

# A Continuous Chirality Analysis of Homoleptic Hexacoordinated Complexes

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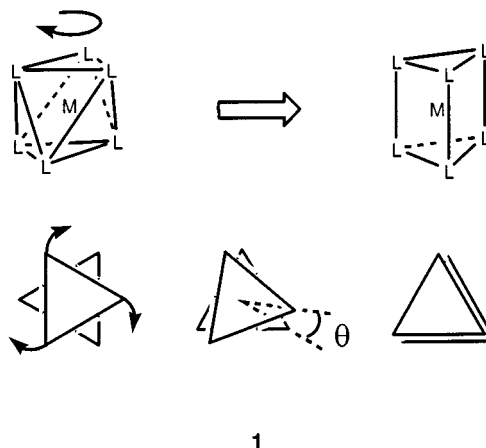
Hexacoordinated complexes are generally considered to be potentially chiral if they have either at least two bidentate ligands or at least three different monodentate ligands. Here we draw attention to a neglected general possibility, namely that homoleptic hexacoordinated complexes with molecular structures in between octahedral and trigonal prismatic, following the Bailar twisting route, are chiral. A quantitative evaluation of the degree of chirality of such hexakis(mon-

dentate) complexes shows that they reach maximum chirality when the trigonal rotation angle of the prism reaches 23°. Model calculations and analysis of experimental X-ray structures are in good agreement. The most chiral of the complexes with monodentate ligands that have been analyzed is  $[\text{Zr}(\text{SC}_6\text{H}_4\text{-4-OMe})_6]^{2-}$ . The validity of the theoretical prediction is also corroborated by an analysis of the chirality of the coordination sphere in twisted tris(chelate) complexes.

## Introduction

The chirality of transition metal complexes is of much current interest mainly because of their potential applications as catalysts for asymmetric synthesis.<sup>[1]</sup> Following von Zelewsky (and somewhat modifying his list),<sup>[2]</sup> we note that chirality can be induced in coordination compounds by: (i) the existence of different ligands (as in  $[\text{Mabcdef}]$ ); (ii) a special spatial arrangement of ligands (as in one of the stereoisomers of  $[\text{Ma}_2\text{b}_2\text{c}_2]$ ); (iii) the removal of an improper symmetry element of a bidentate ligand through formation of chelate rings (including the mutual breaking of an improper rotation present in such ligands); (iv) coordination of chiral ligands, of ligands which assume chiral conformations or of prochiral ligands (i.e., ligands which become chiral upon coordination because an improper symmetry is broken); or (v) rotational symmetry wrapping of the ligands around the metal. Within the rotational wrapping option, we distinguish several sub-types, namely helical wrapping,<sup>[3]</sup> the propeller-type arrangement in bis- and tris(chelate) complexes and, of relevance to this report, the Bailar-type twist,<sup>[4]</sup> which links octahedricity and trigonal prismaticity in hexacoordinated complexes, as shown in **1**.

Perhaps the most elementary option for obtaining chirality is the Bailar twist, which reduces the achiral point groups  $O_h$  and  $D_{3h}$  to the chiral  $D_3$  symmetry point group. The simplicity of this option originates from the fact that it



allows *homoleptic*  $[\text{ML}_6]$  complexes to be chiral, with no special requirement for chirality or pro-chirality of the six ligands. Yet, to the best of our knowledge, no enantiomeric crystals of the two  $D_3$  enantiomers have been reported. It is interesting to note that of all the options for obtaining chirality, the one that was highlighted since the dawn of coordination chemistry was option (iii), i.e. the use of bidentate ligands. Starting with the pioneering work of Alfred Werner, who resolved the two enantiomers of the cationic complexes  $[\text{CoX}(\text{NH}_3)(\text{en})_2]^{2+}$  ( $\text{X} = \text{Cl}, \text{Br}$ ),<sup>[5]</sup> many other octahedral metal complexes with two or three bidentate ligands have been shown to be chiral.<sup>[2,6–12]</sup> In fact, option (iii) has overshadowed over the years all the other options for obtaining chirality in hexacoordinated complexes. Thus, it is common to find in textbooks statements such as: “Important examples [of chiral molecules] are bischelate and trischelate octahedral complexes” (ref.<sup>[11]</sup>); “Chiral complexes occur mainly when chelate rings are formed” (ref.<sup>[11]</sup> p. 683) “In practice, optical activity is largely confined to octahedral complexes of chelating ligands”;<sup>[6]</sup> “The absolute configuration of a chiral complex is described by imagining a view along a threefold rotation axis of a regular octahedron and noting the handedness of the helix formed

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by the ligands", but again, the figure that accompanies the text shows a complex with bidentate ligands.<sup>[8,13]</sup>

The main purpose of this paper is to draw attention to the largely neglected possibility of obtaining chiral homoleptic  $[\text{ML}_6]$  complexes through the Bailar twist. We do so by reporting the results of a quantitative analysis of the chirality of homoleptic hexacoordinated complexes and its variation along the  $D_3$  route, comparing in detail experiment with theory. It was found that *chirality in crystalline hexacoordinated complexes is much more common than previously appreciated*. While it is true that crystalline chirality may not show up in solution if the racemization process has a low energy barrier, one should recall that chiral crystals have been used successfully for product enantiocontrol in many chiral catalytic reactions<sup>[28]</sup> and that growing interest in crystals as useful materials for optical purposes renders crystal-packing-induced chirality an important issue. Furthermore, even if the handedness flips between the two enantiomers in solution it may be of importance in catalytic processes with chiral substrates since diastereomeric interactions will prefer one of the two enantiomers. We also mention here, computational analysis in progress in our laboratories shows that the energy barriers for racemization of  $D_3$ -chiral homoleptic  $[\text{ML}_6]$  complexes may be surprisingly high (e.g. of the order of 20 kcal/mol for the  $\text{Zr}^{\text{IV}}$  thiolato complex analyzed below).

## Results and Discussion

### Chirality Changes Along the Bailar-Twist Route

The  $\text{ML}_6$  structures can be characterized by the Bailar twist angle  $\theta$  (**1**) that indicates their deviations from the trigonal prism ( $\theta = 0^\circ$ ) or from the octahedron ( $\theta = 60^\circ$ ). While classically one labels all the intermediate  $D_3$  geometries as simply "chiral", the intuitive need arises to express that, for example, a  $\theta$  value of  $0.1^\circ$  represents much lower chirality than a  $\theta$  value of  $10^\circ$ . A quantitative evaluation of the degree of chirality is therefore needed here, and such a structural measurement tool will allow one to follow, in a continuous way, how chirality changes with  $\theta$ . The methodology we use for this purpose is the Continuous Chirality Measures approach,<sup>[14]</sup> which has already proved useful in numerous applications.<sup>[15]</sup> In short (readers interested in more details are referred to ref.<sup>[14]</sup>), the method seeks the minimal distances that the vertices of an object have to undergo to attain achirality. On the scale, which is a function of these distances, an achiral molecule has a chirality value of  $S = 0$  and as the structure is more chiral  $S$  increases (up to a maximum value of 100). In most cases — and in all cases reported here — the nearest achiral structure has at least one reflection plane.<sup>[16]</sup>

The results of computing the  $S$  values along a hypothetical Bailar route are shown in Figure 1 (full line) beginning with the ideal, all-equal-edges trigonal prism (TP) at  $\theta = 0^\circ$  and ending at  $\theta = 60^\circ$  with the ideal octahedron.<sup>[17]</sup> Since the end points are achiral while those at intermediate  $\theta$

values are  $D_3$ -chiral, one expects that (at least one) maximum chirality value will appear in between the two achiral ends. This is indeed found for the model at  $\theta = 23^\circ$  (Figure 1). In a way, this result resembles the chirality analysis of rotating ethane<sup>[18]</sup> for which an angle of  $30^\circ$  was found to give the maximal chiral rotamer. We proposed therefore to term conformers of maximal chirality *chiramer*s, and this term can be used here as well, i.e., the  $23^\circ$  conformer of the hexacoordinated  $\text{ML}_6$  group is its chiramer.

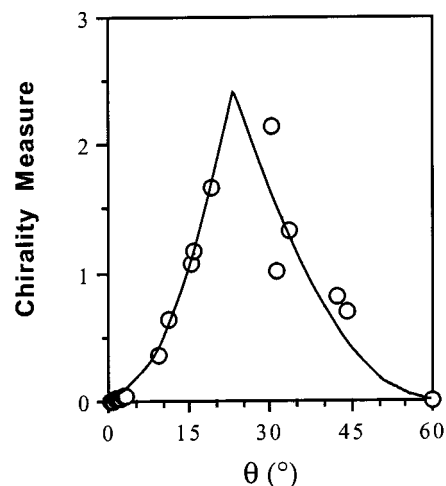


Figure 1. Chirality measure for a model  $\text{MX}_6$  molecule (continuous line) along the trigonal twist (see **1**); the experimental chirality measures of heptaatomic  $\text{MX}_6$  cores of homoleptic organometallic and thiolato complexes are shown as circles (more information can be found in Table 1)

The fact that the chiramer of the hexacoordinated complexes does not appear halfway (i.e., at  $30^\circ$ ) between the two ideal shapes may seem at first sight surprising, but is explained as follows: One of the main features of the CCM approach is that it not only computes the chirality content, but also provides the actual shape of the nearest achiral object. When these objects are observed for the full line in Figure 1, it is seen that from the maximum and to the right ( $\theta = 60^\circ$ ), the nearest achiral structure is a distorted octahedron of  $C_{2v}$  symmetry, namely an octahedron that is bent along the  $z$ -axis, as shown by **2**. Between the ideal TP on the left of Figure 1 ( $\theta = 0^\circ$ ) and the maximum at  $\theta = 23^\circ$ , the nearest achiral structure is always a  $D_{3h}$ -TP varying in height from point to point (although not very much. Thus, for  $\theta = 0^\circ$ ,  $10^\circ$  and  $20^\circ$ , the edge-to-height ratios are 1.000, 1.028 and 1.049, respectively). The reason why it is that the two branches do not cross at the halfway angle but closer to the achiral distorted octahedron branch is now clear: Unlike the right branch of Figure 1, the left branch represents a more demanding nearest achiral structure in the sense that it does not have two reflection planes but four; therefore, departure from that branch to the less-demanding two-planes branch occurs earlier than  $30^\circ$ . Finally, it should be noted that at the peak ( $\theta = 23^\circ$ ), the chirality measure represents an equal minimum distance to *two* achiral structures: a TP and a bent  $z$ -axis octahedron.

## Chirality of Homoleptic Complexes

Does the theoretical line of Figure 1 represent a reality for  $[\text{ML}_6]$  complexes? We have selected for the present study



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the families of organometallic and thiolato homoleptic compounds,<sup>[19]</sup> and the chirality measures of their  $\text{MX}_6$  cores (Table 1) are superimposed in Figure 1 on the Bailar

Table 1. Chirality measures, twist angle ( $\theta$ ), space group, and references for the hexacoordinated homoleptic metal complexes presented in Figure 1

Compd. <sup>[a]</sup>	Refcode <sup>[b]</sup>	$\theta$	S(chir)	Group	ref.
$[\text{Ta}(\text{CCSi}t\text{Bu}_3)_6]^-$	HEQDIQ	18.8	1.67	$P\bar{1}$	[c]
$[\text{Zr}(\text{CCSi}t\text{Bu}_3)_6]^{2-}$	HEQDOW	60.0	0.00	$R\bar{3}$	[c]
$[\text{Hf}(\text{CCSi}t\text{Bu}_3)_6]^{2-}$	HEQDUC	60.0	0.00	$R\bar{3}$	[c]
$[\text{TaPh}_6]^-$	REZBAZ	15.1	1.08	$P\bar{1}$	[d]
$[\text{Ta}(p\text{-Tol})_6]^-$	REZBED	15.9	1.18	$P2_1/n$	[d]
$[\text{ZrMe}_6]^{2-}$	JAMWOJ	11.2	0.63	$Aba2$	[e]
$[\text{RhMe}_6]^{3-}$	KAWVAF	44.0	0.70	$R\bar{3}c$	[f]
$[\text{IrMe}_6]^{3-}$	KAWVEJ	42.3	0.82	$R\bar{3}c$	[f]
$*[\text{TaMe}_6]^-$	POZHUH	3.2	0.04	$P2_12_12_1$	[g]
$*[\text{NbMe}_6]^-$	POZJAP	3.0	0.03	$P2_12_12_1$	[g]
$[\text{WMe}_6]$	ZOSXEK01	2.2	0.01	$Pbc2_1$	[g]
		0.6	0.01		
$[\text{ReMe}_6]$	ZOSXEL	1.1	0.01	$P2_1/n$	[g]
$[\text{Co}(\text{oxazolidyl})_6]^{2+}$	CUXRUI	57.0	0.16	$P2_1/n$	[h]
$[\text{MnMe}_6]^{2-}$	GINZEI	60.0	0.00	$Pbca$	[i][j]
$[\text{CrMe}_6]^{3-}$	MCRLDX	47.1	0.42	$R\bar{3}c$	[k]
$[\text{MoMe}_6]$		1.7	0.02	$Cc$	[l]
		1.4	0.01		
$[\text{Ti}_2(\mu\text{-SMe})_3(\text{SMe})_6]^{2-}$	POJFOJ	31.1	1.01	$P2_1/a$	[m]
		33.3	1.34		
$[\text{Zr}(\text{SC}_6\text{H}_4\text{-4-Me})_6]^{2-}$		9.2	0.35	$P\bar{1}$	[n]
$*[\text{Zr}(\text{SC}_6\text{H}_4\text{-4-OMe})_6]^{2-}$		30.4	2.16	$R3_2$	[n]

[a] Compounds marked with an asterisk crystallize in enantiomorphic space groups. — [b] Cambridge Structural Database refcodes. — [c] T. P. Vaid, A. S. Veige, E. B. Lobkovsky, W. V. Glassey, P. T. Wolczanski, L. M. Liable-Sands, A. L. Rheingold, T. R. Cundari, *J. Am. Chem. Soc.* **1998**, *120*, 10067–10079. — [d] S. Kleinhenz, M. Schubert, K. Seppelt, *Chem. Ber.* **1997**, *130*, 903–905. — [e] P. M. Morse, G. S. Girolami, *J. Am. Chem. Soc.* **1989**, *111*, 4114–4116. — [f] R. S. Hay-Motherwell, G. Wilkinson, B. Hussain, M. B. Hursthouse, *J. Chem. Soc., Chem. Commun.* **1989**, 1436–1437. — [g] S. Kleinhenz, V. Pfennig, K. Seppelt, *Chem. Eur. J.* **1998**, *4*, 1687–1691. — [h] U. Plaia, H. Stolzenberg, W. P. Fehlhammer, *J. Am. Chem. Soc.* **1985**, *107*, 2171–2172. — [i] R. J. Morris, G. S. Girolami, *J. Am. Chem. Soc.* **1988**, *110*, 6245–6246. — [j] R. J. Morris, G. S. Girolami, *Organometallics* **1991**, *10*, 792–799. — [k] J. Krausse, G. Marx, *J. Organomet. Chem.* **1974**, *65*, 215–222. — [l] B. Roessler, K. Seppelt, *Angew. Chem. Int. Ed.* **2000**, *39*, 1259–1261. — [m] W. Stuer, K. Kirschbaum, D. M. Giolando, *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1981–1983. — [n] J. C. Friese, A. Krol, C. Puke, K. Kirschbaum, D. M. Giolando, *Inorg. Chem.* **2000**, *39*, 1496–1500.

model line. It is seen that all structures fall along that line, suggesting that they indeed represent the Bailar pathway from  $O_h$  to TP. It can also be seen that the octahedricity and the trigonal prismaticity of such complexes correspond to the Bailar route, as discussed in more detail elsewhere.<sup>[20]</sup> Analysis of the bonding parameters of the actual structures confirms that these are of  $D_3$ -type, as illustrated in Figure 2 for three representative compounds. This observation indicates that chiral hexacoordinated homoleptic complexes have already been synthesized and structurally characterized *but their chirality not recognized and not reported*. Thus, despite the clear chirality of molecules with intermediate rotation angles, the experimental reports of the compounds presented in Figure 1 do not mention such a property and their optical activity has not been investigated. Most of these complexes, however, crystallize in space groups having improper symmetry operations, namely as racemic mixtures.<sup>[21]</sup> We note that these anionic complexes have been crystallized with achiral cations and propose that obtaining enantiomerically pure compounds may be possible through crystallization with optically pure chiral counter ions. Two complexes,  $[\text{NbMe}_6]^-$  and  $[\text{TaMe}_6]^-$ , that crystallize<sup>[22]</sup> in the enantiomorphic space group  $P2_12_12_1$  are only slightly-distorted from the octahedron ( $\theta \approx 3^\circ$ ) and have small chirality measures. To the best of our knowledge, only a  $\text{Zr}^{\text{IV}}$  thiolato complex reported recently<sup>[23]</sup> is expected to be optically active, since it crystallizes in the enantiomorphic  $R3_2$  group and has a  $\text{ZrS}_6$  core with a high chirality measure ( $S = 2.16$  at  $\theta = 30.4^\circ$ ).

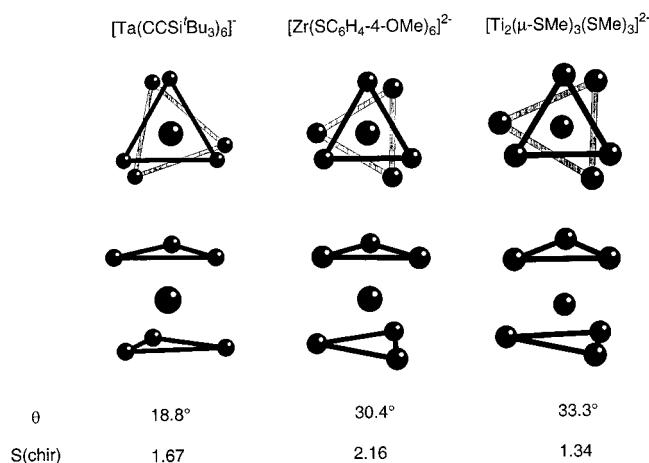


Figure 2. Perspective view and projection about the trigonal axis of the coordination spheres of three chiral homoleptic complexes with monodentate ligands that fall along the Bailar twist pathway 1 (see Table 1 for references)

As a further test of these observations and of the validity of the theoretical chirality line, we also analyzed the chirality of tris(chelate) complexes with twisted octahedra. Since the above analysis focused only on the  $\text{MX}_6$  core, a corollary is that in the case of twisted tris(chelate) complexes the chirality is not associated only with the backbone of the bidentate ligands but also with the spatial arrangement of the donor atoms. To check this conclusion we have chosen

the tris(dithiolene), tris(diselenolene), tris(bipyridine) and tris( $\beta$ -diketonato) metal complexes (structural information, references and symmetry measures are given as Supporting Information),<sup>[24]</sup> which are known to present structures throughout the whole range of twist angles. The chirality measures of the inner  $\text{MX}_6$  core of such complexes, obtained from their crystal structural data (Figure 3 and 4) indeed corroborate the result of Figure 1. Note that the tris(bipyridine) and tris( $\beta$ -diketonato) complexes appear at the ends of the twist-angle scale: most cluster in the range  $45^\circ < \theta \leq 68^\circ$  but two structures are also found at  $\theta \approx 2^\circ$ . It has been found<sup>[20]</sup> that the twist angle in nearly octahedral structures of bipyridine and diketonato complexes is associated with the normalized bites ( $b = \text{L} \cdots \text{L}/\text{M} \cdots \text{L}$ ) of these ligands. Since bipyridine has a smaller bite than diketonates [the averages for first row transition metals are  $b = 1.27(4)$

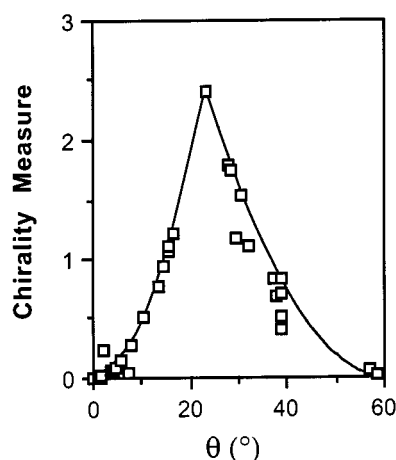


Figure 3. Chirality measures of the  $\text{MX}_6$  cores of tris(dithiolene) and tris(diselenolene) complexes ( $\text{X} = \text{S}$  and  $\text{Se}$ ), calculated from the experimental structural data as a function of the twist angle along the trigonal prism to octahedron interconversion path (data provided as Supporting Information); the solid line corresponds to a geometrical model, as in Figure 1

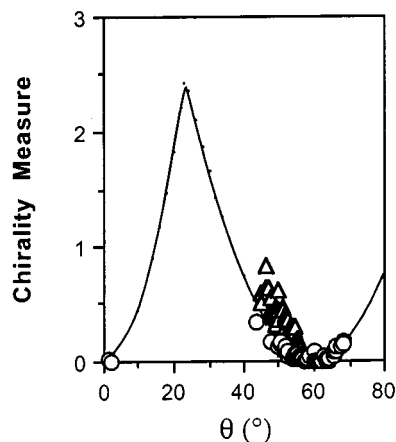


Figure 4. Chirality measures of the  $\text{MX}_6$  cores of tris(bipyridine) ( $\text{X} = \text{N}$ , triangles) and tris( $\beta$ -diketonato) ( $\text{X} = \text{O}$ , circles) complexes, calculated from the experimental structural data as a function of the twist angle along the trigonal prism to octahedron interconversion path (data provided as Supporting Information); the solid line corresponds to a geometrical model, as in Figure 1

and  $1.41(5)$ , respectively], the twist angles of the former family are smaller than in the latter. The existence of structures with twist angles larger than  $60^\circ$  corresponds to a rotation towards a trigonal prism (characterized by  $\theta = 120^\circ$ ) in which the bidentate ligand would be placed along the diagonal of a square face rather than along the edges (as happens for  $\theta = 0^\circ$ ). The two nearly trigonal prismatic structures of diketonato complexes correspond to complexes of  $\text{Y}^{\text{III}}$  and  $\text{Cd}^{\text{II}}$  with  $d^0$  and  $d^{10}$  electron configurations ( $b = 1.21$  and  $1.28$ , respectively). We will return to these complexes in a separate report on a different issue, namely the relation between the chirality of the inner  $\text{MX}_6$  core and the chirality of the ligand sphere.<sup>[25]</sup>

In conclusion, we draw attention to  $[\text{Zr}(\text{SC}_6\text{H}_4\text{-4-OMe})_6]^{2-}$  which is the most chiral homoleptic complex with monodentate ligands among those that have been analyzed, and to the fact that the theoretical maximum at  $23^\circ$  is occupied in Figure 3 by the inner  $\text{WS}_6$  core of  $(\text{AsPh}_4)_2[\text{W}(\text{S}_2\text{C}_6\text{H}_4)_3]$ ,<sup>[27]</sup> with  $S = 2.40$  making it the most chiral of all  $\text{MS}_6$  coordination spheres analyzed in this report. To the best of our knowledge, these pronounced chiralities often go unnoticed. Thus our main message is that *chirality in hexacoordinated complexes with monodentate ligands is a more common phenomenon than currently appreciated*. We hope the stereochemical analysis presented in this report will encourage experimental search for as-yet undetected manifestations of chirality in transition metal complexes.

## Acknowledgments

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[1] See, for example: *Catalytic Asymmetric Synthesis* (Ed.: I. Ojima), VCH, New York, **1993**; *Comprehensive Asymmetric Catalysis* (Eds.: E. N. Jacobsen, A. Pfaltz, H. Yamamoto), Springer, Berlin, Vols. 1–3, **1999**; F. Gelman, D. Avnir, H. Schumann, J. Blum, *J. Mol. Catal., A: Chem.* **1999**, *146*, 123–128.

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- [13] Other quotes include the following: "The six-coordinated chelate complexes of the type  $M(\text{bidentate ligand})_3$ ...which has  $D_3$  symmetry...are the commonest cases";(ref.<sup>[11]</sup> p. 639) "...a few cases of optical isomerism are known for planar and tetrahedral complexes involving asymmetric bidentate ligands, but by far the most numerous examples are afforded by octahedral compounds of chelating ligands";(ref.<sup>[12]</sup> p. 919) "Most of these [optically active inorganic molecules] are six-coordinate complexes with  $D_3$  or closely related symmetry. They will be discussed at greater length in Chapter 12 [all examples given in Chapter 12 correspond to bis- or tris(chelate) complexes]";(ref.<sup>[9]</sup> p. 64) "Most of the optically active complexes for which experimental and theoretical study has been made involve chelate rings".(ref.<sup>[10]</sup> p. 53). Other textbooks on Inorganic Chemistry that were consulted also propose as examples of chiral complexes only bis- and tris-chelates.
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- [16] In other cases, the nearest achiral object may have another improper symmetry element.
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