

# Chiral Molecules Containing Metal–Metal Bonds

F. Albert Cotton\*<sup>[a]</sup> and Carlos A. Murillo\*<sup>[a]</sup>

**Keywords:** Metal–metal bonds / Chirality / Chromophores / Orthometalation / Helical molecules

Many chiral compounds having metal–metal bonds are now known in which the M–M unit is the chromophore. In this review they are classified as those where it is either (1) an inherently chiral chromophore owing to helical stacking of metal–ligand bonds, or (2) not inherently chiral but surrounded by a collection of ligands bearing chiral substituents. In only a few cases have the actual CD and/or ORD

spectra been measured and analyzed. These include  $M_2X_4$ –(PP)<sub>2</sub> molecules (PP = a bridging diphosphane) and  $M_2(O_2CR)_4$  molecules where R is chiral. The more recently discovered helical extended metal atom chain (EMAC) molecules are also mentioned.

(© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2006)

## Introduction

The way in which metal–metal (M–M) bonds are influenced by, and exert influence upon, a chiral environment is a topic that has not been comprehensively reviewed. There is now a large enough body of results to justify at least a small (surely at least *micro*) review. In general, metal–metal-bonded compounds are of interest in many areas such as catalysis,<sup>[1]</sup> medicine<sup>[2]</sup> and for synthesizing supramolecular arrays.<sup>[3]</sup>

We preface the main body of the review by reminding the reader that there are two fundamental classes of optically active molecules:<sup>[4]</sup>

- (1) Those with inherently chiral chromophores
- (2) Those with achiral chromophores embedded in chiral surroundings

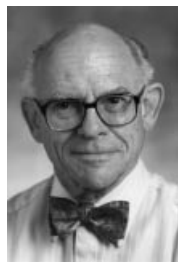
We shall divide this review into two parts based on this difference.

## 1. Inherently Chiral Di- or Polymetal Chromophores

### 1a. M–M Bond Twist Induced by Chiral Diphosphanes

The first examples of molecules with the type of structure shown in Figure 1 were discovered by R. A. Walton and co-workers, in 1975 for rhenium compounds<sup>[5]</sup> and in 1978 for molybdenum compounds.<sup>[6]</sup> Tungsten analogs were reported in 1980.<sup>[7]</sup> The compounds with dppe ( $Ph_2PCH_2CH_2PPh_2$ ) are generally regarded as prototypical, but many are known with other  $R_2PCH_2CH_2PR_2$  and sim-

[a] Department of Chemistry and Laboratory for Molecular Structure and Bonding, A&M University, College Station, P. O. Box 30012, Texas 77842-3012, USA  
E-mail: cotton@tamu.edu  
murillo@tamu.edu



*F. Albert Cotton was born in Philadelphia in 1930. He is the Doherty-Welch Professor of Chemistry and director of the Laboratory for Molecular Structure and Bonding at Texas A&M University. He began his academic career at the Massachusetts Institute of Technology from 1955 to 1971. His successful Ph. D. students number 116. Among his honors are membership in the US National Academy of Sciences and the American Philosophical Society. He received the ACS George C. Pimental Award in Chemical Education in 2006. He is the coauthor of many books and almost 1600 research publications. His main research interest deals with the study of compounds with metal–metal bonds.*



*Carlos A. Murillo received a B. Sc in his native country from the University of Costa Rica in 1973 and a Ph. D. from Texas A&M University (TAMU) in 1976, working with F. A. Cotton. After one year at Princeton University working with M. H. Chisholm he took a position at the University of Costa Rica where he became Professor of Chemistry in 1986. He then moved to TAMU in 1991 where he is a senior lecturer and executive director of the Laboratory for Molecular Structure and Bonding. He is a charter member of the Costa Rican Academy of Sciences, a Fellow of the American Association for the Advancement of Science, a coauthor of Advanced Inorganic Chemistry, a coeditor of Multiple Bonds Between Metal Atoms and coauthor of nearly 250 research publications. His principal research interests are in the synthesis and characterization of compounds with metal–metal bonds.*

ilar bridging diphosphanes.<sup>[8]</sup> The important feature of the  $\text{Re}_2\text{Cl}_4(\text{dppe})_2$  structure shown in Figure 1 is that the conformational requirements of the two six-membered rings that are fused along the metal–metal bond (triple in the rhenium compounds and quadruple for the molybdenum and tungsten ones) induce a partial twist away from an eclipsed conformation. This twist makes the M–M bond an inherently chiral chromophore. For the compounds with quadruple bonds, the  $\delta \rightarrow \delta^*$  transition is a particularly convenient electronic transition for studying the CD/ORD spectra.

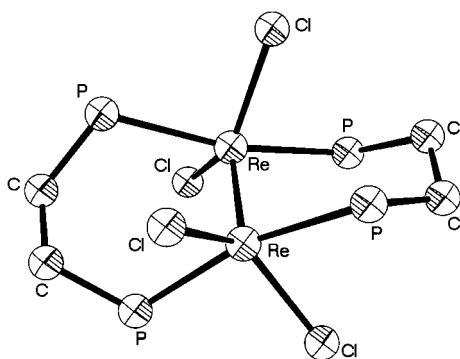


Figure 1. The core of the prototypical  $\text{Re}_2\text{Cl}_4(\text{dppe})_2$  molecule showing the twist away from an eclipsed conformation that produces a chiral chromophore.

No enantiomers of the  $\text{M}_2\text{X}_4(\text{R}_2\text{PCH}_2\text{CH}_2\text{PR}_2)_2$  compounds have been resolved, but by introducing chirality into the backbone of the diphosphane, the chirality of the helix around the M–M core can be predetermined. For such work, the prototype compound is  $\Lambda\text{-}[\text{Mo}_2\text{Cl}_4\{(S,S)\text{-dppb}\}_2]$ , shown along with its CD spectrum in Figure 2, where  $(S,S)\text{-dppb}$  is  $(S,S)\text{-2,3-(diphenylphosphanyl)butane}$ . The structure, with its  $\Lambda$  sense of the twist, is both predicted by conformational analysis and confirmed by X-ray crystallography.<sup>[9,10]</sup>

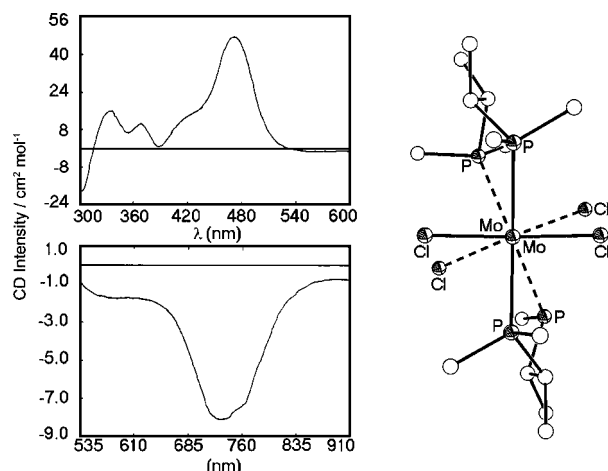


Figure 2. The  $\beta\text{-Mo}_2\text{Cl}_4\{(S,S)\text{dppb}\}_2$  molecule viewed down the Mo–Mo axis (right) and its CD spectrum (left).

The CD spectrum shows two principal features: a negative band at about  $13500\text{ cm}^{-1}$  that corresponds to the

$\delta \rightarrow \delta^*$  absorption band in the electronic spectrum and a positive band at about  $21300\text{ cm}^{-1}$ . These same two principal features are seen in most similar molecules having  $\text{Mo}_2^{4+}$  units.<sup>[11–14]</sup>

There is a very straightforward and unequivocal explanation of these CD results. For the  $\delta \rightarrow \delta^*$  transition, we refer to Figure 3, where it can be seen that there is a shift of charge both along and around the metal–metal bond. Therefore, the  $\delta \rightarrow \delta^*$  transition in such a helical molecule is both electric-dipole- and magnetic-dipole-allowed; it must, therefore, be CD allowed. As shown on the left side, when the  $\Lambda$  twist angle is less than  $45^\circ$ , the signs of the CD bands would be reversed for the  $\Lambda$  and  $\Delta$  isomers. The entire analysis can be conveniently generalized into a sector diagram, as shown in Figure 4. This shows how the CD sign changes, alternating from one octant to the next, as a function of the L–M–L angle. Thus, even if it is known from conformational analysis whether to expect the  $\Lambda$  or  $\Delta$  twist, the extent of the twist must also be known. The first actual test of this octant rule was made with  $\text{Mo}_2\text{Cl}_4\{(R,R)\text{-DIOP}\}_2$ , where  $(R,R)\text{-DIOP}$  is shown in Scheme 1. The twist angle,  $\chi$ , in the dominant isomer of the dimolybdenum compound is  $-45^\circ < \chi < -90^\circ$ , and the sign of the CD for the  $\delta \rightarrow \delta^*$  transition is predicted from the sector diagram to be positive. As shown in Figure 5, this is found experimentally. The diamine molecule,  $\text{Mo}_2\text{Cl}_4[(R)\text{-H}_2\text{NCH}(\text{CH}_3)\text{-CH}_2\text{NH}_2]_2$  was also shown to obey the sector diagram.<sup>[15]</sup>

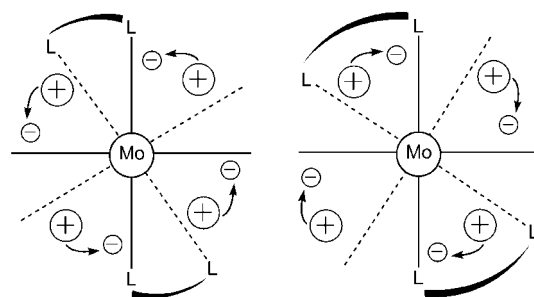


Figure 3. Diagrams of the transient charge distributions for the  $\delta \rightarrow \delta^*$  transition in twisted  $\text{Mo}_2\text{X}_4(\text{LL})_2$  molecules with torsion angle  $\theta$  (a) in the range  $0$  to  $-45^\circ$  and (b) in the range  $-45$  to  $-90^\circ$ . Note that the two ranges, though in the same direction geometrically, give transient charge distributions of opposite rotational sense.

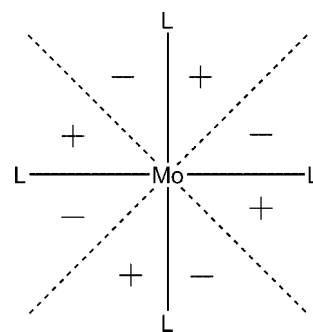
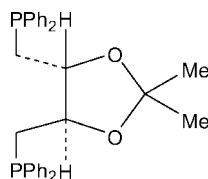
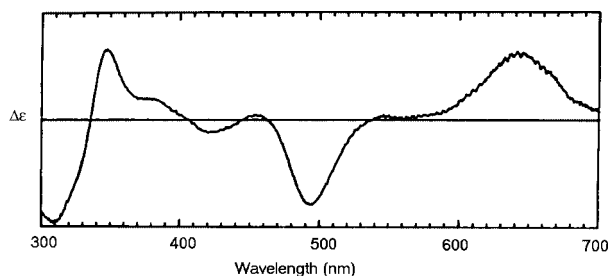


Figure 4. The sign rule for the CD of the  $\delta \rightarrow \delta^*$  transition. The sign of the CD refers to the vector in which the rear set of ligand atoms is found.

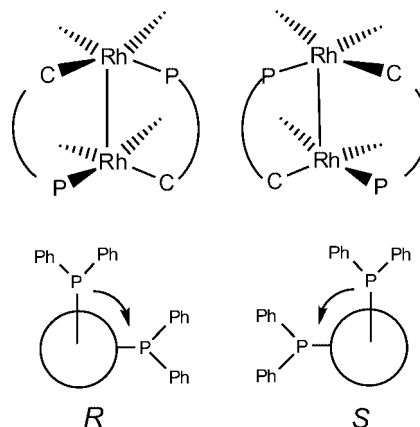
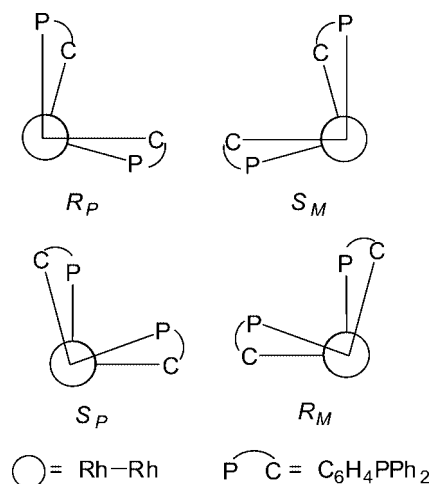
Scheme 1. The (*R,R*)-DIOP molecule.Figure 5. CD spectra of  $\text{Mo}_2\text{Cl}_4\{(\text{R,R})\text{-DIOP}\}_2$  in  $\text{CH}_2\text{Cl}_2$  solution in the range from 300 to 700 nm.

In all of the compounds just discussed, there is a band in the visible spectrum (ca.  $22000\text{ cm}^{-1}$ ) which has the opposite CD sign to that for the  $\delta \rightarrow \delta^*$  transition. This band is due to a  $\delta_{xy} \rightarrow \delta_{x^2-y^2}$  transition, and it has been shown that it follows a sector diagram too, but with all of the signs reversed from those shown in Figure 3 for the  $\delta \rightarrow \delta^*$  transition.

### 1b. Molecules with Orthometalated Bridging Phenylphosphanes

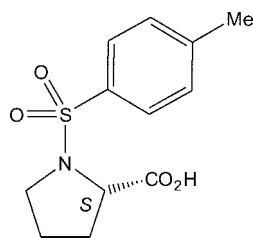
These are compounds with a dimetal unit bridged by two *cisoid* orthometalated phosphanes in a head-to-tail (H,T) arrangement. Two additional equatorial groups such as carboxylates usually complete the paddlewheel arrangement. The compounds *cis*- $\text{Rh}_2(\text{C}_6\text{H}_4\text{PPh}_2)_2(\text{OAc})_2 \cdot 2\text{CH}_3\text{COOH}$ <sup>[16]</sup> and  $\text{Os}_2(\text{C}_6\text{H}_4\text{PPh}_2)_2\text{Cl}_4$ <sup>[17]</sup> were the first to be made. The dirhodium compound and its derivatives have been studied in great detail. Because of the H,T arrangement of the two orthometalated bridging ligands, the *cis*- $\text{Rh}_2(\text{C}_6\text{H}_4\text{PPh}_2)_2$ <sup>2+</sup> unit has only  $C_2$  symmetry and is therefore chiral. The (*R*) and (*S*) conformations are shown in Scheme 2. The interconversion of (*R*) and (*S*) isomers would require bond breaking and such isomers are not expected to interconvert at ordinary temperatures because of the large energy barriers associated with such processes. As shown in Scheme 3, there is also a secondary source of chirality induced by the twist pattern of each phosphane ligand designated as *P* (for positive torsion angle) and *M* (for negative torsion angle along the axis of the helix) following the nomenclature used for helical molecules.<sup>[18]</sup> While for the secondary chirality less energy is expected to be required for interconversion than for the primary source of chirality, this value may still be significant. Molecular mechanics calculations have been used to estimate the relative stability of the (*S<sub>M</sub>*) and (*S<sub>P</sub>*) conformers in *cis*- $\text{Rh}_2(\text{C}_6\text{H}_4\text{PPh}_2)_2(\text{CH}_3\text{CN})_6^{2+}$ ,<sup>[19]</sup> which has a P–Rh–Rh–P torsion angle of  $-23^\circ$ . The results indicate that the experi-

mental (*S<sub>M</sub>*) conformation is  $88.1\text{ kJ mol}^{-1}$  more stable than the (*S<sub>P</sub>*) conformation having the same torsion angle, and that the energy barrier between the conformers is estimated to be much greater than  $kT$  ( $153.3\text{ kJ mol}^{-1}$ )

Scheme 2. The (*R*) and (*S*) chirality imposed by the H,T arrangement of the *cisoid* orthometalated groups.

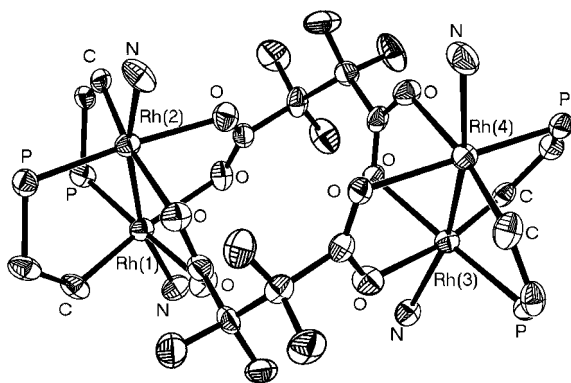
Scheme 3. The second chirality due to the magnitude and sign of the torsion angle along the P–Rh–Rh–P unit.

The stable (*R*) and (*S*) enantiomers have been resolved. The separation procedure makes use of the fact that in (*R,S*)-*cis*- $\text{Rh}_2(\text{C}_6\text{H}_4\text{PPh}_2)_2(\text{OAc})_2 \cdot 2\text{CH}_3\text{COOH}$ , the orthometalated phosphane groups are not labile while the carboxylate groups are. Reaction with ProtosH (*N*-4-methylphenylsulfonyl-L-proline, see Scheme 4) yields (*R,S*)-*cis*- $\text{Rh}_2(\text{C}_6\text{H}_4\text{PPh}_2)_2(\text{Protos})_2 \cdot 2\text{H}_2\text{O}$  and the diastereoisomers are easily separated by column chromatography using silica gel and elution with a mixture of  $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ .<sup>[20]</sup> Many analogs using a great variety of substituted phosphanes have also been synthesized. These compounds have applications in enantioselective C–H insertion of  $\alpha$ -diazo ketones and other catalyzed reactions.<sup>[20,21]</sup>



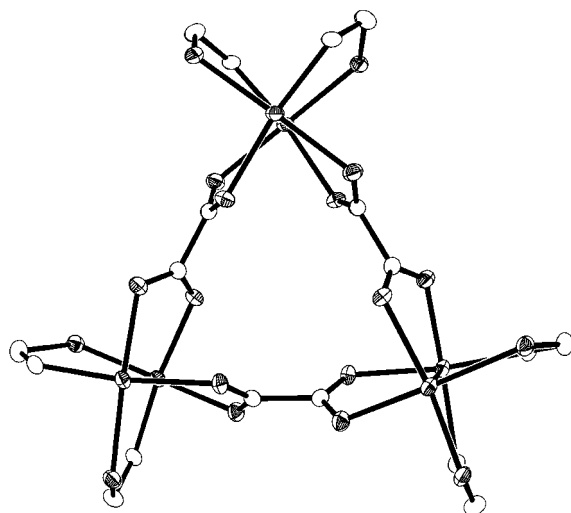
Scheme 4. The chiral ProtosH molecule.

Substitution reactions of the carboxylate groups from the diastereoisomers proceed without racemization, and the group Protos can be easily replaced by other groups such as carboxylates or acetonitrile. The orthometalated dirhodium unit in  $[(R)\text{-}cis\text{-Rh}_2(\text{C}_6\text{H}_4\text{PPh}_2)_2(\text{CH}_3\text{CN})_6](\text{BF}_4)_2$  has been useful as a corner piece for the synthesis of enantiopure supramolecular structures. Reaction with the dicarboxylate anions  $\text{O}_2\text{C}(\text{CF}_2)_n\text{CO}_2$ ,  $n = 2$  and  $3$ , give molecular loops in which each of the two  $\text{Rh}_2(\text{C}_6\text{H}_4\text{PPh}_2)_2$  units is also coordinated by two carboxylate groups from each of the two linkers and two axial pyridine molecules, as shown in Figure 6 for  $n = 2$ .<sup>[22]</sup> In this complex, the P–Rh–Rh–P torsion angles  $[75.7(1)$  and  $74.56(9)^\circ]$  are smaller than those of C–Rh–Rh–C  $[-116.9(4)$  and  $-119.2(4)^\circ]$ . Therefore, the overall chirality of this dirhodium compound is  $(R_M R_M)$ . This is uncommon for simple dirhodium compounds, in which the torsion angle of P–Rh–Rh–P is usually larger than that of C–Rh–Rh–C,<sup>[23]</sup> because of steric repulsions between the bulky phenyl groups in the phosphanes.

Figure 6. The core of the chiral molecular loop  $(RR)\text{-}[cis\text{-Rh}_2(\text{C}_6\text{H}_4\text{PPh}_2)_2(\text{py})_2\text{O}_2\text{CF}_2\text{CF}_2\text{CO}_2]_2$  for which the overall chirality is  $(R_M R_M)$ .

A series of neutral molecular triangles having the formula  $[cis\text{-Rh}_2(\text{C}_6\text{H}_4\text{PPh}_2)_2]_3(\text{dicarboxylate})_3(\text{L}_{\text{ax}})_6$  where  $\text{L}_{\text{ax}}$  may be one of a variety of donor molecules such as DMF, MeOH or py,  $\text{CH}_2\text{Cl}_2$  have also been made. These compounds, for which a representative core is shown in Figure 7, were first prepared by reaction of racemic  $[cis\text{-Rh}_2(\text{C}_6\text{H}_4\text{PPh}_2)_2(\text{CH}_3\text{CN})_6](\text{BF}_4)_2$  and tetraethylammonium salts of linear dicarboxylates such as, oxalate, terephthalate and 4,4'-biphenyldicarboxylate.<sup>[19]</sup> The relative chiralities of the dirhodium units in these triangles were established using a combination of data from X-ray crystallography and  $^{31}\text{P}$  NMR spectroscopy. It should be noted

that the combination of the racemic mixture of  $cis\text{-Rh}_2(\text{C}_6\text{H}_4\text{PPh}_2)_2^{2+}$  units with dicarboxylate anions to form triangles can produce four possible stereoisomers:  $(RRR)$ ,  $(RRS)$ ,  $(SSR)$ , and  $(SSS)$ , and each of these can be either  $(R_P)$  and  $(R_S)$ , or  $(S_P)$  and  $(S_M)$  (see Scheme 3). For the oxalate compound, all the  $\text{Rh}_2$  units in each triangle have the same chirality, and this compound exists as a mixture of  $(R_P R_P R_P)$  and  $(S_M S_M S_M)$  isomers having  $D_3$  symmetry. It is notable that no  $(R_M)$  or  $(S_P)$  conformers were observed. For the terephthalate analog, the structure shows two dirhodium units with one chirality and the third one with another chirality  $[(RRS)$  or  $(SSR)]$  but again there are only  $(R_P)$  or  $(S_M)$  conformers.

Figure 7. The core of the neutral molecular triangle  $[cis\text{-Rh}_2(\text{C}_6\text{H}_4\text{PPh}_2)_2]_3(\text{oxalate})_3(\text{L}_{\text{ax}})_6$ . Only the  $\text{Rh}_2\text{PCC}$  portions of the orthometalated  $\text{Rh}_2\text{C}_6\text{H}_4\text{PPh}_2$  units are shown. Axially coordinated ligands have also been removed for clarity. Carbon atoms are shown as open ellipsoids.

The  $^{31}\text{P}$  NMR spectra, shown in Figure 8, suggest that the structures observed in the solid state remain unchanged in solution, and that there are no interconversions in solution to other types of oligomers such as squares. For the compounds with oxalate and 4,4'-biphenyldicarboxylate linkers, the doublets are consistent with the high symmetry in the crystal, whereby all the orthometalated phosphane ligands are equivalent. Here, the doublets are due to coupling of the P atoms with the  $I = 1/2$   $^{103}\text{Rh}$  nucleus. For the terephthalate analog, the three doublets with nearly identical coupling indicate that the  $(RRS)$  or  $(SSR)$  chirality of the solid state is again present in solution. The enantiopure analogs  $[(RRR)$  or  $(SSS)]$  have also been prepared from reaction of  $(R)$ - or  $(S)$ - $[cis\text{-Rh}_2(\text{C}_6\text{H}_4\text{PPh}_2)_2(\text{CH}_3\text{CN})_6](\text{BF}_4)_2$  and the dicarboxylate salts.<sup>[24]</sup> The core structure of  $(SSS)\text{-}[cis\text{-Rh}_2(\text{C}_6\text{H}_4\text{PPh}_2)_2]_3(\text{terephthalate})_3(\text{py})_6$  is shown in Figure 9 along with the packing diagram. Catalytic evaluation of these enantiopure triangles show that they are catalytically active and provide good results for the intermolecular cyclopropanation between styrene and ethyl diazoacetate.



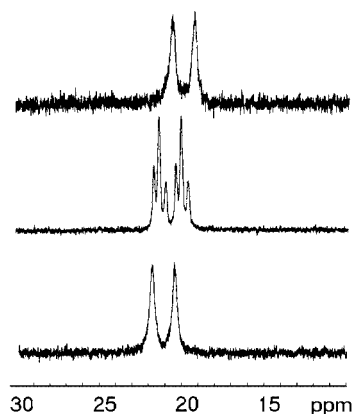


Figure 8.  $^{31}\text{P}$  NMR in  $\text{CD}_3\text{Cl}$  of the racemic triangular compounds with oxalate, terephthalate and 4,4'-biphenyldicarboxylate linkers shown in the same order from top to bottom.

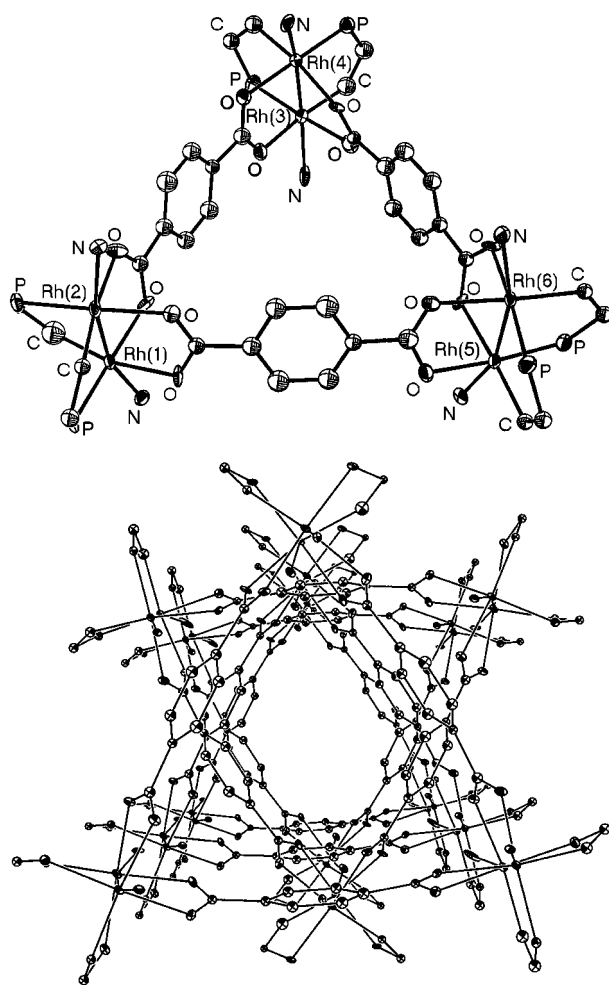


Figure 9. The core structure (top) and packing pattern (bottom) of  $(\text{SSS})\text{-}[\text{cis-Rh}_2(\text{C}_6\text{H}_4\text{PPh}_2)_2]_3(\text{terephthalate})_3(\text{py})_6$ . Note that the molecules stack on top of each other, but alternately out of register, leaving a chiral channel. For the oxalate analog, the triangular molecules stack in register.

The same dirhodium corner piece has been used to build a molecule with pure rotational symmetry  $T$  by reaction of  $(R)\text{-}[\text{cis-Rh}_2(\text{C}_6\text{H}_4\text{PPh}_2)_2(\text{CH}_3\text{CN})_6](\text{BF}_4)_2$  and the trianion

of benzene-1,3,5-tricarboxylic (trimesic) acid.<sup>[25]</sup> The compound  $\{\text{NEt}_4\}[(R)\text{-cis-Rh}_2(\text{C}_6\text{H}_4\text{PPh}_2)(\text{py})_2]_6(1,3,5\text{-C}_6\text{H}_3(\text{CO}_2)_3)_4\}\text{BF}_4$ , prepared by a designed synthesis and shown in Figure 10, has only eight  $\text{C}_3$  and three  $\text{C}_2$  rotations of the group  $T$ . It encapsulates a  $\text{NEt}_4^+$  cation within the chiral spheroidal cavity of the cage. In this chiral carceplex there are six *cisoid*  $(R)\text{-Rh}_2(\text{C}_6\text{H}_4\text{PPh}_2)_2^{2+}$  units (B) linked by four trimesate anions (A), each connecting to three different  $\text{Rh}_2^{4+}$  units to give an  $\text{A}_4\text{B}_6$  type molecule. All oxygen atoms of the trimesate anions are *trans* to either carbon or phosphorus atoms in the orthometalated ligands. The midpoints of the dirhodium units roughly describe an octahedron while the centers of the aryl groups of the anions describe a tetrahedron. Pyridine molecules are found at both axial positions of each dirhodium unit. This carceplex is an all  $(R)$  isomer.

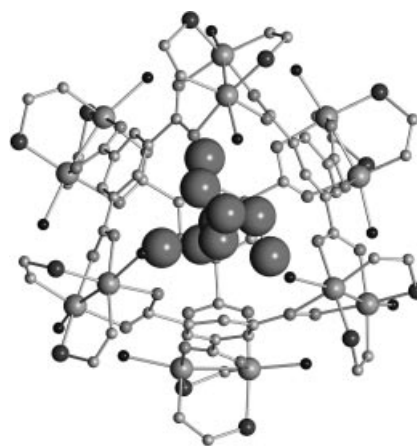


Figure 10. A view of the core structure of the carceplex  $\Lambda\text{-}\{\text{NEt}_4\}[(R)\text{-cis-Rh}_2(\text{C}_6\text{H}_4\text{PPh}_2)(\text{py})_2]_6(1,3,5\text{-C}_6\text{H}_3(\text{CO}_2)_3)_4\}\text{BF}_4$  showing the encapsulated tetraethylammonium cation.

The  $^1\text{H}$  NMR spectrum offers clear evidence that the tetraethylammonium cation remains encapsulated in solution, and shows two signals at high field ( $-0.035$  and  $-0.278$  ppm) in a ratio of 3:2. The large upfield displacement of these signals relative to those of a non-encapsulated  $\text{NEt}_4^+$  cation is due to strong shielding by the cage. The  $^{31}\text{P}$  NMR spectrum of the compound in  $\text{CD}_2\text{Cl}_2$  in the presence of excess pyridine is consistent with the existence of only one highly symmetrical species in solution as it shows only one doublet because of coupling of each P atom to the adjacent  $^{103}\text{Rh}$  nucleus.

### 1c. Helical Molecules with Three or More Metal Atoms

The best known compounds are of the type  $\text{M}_3(\text{dpa})_4\text{X}_2$ , where dpa = the anion of dipyridylamine, X is a monodentate group, typically a monoanion such as a halide,  $\text{PF}_6$ , acetylide, and others and  $\text{M} = \text{Co}, \text{Cr}, \text{Rh}, \text{Ru}, \text{Ni}$ .<sup>[26]</sup> One remarkable feature of compounds of this type is the tunable metal-to-metal interactions within the trinuclear unit and symmetrical and unsymmetrical arrangements may be obtained depending on the nature of the axial ligands. More importantly for this review is the typical helical arrangement of the four dpa anions about the  $\text{M}_3$  unit as shown in

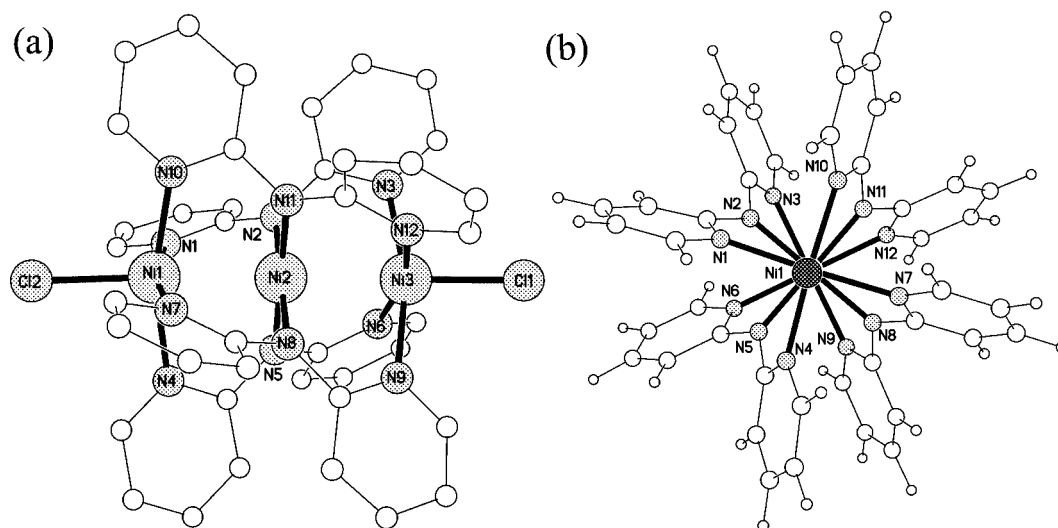


Figure 11. A typical structure of an  $M_3(dpa)_4X_2$  as represented by  $Ni_3(dpa)_4Cl_2$ . The structure is shown (a) perpendicular to the  $Ni_3$  axis, and (b) looking down the  $Ni_3$  axis to emphasize the helical arrangement of the dpa ligands.

Figure 11 for a typical  $M_3$  compound. While the set of four dpa ligands has the capacity to organize an extended metal atom chain (EMAC), it is also forced by internal non-bonded ( $H\cdots H$ ) contacts to form an overall molecular structure with a helical configuration having right- or left-handed helicity (referred to as  $\Delta$  or  $\Lambda$ , respectively) as shown in Figure 12.

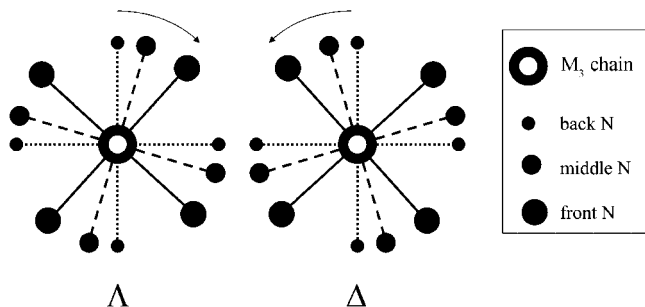


Figure 12. A schematic representation of the  $\Delta$  and  $\Lambda$  isomers of an EMAC of the type  $M_3(dpa)_4X_2$ .

Most of the structures of these  $M_3(dpa)_4X_2$  compounds are racemic but for  $[Co_3(dpa)_4(CH_3CN)_2](PF_6)_2$  single crystals of the  $\Delta$  and  $\Lambda$  isomers were isolated from solution and manually separated. Their absolute configurations were determined by X-ray crystallography and circular dichroism spectra (Figure 13) were measured on solutions made from crystals of known absolute configuration.<sup>[27]</sup> Both isomers exhibit significant Cotton effects. The bands were assigned from the electronic spectra with that at 312 nm corresponding to a spin-allowed  $\pi-\pi^*$  transition. The transition at 369 nm was assigned to a charge-transfer band and the lower energy bands at 442 and 544 nm were assigned to metal-centered transitions in the  $Co_3^{2+}$  core.<sup>[27]</sup> In general, the anisotropy or dissymmetry factor given by the  $\Delta\epsilon/\epsilon$  ratio of circular dichroic to isotropic absorbance is associated with the nature of the transitions.<sup>[28]</sup> For electric-dipole-allowed

and magnetic-dipole-forbidden transitions (CT and ligand  $\pi-\pi^*$  transitions), the  $\Delta\epsilon/\epsilon$  ratio  $\leq 5 \cdot 10^{-3}$  and for magnetic-dipole-allowed and electric-dipole-forbidden transitions (ligand-field transitions,  $n-\pi^*$  transitions),  $\Delta\epsilon/\epsilon$  ratio  $\geq 5 \cdot 10^{-3}$ . The transition for the  $\Lambda$  isomer at 312 nm has a negative sign ( $\Delta\epsilon/\epsilon = 8.2 \cdot 10^{-4}$ ) in the CD spectrum, while the bands at 369 nm ( $\Delta\epsilon/\epsilon = 1.5 \cdot 10^{-3}$ ), 442 nm ( $\Delta\epsilon/\epsilon = 8.25 \cdot 10^{-3}$ ), and 544 nm ( $\Delta\epsilon/\epsilon = 5.0 \cdot 10^{-3}$ ) are positive. The CD spectra for the  $\Delta$  and  $\Lambda$  isomers are mirror images, as expected for a pair of enantiomers. The CD bands at 312 and 369 nm have small  $\Delta\epsilon/\epsilon$  values with the former corresponding to a ligand  $\pi-\pi^*$  transition and the latter corresponding to a LMCT transition. Both are electric-dipole-allowed and magnetic-dipole-forbidden transitions. The greater dissymmetry factor  $\Delta\epsilon/\epsilon$  for the bands at 442 and 544 nm is consistent with these bands being magnetic-dipole-allowed and electric-dipole-forbidden metal-centered transitions. Importantly, the equal intensity but opposite signs of the spectra from the two solutions of isomers having similar concentrations indicates that the two enantiomers do not interconvert in solution.

Spontaneous resolution upon crystallization as just described, is very rare. Normally only racemic crystals are obtainable. However, chromatographic resolution on columns of chiral adsorbants has recently been applied with success to several  $M_3(dpa)_4X_2$  compounds.<sup>[29]</sup> There are two ways to determine the absolute helicity of each enantiomer. The most obvious is to crystallize one (or both) and employ X-ray crystallography. When this cannot be done, vibrational circular dichroism can be used. This has been done in the case of  $Ni_3(dpa)_4(OH)_2$ .<sup>[30]</sup> There are preliminary results showing that many other helical EMACs will be treatable by similar methods.

There are also structurally characterized EMACs with longer polypyridylamides having linear  $M_5$ ,  $M_7$  and  $M_9$  cores. The structures resemble those with  $M_3$  cores in that the molecules are helical. An example is that of  $Ni_9$ -

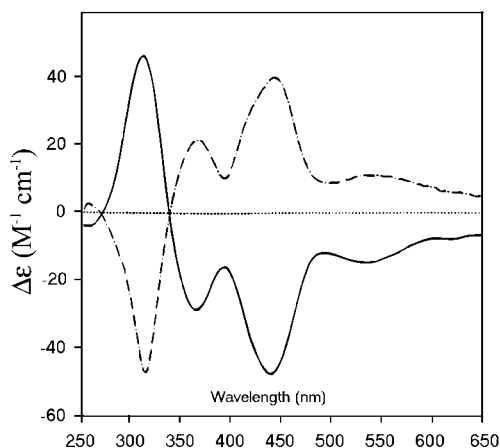


Figure 13. CD spectra of  $\Delta$ - (solid line) and  $\Lambda$ - (dashed line)  $[\text{Co}_3(\text{dpa})_4(\text{NCCH}_3)_2](\text{PF}_6)_2$ .

(peptea) $_4\text{Cl}_2$  (peptea = the anion of pentapyridyltetra-amine),<sup>[31]</sup> which is shown in Figure 14. Recently examples of complexes with four anions derived from polypyridyl-naphthyridine groups (Scheme 5) have been made containing  $\text{Co}_6^{12+}$  and  $\text{Co}_6^{11+}$  cores,<sup>[32]</sup> and  $\text{Ni}_6^{12+}$  and  $\text{Ni}_6^{11+}$  cores.<sup>[33]</sup> A schematic representation of the  $\text{Co}_6^{n+}$  compounds is given in Figure 15. However, none of these racemic mixtures have been resolved.

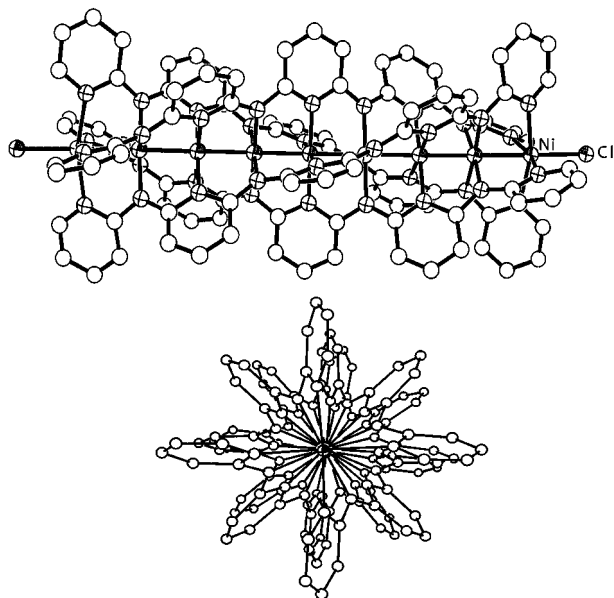
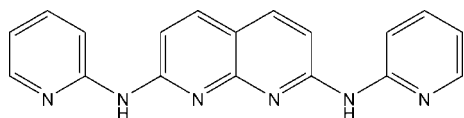


Figure 14. The structure of one of the enantiomers of  $\text{Ni}_9(\text{peptea})_4\text{Cl}_2$  (top). A view along the main axis of this molecule emphasizing the helical arrangement of the polypyridylamido ligands is at the bottom.



Scheme 5. A schematic drawing of 2,7-bis( $\alpha$ -pyridylamido)-1,8-naphthyridine used in the syntheses of compounds with  $\text{M}_6^{12+}$  and  $\text{M}_6^{11+}$  cores,  $\text{M} = \text{Co}$  and  $\text{Ni}$ .

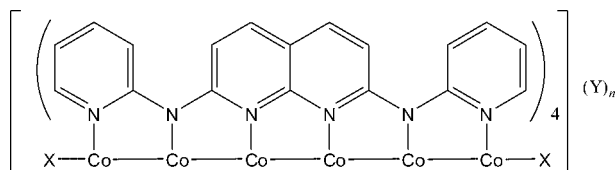


Figure 15. A 2-dimensional representation of the  $\text{Co}_6^{n+}$  compounds synthesized with the ligand in Scheme 5,  $\text{X} = \text{NCS}$  or triflate anions, and  $\text{Y} = \text{PF}_6$  or triflate anions. The way the EMACs twist is not shown.

## 2. Achiral Dimetal Chromophores in Chiral Environments

It appears that the first structurally characterized quadruply bonded  $\text{Mo}_2^{4+}$  compound containing chiral ligands was  $\text{Mo}_2(\text{L-isoleucine})_2(\text{NCS})_4 \cdot 4.5\text{H}_2\text{O}$ , but no spectroscopic data were collected.<sup>[34]</sup> Later,  $\text{Mo}_2(\text{L-leucine})_4\text{Cl}_2(p\text{-toluenesulfonate})_2 \cdot 2\text{H}_2\text{O}$  was prepared, structurally characterized, and, because of very favorable alignment of the molecules in the crystal, used for detailed studies of the polarization and vibronic structure of the  $\delta \rightarrow \delta^*$  absorption band.<sup>[35]</sup> Again, however, no ORD or CD data were collected.

Chiral dicarboxylic acid anions, L-tartrate and D-aspartate, have been used to link  $\text{Mo}_2(\text{DAniF})_3^+$  units ( $\text{DAniF}$  = the  $N,N'$ -di- $p$ -anisylformamidinate anion).<sup>[36]</sup> The structure of the tartrate is shown in Figure 16. An enantiomerically pure compound in the form of a loop has two  $\text{cis-Mo}_2(\text{DAniF})_2^{2+}$  units and two chiral dicarboxylates made from hydroquinone and ethyl ( $S$ )-lactate,<sup>[37]</sup> **L1-para**, shown in Scheme 6. The structure of the loop  $[\text{cis-Mo}_2(\text{DAniF})_2]_2(\text{L1-para})_2$  is shown in Figure 17. In the crystal, the molecules stack forming channels capable of hosting guest molecules such as  $\text{CH}_2\text{Cl}_2$ , as shown in Figure 18.

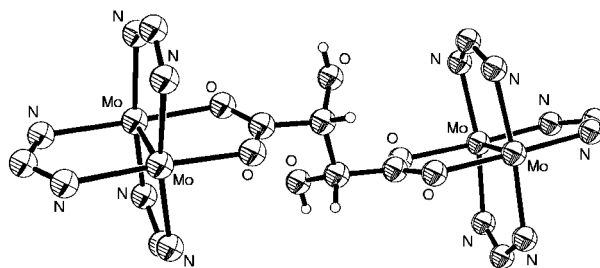
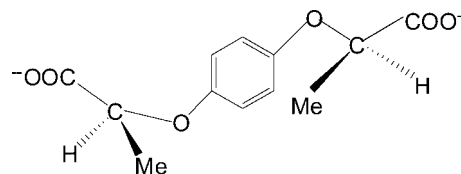


Figure 16. The structure of  $[\text{Mo}_2(\text{DAniF})_3]_2(\text{L-tartrate})$ .



Scheme 6. The ligand **L1-para**,  $p\text{-O}_2\text{C}(\text{CH}_3)(\text{H})(\text{O})\text{-C}_6\text{H}_4\text{-(O)C}(\text{CH}_3)(\text{H})\text{CO}_2^-$ , made from hydroquinone and ethyl ( $S$ )-lactate.

Other early work in this area was done by Snatzke,<sup>[38]</sup> whose goal was to employ the  $\delta \rightarrow \delta^*$  transition in the  $\text{Mo}_2^{4+}$  chromophore, which is conveniently located at about

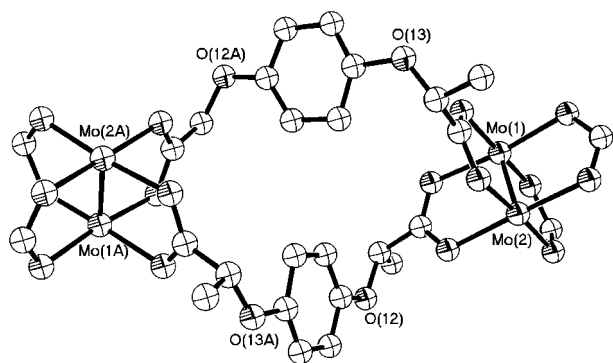


Figure 17. The structure of the molecular loop  $[cis-Mo_2(DAniF)_2]_2-(L1-para)_2$ .

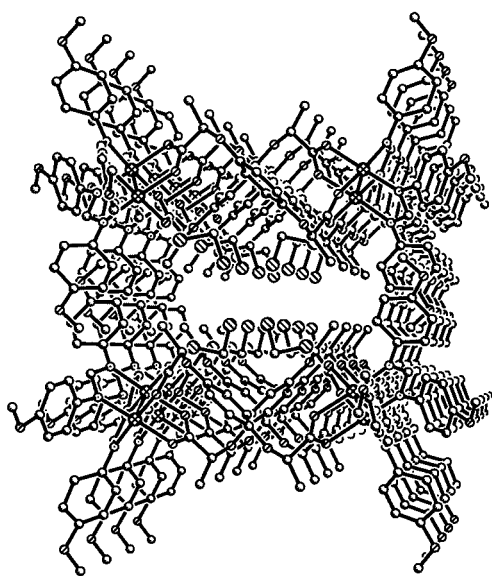


Figure 18. The packing of  $[cis-Mo_2(DAniF)_2]_2-(L1-para)_2$  showing the chiral interstices.

$20000\text{ cm}^{-1}$ , to determine the absolute configurations of functionalized organic molecules. Direct ORD or CD measurements of the organic molecules themselves was challenging because their lowest-energy transition was generally in the ultraviolet. Snatzke's approach was rather empirical; it consisted in simply adding  $Mo_2(O_2CCH_3)_4$  to a solution of the organic compound of interest and measuring the CD spectrum in the visible region due to some generally undefined complex between the organic compound and some fragment of the  $Mo_2(O_2CCH_3)_4$  molecule that had been introduced. Results varied with absolute and relative concentrations.

It was later proposed<sup>[39]</sup> that the ability of  $Rh_2(O_2CCF_3)_4$  to bind almost every possible organic functionality including simple olefins, at its axial position might lead to a more reliable realization of Snatzke's concept, but there has been no follow up on this. It does not appear that the use of "spectator" dimetal units, either  $Mo_2^{4+}$  or  $Rh_2^{4+}$  is a very promising technique.

## Dirhodium Compounds

In 1986 two  $Rh_2(O_2CR)_4L_2$  compounds, one with  $R = CPh(OH)H$  and  $L = EtOH$  and the other with  $R = CPh(OMe)H$  and  $L = THF$  were structurally characterized and their CD spectra were measured and interpreted.<sup>[40]</sup> The structure of the (*S*)-mandelate is shown in Figure 19 and it resembles that of the  $Mo_2^{4+}$  analog, except for the absence of axial ligands in the latter.<sup>[41]</sup> The electronic absorption and CD spectra of  $Rh_2[(S)\text{-mandelate}]_4(EtOH)_2$  are shown in Figure 20. The interpretation, which is much too complex to recapitulate here, was carried out assuming that the central  $Rh_2(O_2C-)_4$  core is inherently achiral, having  $D_{4h}$  symmetry. A one-electron model of a type previously proposed by others<sup>[42]</sup> was employed and was found to be consistent with the fact that the CD signs associated with the two prominent absorption bands (at ca. 450 and 600 nm) have the same sign. The fact that both are negative (rather than both positive) was not predictable. However, because both have the same sign, a reversal of the absorption band assignments from those accepted at the time is not ruled out, and indeed MCD measurements reported se-

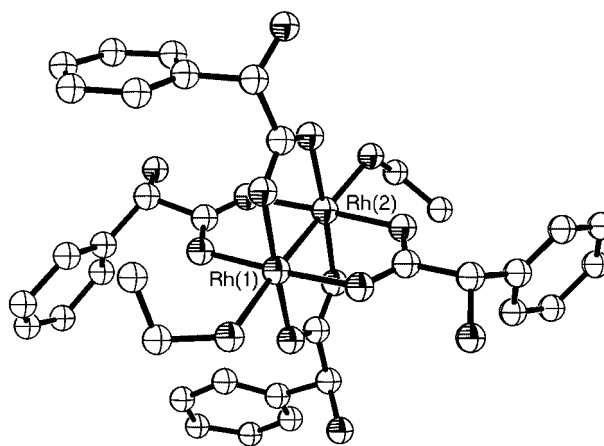


Figure 19. The structure of  $Rh_2[(S)\text{-mandelate}]_4(EtOH)_2$ .

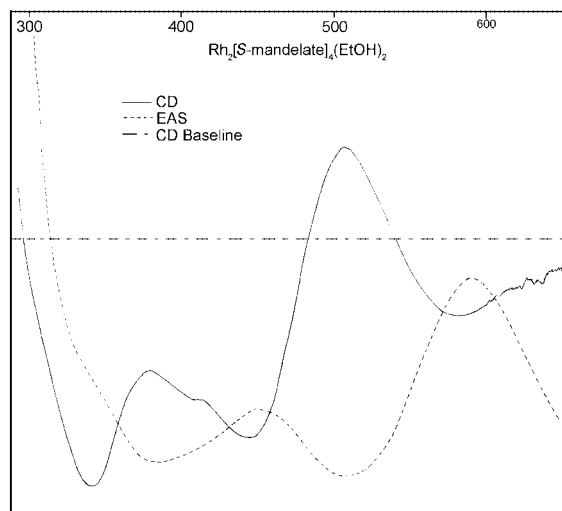


Figure 20. CD and UV-vis spectra of  $Rh_2[(S)\text{-mandelate}]_4(EtOH)_2$ .



veral years later<sup>[43]</sup> showed that such a reversal was required. Thus, while the CD results offer valuable evidence for assigning the electronic spectrum, they are not by themselves definitive.

Chiral dirhodium compounds are some of the most widely studied species with metal–metal bonds due to their applications in catalysis. Because this topic has been reviewed recently we will not elaborate any further here.<sup>[44]</sup>

## Conclusions

There is considerable diversity of chiral compounds that contain dimetal units. Those cited in this review suggest that there is great scope for further development, along both of the main avenues: (1) compounds in which the ligand arrangement renders the  $M_2$  unit itself chiral, and (2) compounds in which the  $M_2$  unit is not itself a seat for chirality but is the linchpin for a surrounding set of chiral ligands.

## Acknowledgments

We thank the Robert A. Welch Foundation and Texas A&M University for financial support.

- [1] a) M. P. Doyle, T. Ren, *Prog. Inorg. Chem.* **2001**, 49, 113; b) R. D. Adams, F. A. Cotton (Eds.), *Catalysis by Di- and Polynuclear Metal Cluster Complexes*, Wiley-VCH, New York, **1998**; c) K. Matsumoto, in: *Cisplatin: Chemistry and Biochemistry of a Leading Anticancer Drug* (Ed.: B. Lippert), Wiley-VCH, New York, **1999**, p. 455; d) N. Saeki, N. Nakamura, T. Ishibashi, M. Arime, H. Sekiya, K. Ishihara, K. Matsumoto, *J. Am. Chem. Soc.* **2003**, 125, 3605; e) M. Pillinger, I. S. Gonçalves, P. Ferreira, J. Rocha, M. Schafer, D. Schon, O. Nuyken, F. E. Kühn, *Macromol. Rapid Commun.* **2001**, 22, 1302; f) E. Whelan, M. Devereux, M. McCann, V. McKee, *Chem. Commun.* **1997**, 427.
- [2] a) J. M. Asara, J. S. Hess, E. Lozada, K. R. Dunbar, J. Allion, *J. Am. Chem. Soc.* **2000**, 122, 8; b) K. V. Catalan, J. S. Hess, M. M. Maloney, D. J. Mindiola, D. L. Ward, K. R. Dunbar, *Inorg. Chem.* **1999**, 38, 3904; c) L. D. Dale, T. M. Dyson, D. A. Tocher, J. H. Tocher, D. I. Edwards, *Anti-Cancer Drug Des.* **1989**, 4, 295; d) K. Aoki, H. Yamazaki, *J. Chem. Soc., Chem. Commun.* **1980**, 186; e) R. A. Howard, A. P. Kimball, J. L. Bear, *Cancer Res.* **1979**, 39, 2568; f) P. Fu, P. M. Bradley, C. Turro, *Inorg. Chem.* **2001**, 40, 2476; g) K. Aoki, M. A. Salam, *Inorg. Chim. Acta* **2001**, 316, 50; h) B. Lippert, *Prog. Inorg. Chem.* **1989**, 37, 1; i) W. Micklitz, G. Müller, B. Huber, J. Riede, F. Rashwan, J. Heinze, B. Lippert, *J. Am. Chem. Soc.* **1988**, 110, 7084; j) H. T. Chifotides, K. R. Dunbar, *Acc. Chem. Res.* **2005**, 38, 146.
- [3] a) F. A. Cotton, C. Lin, C. A. Murillo, *Acc. Chem. Res.* **2001**, 34, 759; b) F. A. Cotton, C. Lin, C. A. Murillo, *Proc. Natl. Acad. Sci. USA* **2002**, 99, 4810; c) M. H. Chisholm, A. M. McIntosh, *Chem. Rev.* **2005**, 105, 2949.
- [4] A. Moscovitz, *Tetrahedron* **1961**, 13, 48.
- [5] a) J. A. Jaeger, D. P. Murtha, R. A. Walton, *Inorg. Chim. Acta* **1975**, 13, 21; b) J. R. Ebner, D. R. Tyler, R. A. Walton, *Inorg. Chem.* **1976**, 15, 833; c) F. A. Cotton, G. G. Stanley, R. A. Walton, *Inorg. Chem.* **1978**, 17, 2099.
- [6] a) S. A. Best, T. J. Smith, R. A. Walton, *Inorg. Chem.* **1978**, 17, 99; b) H. D. Glicksman, R. A. Walton, *Inorg. Chem.* **1978**, 17, 3197.
- [7] a) F. A. Cotton, T. R. Felthouse, D. G. Lay, *J. Am. Chem. Soc.* **1980**, 102, 1431; b) F. A. Cotton, T. R. Felthouse, *Inorg. Chem.* **1981**, 20, 3880.
- [8] For full references, see chapters on Mo, W and Re, in: *Multiple Bonds Between Metal Atoms* (Eds.: F. A. Cotton, C. A. Murillo, R. A. Walton), Springer Science and Business Media Inc., New York, **2005**.
- [9] P. A. Agaskar, F. A. Cotton, I. F. Fraser, R. D. Peacock, *J. Am. Chem. Soc.* **1984**, 106, 1851.
- [10] P. A. Agaskar, F. A. Cotton, I. F. Fraser, L. Manojlovic-Muir, K. W. Muir, R. D. Peacock, *Inorg. Chem.* **1986**, 25, 2511.
- [11] J.-D. Chen, F. A. Cotton, L. R. Falvello, *J. Am. Chem. Soc.* **1990**, 112, 1076.
- [12] R. D. Peacock, *Polyhedron* **1987**, 6, 715.
- [13] I. F. Fraser, A. McVitie, R. D. Peacock, *Polyhedron* **1986**, 5, 39.
- [14] I. F. Fraser, R. D. Peacock, *J. Chem. Soc., Chem. Commun.* **1985**, 1727.
- [15] R. D. Peacock, I. F. Fraser, *Inorg. Chem.* **1985**, 24, 988.
- [16] A. R. Chakravarty, F. A. Cotton, D. A. Tocher, J. H. Tocher, *Organometallics* **1985**, 4, 8.
- [17] F. A. Cotton, R. Poli, *Organometallics* **1987**, 6, 1743.
- [18] R. S. Cahn, C. Ingold, V. Prelog, *Angew. Chem. Int. Ed. Engl.* **1966**, 5, 385.
- [19] F. A. Cotton, C. A. Murillo, X. Wang, R. Yu, *Inorg. Chem.* **2004**, 43, 8394.
- [20] F. Estevan, K. Herbst, P. Lahuerta, M. Barberis, J. Pérez-Prieto, *Organometallics* **2001**, 20, 950.
- [21] a) M. Barberis, J. Pérez-Prieto, K. Herbst, P. Lahuerta, *Organometallics* **2002**, 21, 1667; b) M. Barberis, P. Lahuerta, J. Pérez-Prieto, M. Sanaú, *Chem. Commun.* **2001**, 439; c) F. Estevan, P. Lahuerta, J. Pérez-Prieto, I. Pereira, S.-E. Stiriba, *Organometallics* **1998**, 17, 3442; d) F. Estevan, P. Lahuerta, J. Pérez-Prieto, M. Sanaú, S.-E. Stiriba, A. M. Ubeda, *Organometallics* **1997**, 16, 880.
- [22] F. A. Cotton, C. A. Murillo, R. Yu, *Inorg. Chem.* **2005**, 44, 8211.
- [23] a) F. Barceló, F. A. Cotton, P. Lahuerta, M. Sanaú, W. Schwotzer, M. A. Ubeda, *Organometallics* **1987**, 6, 1105; b) P. Lahuerta, R. Martínez-Mañez, J. Paya, E. Peris, *Inorg. Chim. Acta* **1990**, 173, 99; c) E. C. Morrison, D. A. Tocher, *J. Organomet. Chem.* **1991**, 408, 105; d) P. Lahuerta, J. Payá, E. Peris, A. Aguirre, S. García-Granda, F. Gómez-Beltrán, *Inorg. Chim. Acta* **1992**, 192, 43; e) M. V. Borrachero, F. Estevan, S. García-Granda, P. Lahuerta, J. Latorre, E. Peris, M. Sanaú, *J. Chem. Soc., Chem. Commun.* **1993**, 1864; f) F. Estevan, P. Lahuerta, E. Peris, M. A. Ubeda, S. García-Granda, F. Gómez-Beltrán, E. Pérez-Carreño, G. González, M. Martínez, *Inorg. Chim. Acta* **1994**, 218, 189; g) F. Estevan, S. García-Granda, P. Lahuerta, J. Latorre, E. Peris, M. Sanaú, *Inorg. Chim. Acta* **1995**, 229, 365; h) P. Lahuerta, I. Pereira, J. Pérez-Prieto, M. Sanaú, S.-E. Stiriba, D. F. Taber, *J. Organomet. Chem.* **2000**, 612, 36; i) F. Estevan, P. Krueger, P. Lahuerta, E. Moreno, J. Pérez-Prieto, M. Sanaú, H. Werner, *Eur. J. Inorg. Chem.* **2001**, 105.
- [24] F. A. Cotton, C. A. Murillo, R. Yu, *Inorg. Chem.* **2005**, 44, 8223.
- [25] F. A. Cotton, C. A. Murillo, R. Yu, *Dalton Trans.* **2005**, 3161.
- [26] J. F. Berry, in: *Multiple Bonds Between Metal Atoms* (Eds.: F. A. Cotton, C. A. Murillo, R. A. Walton), Springer Science and Business Media Inc., New York, **2005**, pp. 669–706. (A review of EMACs with 86 references)
- [27] R. Clérac, F. A. Cotton, K. R. Dunbar, T. Lu, C. A. Murillo, X. Wang, *Inorg. Chem.* **2000**, 39, 3065.
- [28] E. L. Eliel, S. H. Wilen, *Stereochemistry of Organic Compounds*, John Wiley & Sons, New York, **1994**.
- [29] D. W. Armstrong, F. A. Cotton, unpublished results.
- [30] A. G. Petrovic, P. L. Polavarapu, F. A. Cotton, unpublished results.
- [31] S.-M. Peng, C.-C. Wang, Y.-L. Yang, Y.-H. Chen, F.-Y. Li, C.-Y. Mou, M.-K. Leung, *J. Magn. Magn. Mater.* **2000**, 209, 80.

- [32] C.-H. Chien, J.-C. Chang, C.-Y. Yeh, G.-H. Lee, J.-M. Fang, S.-M. Peng, *Dalton Trans.* **2006**, 2106.
- [33] C.-H. Chien, J.-C. Chang, C.-Y. Yeh, G.-H. Lee, J.-M. Fang, Y. Song, S.-M. Peng, *Dalton Trans.* **2006**, 3249.
- [34] A. Bino, F. A. Cotton, *Inorg. Chem.* **1979**, *18*, 1381.
- [35] A. Bino, F. A. Cotton, P. E. Fanwick, *Inorg. Chem.* **1980**, *19*, 1215.
- [36] F. A. Cotton, J. P. Donahue, C. A. Murillo, *Inorg. Chem. Commun.* **2002**, *5*, 59.
- [37] J. F. Berry, F. A. Cotton, S. I. Ibragimov, C. A. Murillo, X. Wang, *Dalton Trans.* **2003**, 4297.
- [38] a) G. Snatzke, *Angew. Chem. Int. Ed. Engl.* **1979**, *18*, 363; b) G. Snatzke, V. Wagner, H. P. Wolff, *Tetrahedron* **1981**, *37*, 349; c) V. J. Engel, R. Gerger, G. Snatzke, V. Wagner, *Chem.-Ztg.* **1981**, *105*, 85.
- [39] F. A. Cotton, L. R. Falvello, M. Gerards, G. Snatzke, *J. Am. Chem. Soc.* **1990**, *112*, 8979.
- [40] P. A. Agaskar, F. A. Cotton, L. R. Falvello, S. Han, *J. Am. Chem. Soc.* **1986**, *108*, 1214.
- [41] F. A. Cotton, L. R. Falvello, C. A. Murillo, *Inorg. Chem.* **1983**, *22*, 382.
- [42] a) S. F. Mason, in: *Optical Activities and Chiral Discrimination* (Ed.: S. F. Mason), D. Riedel, Boston, **1979**, pp. 1–24; b) J. A. Schellman, *Acc. Chem. Res.* **1968**, *1*, 144.
- [43] J. W. Trexler Jr, A. F. Schreiner, F. A. Cotton, *Inorg. Chem.* **1988**, *27*, 3265.
- [44] D. J. Timmons, M. P. Doyle, in: *Multiple Bonds Between Metal Atoms* (Eds.: F. A. Cotton, C. A. Murillo, R. A. Walton, Eds.), Springer Science and Business Media Inc.: New York, **2005**, pp. 591–632. (A review with 200 references on the catalytic activity of chiral  $\text{Rh}_2^{4+}$  compounds)

Received: May 24, 2006

Published Online: July 31, 2006