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Preparation of the Chiral Hexadentate Ligand *N,N',N''*-Tris[(S)-2-hydroxypropyl]-1,4,7-triazacyclononane and Preparation and Circular Dichroism Spectra of its Co(III) Complexes

JOHN ROBB and ROBERT D. PEACOCK*

Department of Chemistry, The University, Glasgow G12 8QQ, U.K.

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The macrocyclic triamine triazacyclononane (tacn) and its C-methyl substituted derivative (Me-tacn) have proved to be excellent ligands for the synthesis of optically active metal complexes with interesting spectroscopic properties. Despite the fact that the two sets of three nitrogen ligating atoms are not connected by chelate rings, $[Co(Metacn)_2]^{3+}$ has a trigonal twist of 7.6° and is substantially elongated [1]. The CD spectrum of the complex is unusual [2, 3] in that the difference in rotational strengths of the A_2 and E components of the $^1A_1 \rightarrow {}^1T_1$ transition is one of the largest measured for a cobalt complex with six nitrogen donor atoms. The cobalt and chromium complexes of tacn itself form enantiomeric single crystals and $[Cr(tacn)_2]Cl_3$ has a very interesting CPL spectrum [4]. More recently tacn has been N-methylated [5] and has been used to synthesise hexadentate ligands containing carboxylate [6], hydroxyethyl [7] and aminoethyl [8] groups attached to the nitrogen atoms. The ligand *N,N',N''*-tris(2-hydroxyethyl)-1,4,7-triazacyclononane (thetacn) has been used to form Cu(II) and Zn(II) complexes [7]. Models suggest that complexes with Co(III) or Cr(III) should be quite badly strained. By placing a methyl substituent on the ethane backbone of the hydroxyethyl units the ligand is made chiral while retaining its C_3 symmetry. We wish to report the synthesis of this novel chiral hexadentate ligand ((S)-Methetacn) and the preparation, characterisation and CD spectra of its Co(III) complexes.

Experimental

Ligand Preparation

N,N',N''-Tris[(S)-2-hydroxypropyl]-1,4,7-triazacyclononane ((S)-Methetacn) was synthesised by neutralising one mole of tacn·3HBr with KOH in slightly aqueous ethanol, filtering off the KCl produced and reacting the liberated tacn with three moles of (S)-propylene oxide overnight at room temperature. On removal of the solvent (S)-Methetacn is obtained as a viscous liquid. Residual KCl is removed by extracting the ligand into isopropanol in which it is very soluble. [NMR ($CHCl_3$) 1.1 ppm, doublet, 9 protons, CH_3; 2.4–2.9 ppm, 21 protons, CH_2; 3.4 ppm, multiplet, 1 proton, NH; 3.9 ppm multiplet, 3 protons, CH].

Cobalt(III) Complexes

Mixing equimolar quantities of $CoCl_2 \cdot 6H_2O$ and (S)-Methetacn in aqueous solution, warming to 70 °C for 30 min, cooling and adding H_2O_2 gives a red–purple solution which is a mixture of the acid and basic forms of the Co(III) complex (see 'Discussion'). The basic form may be obtained as a solid by dehydrating a basic solution of the complex at ~100 °C, extracting the blue solid into ethanol and removing the solvent. The very hygroscopic complex analyses as $[Co\{(S)\text{-Methetacn}\}]Cl_3$. *Anal.* Found: C, 38.6; H, 7.4%; N, 9.0. Calc.: C, 38.4; H, 7.0; N, 9.0%. The red acid form may be obtained in solution by acidifying solutions of the mixture to pH ~1 and the two complexes may be separated by elution from an SP Sephadex cation exchange column, the blue complex being eluted first.

Results and Discussion

The tacn nitrogen atoms could, in principle, attack either the CH_2 or CH(Me) carbons of the propylene oxide. The NMR spectrum shows that only one product is formed and both chemical reasoning (attack at the least hindered carbon) and the chemical shift of the CH proton (3.9 ppm compared with 3.7 in 2-aminopropan-1-ol and 3.4 in 1-aminopropan-2-ol) lead us to believe that (S)-Methetacn has the structure shown in Fig. 1. As was found for thetacn

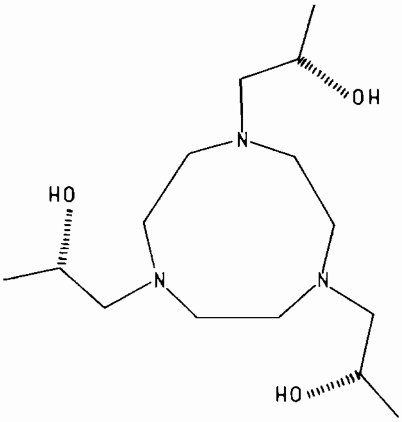

Fig. 1. *N,N',N''*-Tris[(S)-2-hydroxypropyl]triazacyclononane ((S)-Methetacn).

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*Author to whom correspondence should be addressed.

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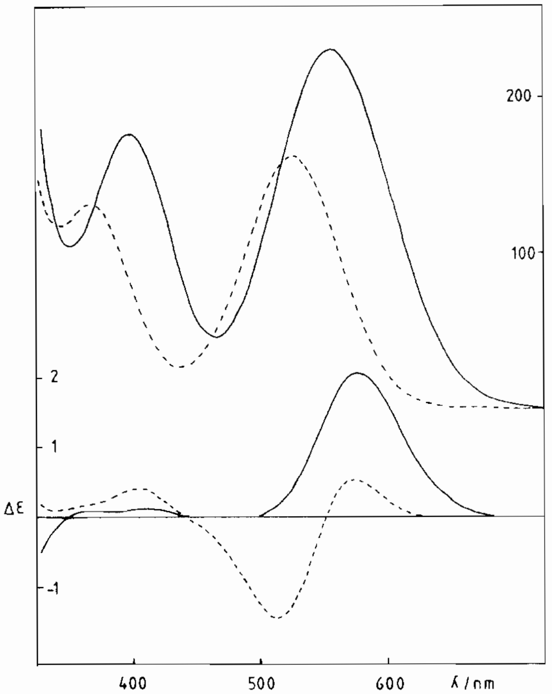

Fig. 2. Absorption and CD spectra of $[Co\{(S)\text{-Methetacn}\}]^{3+}$ in aqueous solution. The solid line spectra are at pH 14 (NaOH) and the dashed line spectra at pH 1 (HCl).

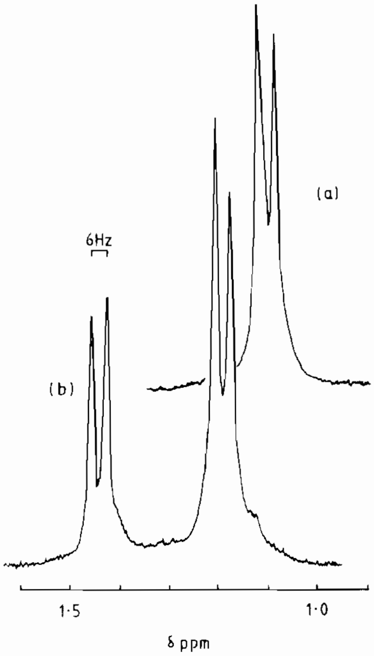

Fig. 3. NMR spectra of $[Co\{(S)\text{-Methetacn}\}]^{3+}$ in D_2O solution: (a) basified with NaOD to pH 14, (b) acidified with DCl to pH 1.

itself [7], (S)-Methetacn is isolated as the HBr salt. The NH proton is detected at 3.4 ppm in the NMR in $CHCl_3$ solution and the parent ion in the mass spectrum is $[\text{MethetacnH}]^+$ ($m/e = 304$).

The absorption and CD spectra of the Co(III) complex are pH dependent. The spectra obtained at pH values of 14 and 1 are shown in Fig. 2. Our first thought was that one of the OH groups was becoming protonated and dissociating at low pH thus producing a pentadentate ligand with the sixth coordination site filled, presumably, by water. This is substantiated by the NMR spectra of the complexes in D_2O acidified by DCl and basified by NaOD (Fig. 3). The spectrum in basic solution (Fig. 3a) is very similar to that of the free ligand. There is only one type of methyl group, at 1.09 ppm, the CH_2 resonances appear at 2.5–3.1 ppm and the CH signals are lost in the wings of the DOH band. The spectrum of the acid form of the complex is quite different (Fig. 3b). There are clearly two types of methyl group in the ratio 2:1. The two equivalent methyls resonate at 1.19 ppm, while the unique methyl group comes at 1.44 ppm. Once again the CH_2 resonances are broad and it is impossible to identify the CH signals. The NMR spectra clearly show that in its basic form the complex is symmetric and is coordinated by all three arms of the (S)-Methetacn ligand. The acid form, on the other hand, contains a ligand in which either one or two of the OH groups are protonated. We detect only one pK_a for the complex (8.2 ± 0.15) and so suggest that the unique methyl group in the NMR spectrum is on an arm containing a protonated OH group. It is very unlikely that a $-CH_2-OH_2+$ group could coordinate to a Co^{3+} ion and so we presume that the third arm of the (S)-Methetacn ligand is dissociated, the sixth coordination site of the Co ion being occupied by a water molecule.

We have not yet completed the crystal structure of $[Co\{(S)\text{-Methetacn}\}]^{3+}$. Fortunately the crystal structure of the related complex Δ-$[Co(\text{taetacn})]^{3+}$ has been determined [9]. In the Δ enantiomer the three five-membered chelate rings formed by the aminoethyl arms of the ligand adopt the δ conformation while the chelate rings formed by the tacn moiety are in the λ conformation. Molecular mechanics calculations [9] confirmed that the relative conformations adopted by the two types of ring are a consequence of the coupling of the rings through the nitrogen atoms and is not an artefact of the solid state structure. The same relative conformations are therefore expected in analogous complexes such as $[Co\{(S)\text{-Methetacn}\}]^{3+}$. The calculations also confirm that the Δ absolute configuration of the taetacn complex is a consequence of the ring conformations about the metal ion. In the basic form of $[Co\{(S)\text{-Methetacn}\}]^{3+}$ the S methyl groups will force the exocyclic CoOCCN rings to adopt the δ conformation and so the endocyclic tacn rings adopt the λ conformation. It is expected, therefore, that this complex will also have the Δ absolute configuration.

Unfortunately there is no direct relationship between the absolute configuration of a Co(III) complex and its CD spectrum in the d → d region [10]. A good example of this is given by the tris-chelates of 1,2-diaminoethane and 1,3-diaminopropane where enantiomers of the same chirality have opposite signed CD under the d → d transitions. There is, however, a relationship between the sign of the CD and the sense of the twist between the two triangles of ligator atoms in a tris-chelate complex containing unsaturated ligands [10, 11]. If the upper triangle of ligators is rotated counterclockwise with respect to the lower, the CD of the $^1A_1 \rightarrow {}^1E(T_1)$ transition is positive and vice versa. This correlation has been experimentally verified in all cases where single crystal studies have established the positions of the ^1E and $^1A_2$ components of the transition and is theoretically reproduced by Ligand Polarisability Theory calculations [12]. In Δ-[Co(taetacn)]$^{3+}$ the twist is clockwise and so the CD of the $^1A_1 \rightarrow {}^1E(T_1)$ transition should be negative. There is also an empirical rule which relates the energy order of the A_2 and E components of the $^1T_1$ state to the axial compression or elongation of a complex [10]. Δ-[Co(taetacn)]$^{3+}$ is axially compressed (NH–Co–NH_2 = 84.9°) and so the E component should come to lower energy of the A_2 component. The CD spectrum of this complex is therefore predicted to have a positive sign to lower and a negative sign to higher energy under the $^1T_1$ transition which is in contrast to what has been found [9]. We feel that the energy argument is far less sound than the sign-twist correlation especially in view of the facts that the complex has both very substantial trigonal twist and that the compression along the trigonal axis is not the same for the two halves of the molecule (the tacn 'half' of the complex is in fact trigonally elongated, the Co–N bond making an angle of approximately 51° to the C_3 axis). While the assignment is not entirely satisfactory we are reasonably confident that the negative CD band under the $^1A_1 \rightarrow {}^1T_1$ transition of Δ-[Co(taetacn)]$^{3+}$ is due to the E component and the positive CD due to the A_2 component. The absorption and CD spectra of the protonated form of Δ-[Co{(S)-Methetacn}]$^{3+}$ closely resemble those of Δ-[Co(taetacn)]$^{3+}$ apart from the frequency shift consequent upon replacing amino by hydroxyl ligators. The basic form of the complex, however, has a CD spectrum with single positive band under the $^1A_1 \rightarrow {}^1T_1$ transition which must be assigned to the A_2 component. When the CD of a configurationally chiral Co(III) complex has only one sign under the $^1A_1 \rightarrow {}^1T_1$ transition it is indicative that the splitting between the A_2 and E components is very small and the CD of the acid and basic forms of Δ-[Co{(S)-Methetacn}]$^{3+}$ are a good example of how sensitive this splitting is to small perturbations. It is interesting that the CD spectrum of the basic form closely resembles that of (λλλ,λ'λ'λ')-[Co[{(R)-Metacn}]$^{3+}$ which has the same conformation tacn ring and is known to be trigonally elongated [1]. Further work on the CD spectra of these and other metal complexes of (S)–Methetacn is in progress.

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