ-[Co(*S*,*S*-peaen)Cl_2]ClO_4 (0.051 g, 0.1 mmol) and sodium oxalate (0.022 g, 0.16 mmol) in water (1 ml) was warmed on a steam bath for 2 h, during which time all solids dissolved to give a red solution. The solution was set aside to cool at room temperature and over 24 h salmon-pink crystals of the title complex formed. These were collected at the pump, washed with a drop of ice-cold water, and air dried. Yield: 90%. *Anal.* Calc. for $C_{18}H_{22}N_4O_8ClCo$: C, 41.8; H, 4.3; N, 10.8%. Found: C, 41.9; H, 4.3; N, 11.1%. Measurement of the CD spectrum of the supernatant gave no indication of the formation of any other diastereoisomer. Reaction of Δ-α-[Co(*S*,*S*-peaen)Cl_2]$^+$ or its Δ-β-analogue with oxalate under the same conditions yielded the same Λ-α-[Co(*S*,*S*-peaen)ox]$^+$ product.

Elemental analyses were carried out by Mrs. A. Dams of the Department of Chemistry, University College Cardiff. Rotations were measured using a Thorn NPL 243 polarimeter and CD and electronic spectra recorded using a Jobin-Yvon CNRS Dichrographe III and a Perkin-Elmer SP8000 spectrophotometer, respectively. 360 MHz ^1H NMR spectra were recorded using a Bruker WM360 instrument at 298K on solutions in dmso-d_6 with TMS as internal standard.

Results and Discussion

The least soluble α-[Co(*S*,*S*-peaen)Cl_2]ClO_4 diastereoisomer has the Δ absolute configuration. Electronic and CD spectral data are given in Table I and the maxima in the former and extrema in the latter correspond with those reported by Suzuki *et al.* [3]. Our complex is somewhat more optically

TABLE II. Characteristic 360 MHz ^1H NMR Data for the Complexes

δ or J^b	Complex[a]		
	Λ-α-$[Co(L)Cl_2]^+$	Δ-α-$[Co(L)Cl_2]^+$	Δ-β-$[Co(L)Cl_2]^+$
H(12)	7.61	7.65	7.60
H(13)	8.20	8.13	8.31
H(14)	7.78	7.70	8.08
H(15)	9.43	9.43	9.37
H(42)			7.73
H(43)			7.89
H(44)			7.44
H(45)			7.10
H(Cl)	5.14	4.51	5.33
$C(M1)H_3$	1.69	1.83	1.69
H(N2)	7.33	6.96	8.44[d]
H(C4)			4.73
$C(M4)H_3$			1.75
H(N3)			6.86[d]
H(C21)	2.32[c]	2.38[c]	3.46[d,e]
H(C22)	2.32[c]	2.38[c]	3.24[d]
H(C31)			2.69[d]
H(C32)			2.45[d,f]
$J_{12,13}$	7.6	7.8	7.9
$J_{13,14}$	7.8	7.6	7.7
$J_{14,15}$	5.7	5.7	5.8
$J_{42,43}$			8.0
$J_{43,44}$			7.5
$J_{44,45}$			5.8
$J_{C1,M1}$	7.2	7.0	6.9
$J_{C4,M4}$			7.0

[a] L = *S*,*S*-peaen. [b] δ in ppm relative to TMS, *J* in Hz. [c] Overlapping multiplets. [d] We do not distinguish between these pairs of protons. [e] Partly obscured by HDO peak. [f] Partly obscured by solvent impurity.

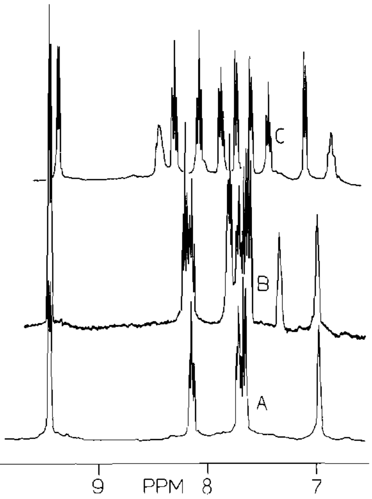
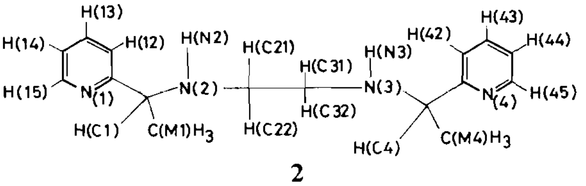


Fig. 1. 360 MHz ^1H NMR spectra of the aromatic regions of A: Δ-α-$[Co(S,S\text{-peaen})Cl_2]ClO_4$, B: Δ-Λ-α-$[Co(S,S\text{-peaen})Cl_2]ClO_4$ and C: Δ-β-$[Co(S,S\text{-peaen})Cl_2]ClO_4$ in dmso-d_6.

active however, possibly by virtue of its being uncontaminated with any of the Λ-α-isomer. The CD spectrum is virtually enantiomorphic with those of Λ-α-$[Co(R\text{-picpn})Cl_2]^+$ [9, 10], Λ-α-$[Co(3S,8S\text{-dimetrien})Cl_2]^+$ [11], and Λ-α-$[Co(trien)Cl_2]^+$ [12]. The α-topology is confirmed by the high resolution ^1H NMR spectrum of the complex as shown in Fig. 1, data for this being given in Table II. Only four resonances are seen in the aromatic region of the spectrum and only one methyl doublet is observed. A *trans* diastereoisomer would have a green colour, so this violet species is the Δ-α-complex, which also possesses two-fold symmetry. The proton numbering scheme is shown in **2**; for the β isomer, N(1), N(2) and N(3) are disposed meridionally in the Co(III) coordination sphere.



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The second species isolated from the mixture formed in the synthesis of $[Co(S,S\text{-peaen})Cl_2]^+$ complexes is the Δ,Λ-α-$[Co(S,S\text{-peaen})Cl_2]ClO_4$ salt with a Δ:Λ ratio of approximately unity. Its CD spectrum (Table I) is qualitatively similar to that ascribed previous [3] to a β-diastereoisomer. Reference to its ^{1}H NMR spectrum however (Fig. 1, Table II) shows clearly that it is a mixture of the Δ-α-complex and another species which also possesses two-fold symmetry. The only possibility which explains these facts is that the second species present is in fact the Λ-α-complex. We do not know whether or not both α complexes cocrystallize in the same crystal, or whether this product is a crystalline mixture of the two α-diastereoisomers. The similar relative abundance of the two forms in our solid and that indicated by the low resolution NMR spectrum of the methyl resonances of that solid isolated by the earlier workers [3] suggests that the former may be correct.

The third diastereoisomer isolated from the reaction mixture is Δ-β-[Co(*S*,*S*-peaen)Cl_2]ClO_4 and corresponds with the previously isolated β-II isomer [3]. Electronic and CD spectral data for our complex are the same within experimental error, as that found by those workers. Its high resolution ^{1}H NMR spectrum (Fig. 1, Table II) is characteristic of a β isomer [2, and refs. therein]. Thus we find that two α and one β complexes can be formed in the reaction of *S*,*S*-peaen with Co(II) when oxidized by molecular oxygen and that the previously supposed extra β diastereomer is rather a mixture of the two possible α-complexes. Obviously *S*,*S*-peaen shows little stereoselectivity in its formation of these dichloro complexes of trivalent cobalt.

The reaction of all three [Co(*S*,*S*-peaen)Cl_2]ClO_4 salts isolated with oxalate ions gives rise to a single diastereoisomeric product, whose absolute configuration has been established crystallographically [13]. Hence this reaction of Λ-α-[Co(*S*,*S*-pean)-Cl_2]$^+$ as part of the mixture of α-isomers thus proceeds with retention of absolute configuration. The electronic and CD spectra of the oxalate salt (Table I) are virtually identical to those reported earlier [3]. A second example of an $\alpha \rightarrow \alpha$ octahedral inversion is provided by the corresponding reaction with Δ-α-[Co(*S*,*S*-peaen)Cl_2]$^+$ [9]. Furthermore the corresponding transformation of Δ-β-[Co(*S*,*S*-peaen)-Cl_2]$^+$ to Λ-α-[Co(*S*,*S*-peaen)ox]$^+$ is another sample of a rather rare kind of octahedral inversion involving the β to α change of topology [14]. We are inclined to think that these kinds of octahedral inversions are probably more common than has been hitherto realized and that many more may be observed by a judicious choice of starting complex and reaction conditions.

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