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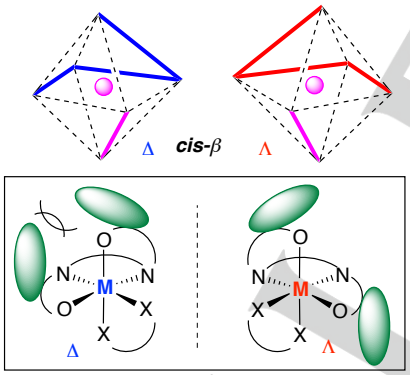
Synthesis of Homochiral Co^{III} and Mn^{IV} [2.2]Paracyclophane Schiff Base Complexes with Predetermined Chirality at the Metal Centre.

Darran Loits,[a] Stefan Bräse,[b] Andrea J. North,[a] Jonathan M. White,[a] Paul S. Donnelly[a] and Mark A. Rizzacasa[a] *

Abstract: The planar chiral Schiff base ligand **2**, derived from (R_p)-5-formyl-4-hydroxy[2.2]-paracyclophane (FHPC) (**1**), was utilised to form a Λ–Co^{III} *cis*-β octahedral metal complex **3** with complete control of the metal centred chirality. In addition, a Λ,Λ-Mn^{IV} di-μ-oxo complex **4** was synthesised with control of both metal centred and *P*-helical chirality.

Introduction

The synthesis of octahedral 'chiral at metal' complexes with control of the metal centred helical chirality is challenging.[1] The potential of chiral at metal octahedral complexes to be useful for asymmetric catalysis[2] and ^{1}H NMR chiral analysis[3] has increased interest in the preparation of homochiral coordination compounds. Cationic enantiopure octahedral metal complexes can be isolated by resolution of diastereoisomeric mixtures[4] by crystallisation with chiral anions but resolution of charge neutral complexes can be more challenging. The isolation of octahedral metal complexes as a single stereoisomer requires judicious design of the ligand and there are few examples that allow complete control of the metal chirality.[1a]



Fiugure 1. Diastereoisomeric *cis*-β octahedral metal complexes with a tetradentate N_2O_2 ligand and a bidentate ligand.

Tetradentate chiral ligands based on chiral linear N_4 ligands derived from chiral diamines and pinenebipyridines (CHIRANGEN)[5] as well as atropisomeric chiral binaphthyl Schiff base type ligands[6] have all been successful in controlling metal chirality to give 'predetermined chirality at the metal centre'.[1a]

We became interested in the stereoselective synthesis of chiral octahedral *cis*-β (*scew-lines convention*)[7] metal complexes (see Fig 1.) as potential chiral catalysts[8] for metal mediated alkene functionalisations[9] using chiral tetradentate N_2O_2 type ligands to control the metal asymmetry present in this type of coordination sphere. Tetradentate N_2O_2 ligands can coordinate to octahedral metal ions in a *cis*-β configuration and a bidentate ligand can be used to complete the coordination sphere (Figure 1).[8] Thus, a sterically demanding chiral functional group on a symmetrical N_2O_2 ligand could direct the formation of a single Δ or Λ helical[7a] twist about the metal ion.

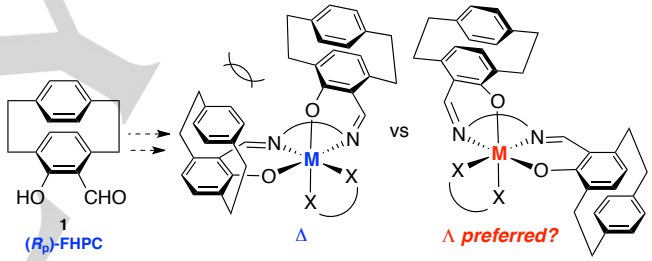


Figure 2. Cis-β octahedral metal complexes based on a 5-formyl-4-hydroxy[2.2]-paracyclophane (**1**) ligand.

With this principle in mind, we reasoned that a ligand based on a planar chiral (R_p)-5-formyl-2-hydroxy[2.2]paracyclophane [(R_p)-FHPC] (**1**)[10] N_2O_2 Schiff base[11] derived from a simple diamine could serve this purpose (Figure 2). A ligand of this type should bind to a metal to form an octahedral cis-β (rather than cis-α)[8] complex as a single stereoisomer with the Λ configuration about the metal centre since there would be a serious steric interaction between the [2.2]paracyclophane rings in the alternative Δ–isomer. Therefore, a symmetrical planar chiral ligand with *no tetrahedral asymmetry* could control the chirality at the metal centre. FHPC derived SALEN ligands have been utilised in the asymmetric Ti catalysed trimethylsilylcyanations[11b] of aldehydes but the catalyst was not characterised. Asymmetric dialkyl zinc additions have also been reported utilising FHPC SALEN ligands[12] and related ligands have been used to prepare square planar Cu^{II} complexes and Mn^{III} complexes with tetragonal pyramidal coordination geometry.[11a] Cis-β Mn^{III} cand Fe^{III} complexes with a single twist about the metal centre have been synthesised[13] using chiral biaryl Schiff base ligands but no cis-β complexes have been reported with FHPC derived ligands..

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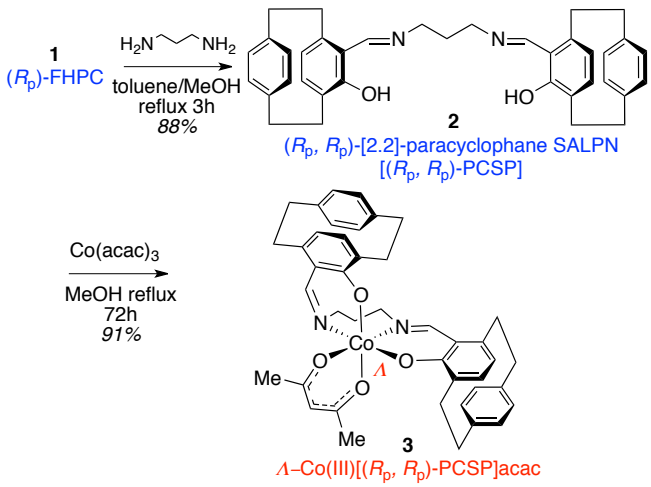


Scheme 1. Synthesis of Co(III) PCSP complex **3**.

The synthesis the FHPC 1,3-propanediamine (SALPN) Schiff base 2 is shown in Scheme 1. Condensation of optically pure (R_p)-FHPC[10b] with 1,3-diaminopropane gave the known[11b] [2.2]**P**ara**C**yclophane **S**AL**P**N (**PCSP**) ligand 2 in 93% e.e.[14] which was further characterised by X-ray crystallography.[14-15]

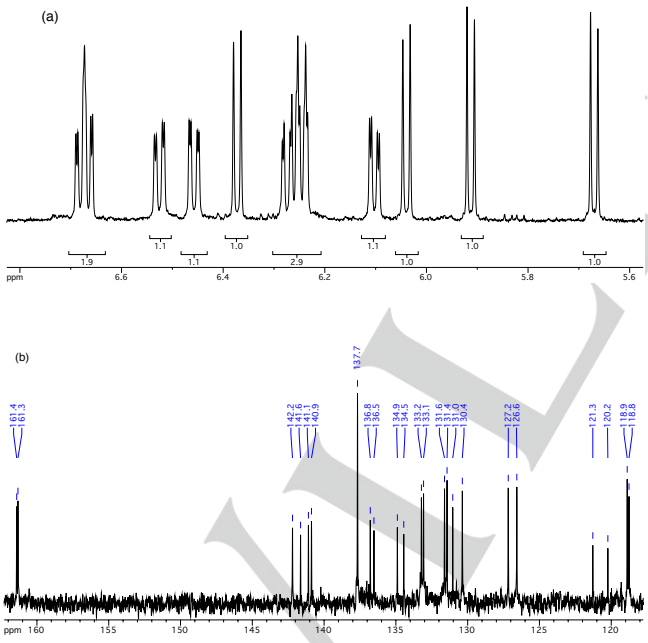


Figure 1: (a) Aromatic region of ^{1}H NMR (b) and proton decoupled ^{13}C NMR spectra of complex **3**.

A solution of [Co(acac)$_3$] (acac = acetylacetonate) and PCSP ligand (**2**) in methanol was boiled for 72h and this resulted in formation of a dark green complex which was identified as Co^{III}(PSCP)acac (**3**) by X-ray crystallography and NMR spectroscopy. Low spin Co^{III} (d^6) complexes are diamagnetic and the ^{1}H NMR spectrum shows the expected resonances for the Schiff base ligand but also reveals that one of the acac ligands remains bound to the metal ion. In the ^{1}H NMR spectrum each of the aromatic protons of the [2.2]paracyclophane are chemical shift non-equivalent reflecting the asymmetry of the complex (Figure 3a). All but one aromatic carbon displayed a different chemical shift in the proton decoupled ^{13}C NMR spectrum (Figure 3b) also suggesting the formation of a single stereoisomer with *cis*-β coordination of the tetradentate ligand.

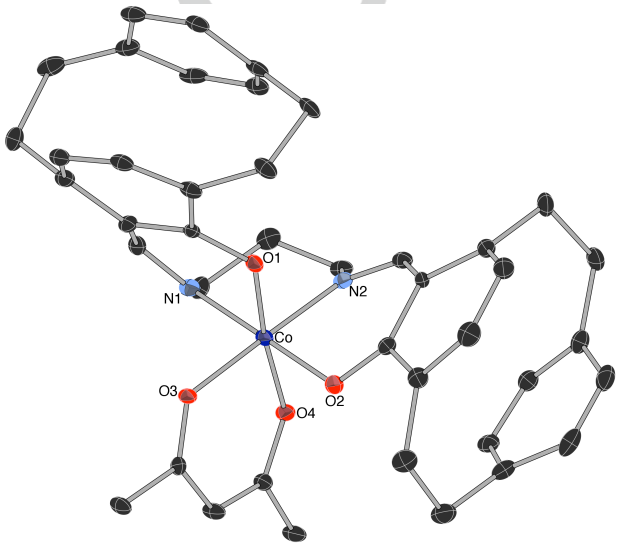
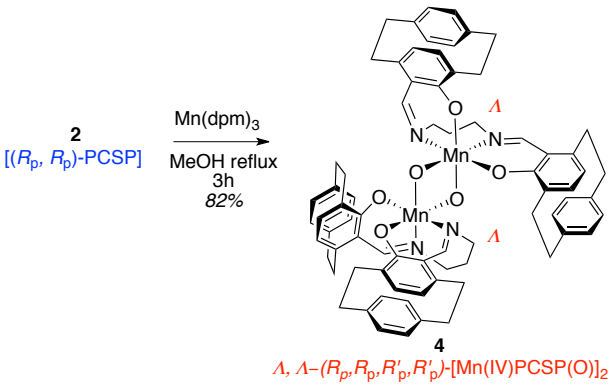


Figure 3. A representation of the X-ray structure of Co^{III}(PCSP)acac (**3**). Ellipsoids are at 30% probably level thermal ellipsoids-H atoms omitted for clarity).

Complex **3** crystallised from CH_2Cl_2 to give crystals suitable for X-ray analysis (space group $P2_12_12_1$)[16] and this revealed that the planar chirality in PCSP ligand results in a predetermined single *Λ* twist[1a] about the metal ion (Figure 3).. The X-ray structure also showed that the complex had recrystallised as a single enantiomer. As expected, the metal ion is a distorted octahedral environment and the Co-N1 [1.903(7) Å] and Co-O1 [1.865(5) Å] bond lengths are similar to those found in a comparable Co^{III}(L)acac complex with a simple Schiff base ligand.[17]



Scheme 2. Synthesis of Mn^{IV} di-μ-oxo PCSP complex **4**.

Heating a methanol solution of ligand **2** and $Mn(dpm)_3$ (where dpm = dipivaloylmethanato) in air resulted in formation of a dark brown solid (Scheme 2). Recrystalisation from a mixture of dimethylformamide and di-*iso*-propyl ether resulted in dark brown crystals suitable for analysis by X-ray crystallography (rhombohedral, space group $P4_32_12$)[14] and this revealed that the dimeric $[Mn^{IV}$-μ-O(PCSP)$]_2$ complex **4** had formed (Figure 5).[18] Both of the Mn^{IV} atoms possessed Λ stereochemistry as was observed for the Co^{III} complex and a single enantiomer was observed.

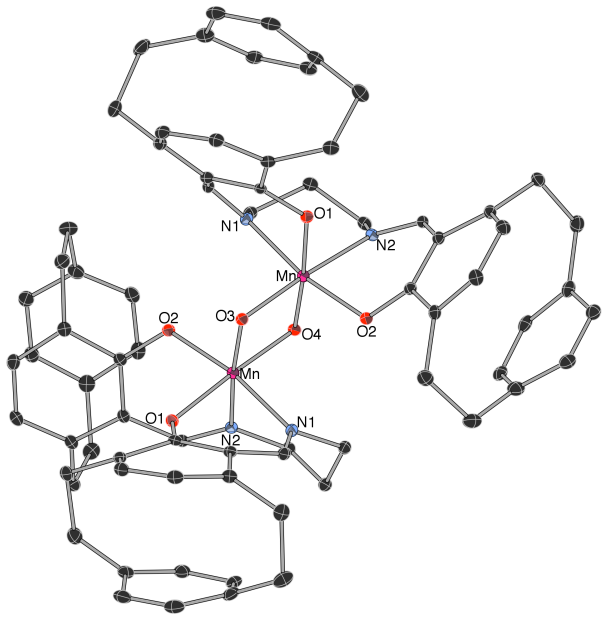


Figure 5. Representation of the X-ray structure of Mn^{IV} complex **4** (30% thermal ellipsoids-H atoms omitted for clarity)

A chiral Mn(IV) di-μ-oxo complex has been previously prepared by oxidative dimerisation of an $[Mn^{III}$(salen)]Cl complex derived from the common chiral unit (*R*,*R*)-trans-cyclohexane-1,2-diamine and this also formed with single metal asymmetry as well as helical chirality.[19] The complex $[Mn^{IV}$-μ-O(PCSP)$]_2$ (**4**) possesses *P* helical (right handed) chirality[19] with the ligands as shown in Figure 6. The bridging O3 atom is *trans* to the imine N2 atoms whilst the O4 atom is *trans* to the phenolic O1 atoms (Figure 5). Formation of the alternative *M*-helical stereoisomer would result in severe steric interactions between the [2.2]paracyclophane units. Thus Mn^{IV} complex **4** is formed as a single stereoisomer with high control of the both the *metal centred* and *helical chirality*. The Mn-Mn bond distance in complex **4** was 2.7350(10) which is slightly shorter than that observed in a related simpler complex [Mn-μ-O(L)] **5** (where L = the Schiff base ligand derived from 1,3-diaminopropane and 3,5-di-*t*-butyl-2-hydroxybenzaldehyde) [Mn-Mn distance 2.7753(8) Å][20] In addition, the Mn-O3-Mn [97.46(17)°] and Mn-O3-Mn [97.16(17)°] angles differed in complex **4** compared to the above reported [Mn-μ-O(L)] complex [Mn-O-Mn angle = 98.03(9)°].[20] Complex **4** also crystallised from DMSO/H_2O to give a structure with non-crystallographic 2-fold symmetry (orthorhombic, $P2_12_12_1$)[21] compared to the previous rhombohedral structure. However, the X-ray structure of these crystals contained some disorder.[14]

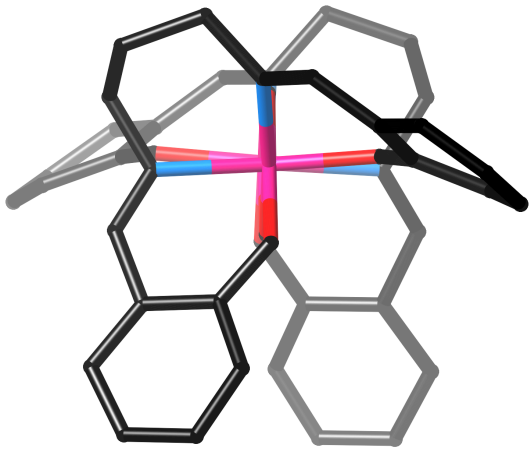


Figure 6. Model of complex **4** with the [2.2]paracyclophane rings truncated looking down the Mn-Mn axis showing *P*-helical chirality.

Conclusions

We have synthesised chiral cis-β octahedral complexes of Co^{III} and Mn^{IV} using the planar chiral PCSP ligand **2** which allowed for high control of asymmetry about the metal centre as well as helical chirality in case of the di-μ-oxo Mn^{IV} complex **4**. The planar chiral [2.2]paracyclophane derived Schiff base **2** is therefore an excellent choice for the preparation of homochiral octahedral metal complexes with high stereoselectivity.

Acknowledgements

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Supporting Information

Experimental, spectral data, and crystallographic data for compounds **2-4**.

Keywords: [2.2]paracyclophane • cis-β octahedral • 'chiral-at-metal' • helical • Schiff base

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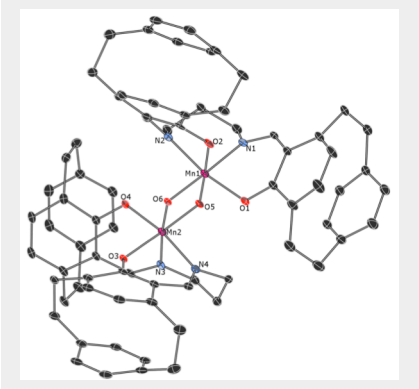
Entry for the Table of Contents

COMMUNICATION

A planar chiral Schiff base [2.2]-paracyclophane derived ligand enable the synthesis of homochiral to form *cis*-β octahedral Co^{III} and Mn^{III} metal complexes owith complete control of the metal centred chirality, and in the case of a Mn^{IV} di-*μ*-oxo complex, *P*-helical chirality.



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Page No. – Page No.

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