Continuous chirality measures of tetracoordinate bis(chelate) metal complexes

Santiago Alvarez *[a] and David Avnir *[b]

[a] *Departament de Química Inorgànica and Centre de Recerca en Química Teòrica, Universitat de Barcelona, Diagonal 647, 08028 Barcelona, Spain*

[b] *Institute of Chemistry and The Lise Meitner Minerva Center for Computational Quantum Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel*

The interconversion pathway between the tetrahedron and the square that is represented by the structures of a large variety of tetracoordinate complexes is the achiral *spread* pathway in the presence of monodentate ligands but the chiral *twist* pathway in bis-chelated complexes. The chirality of several families of bis-chelated metal complexes is evaluated using the Continuous Chirality Measures methodology. The specific contribution to chirality from the innermost MX_4 shell, as well as from the ligands is analyzed. The maximal expected chirality value for the tetrahedral to square planar route is at a torsion angle of 45°, which is realized in $[Cu(p\text{-}C_6H_4\{p\text{-}C_2H_5bipyMe\}_2)_2]^{2+}$. The chiral behavior of double-stranded helicates is compared to that of analogous mononuclear complexes. The present study shows that chirality is a rather common property of bis-chelated complexes, even in the absence of asymmetric ligands.

There is an extended perception that tetracoordinate bis-(chelate) complexes are chiral only if the bidentate ligands are asymmetric.[1,2] As an example of such an extended belief, let us quote two authoritative references: ". . .optical isomerism can occur only when the dihedral angle between the two chelate rings defined by the metal and donor atoms is nonzero, and is possible *only* for M(L–L′)₂," (ref. 1, p. 249). "Coordination units [M(AA)a₂] and [M(AA)ab] have symmetries C_{2v} and C_s, respectively and they cannot give rise to stereoisomers. The same is true for [M(AA)₂] with D_{2d} symmetry. On the other hand, [M(AB)ab] and [M(AB)₂] have C_1 and C_2 symmetries, respectively and they are therefore chiral" (ref. 2, p. 98), where AA and AB represent symmetric and asymmetric bidentate ligands, a and b monodentate ligands. As a further indication of such a belief, we have been unable to find any reference to the chirality of tetracoordinate transition metal complexes in all advanced Inorganic Chemistry textbooks consulted. When reference is made to chirality, one finds statements such as "Tetrahedral complexes. . . are potentially chiral just as is tetrahedral carbon. The simple form of optical isomerism exhibited by most organic enantiomers, namely *four different substituents*, is rarely observed. . ."; or "A form of optical isomerism analogous to that shown by organic spirocyclic compounds has been demonstrated. . . The two enantiomers of bis(benzoyl-acetonato)-beryllium are illustrated. . . the chelating ligand *must be unsymmetric*".[3] However, it is being increasingly recognized by some authors that a bis-chelate complex "can distort towards a square planar geometry, becoming therewith, a chiral species",[4] that "chelating ligands in combination with tetrahedrally coordinated metal ions lead to mononuclear complexes which already possess a helical twist"[5] and that "square planar complexes that deviate significantly from planarity can be chiral".[6]

In recent years we have proposed that chirality can be treated as a continuous property and that it might be useful not only to define a given molecule as chiral, but to provide a measure of how far it is from being achiral.[7–9] In order to translate this definition into practice, we have developed the Continuous Chirality Measure (CCM) methodology and a computational tool which evaluates the distance of a chiral object to the nearest achiral symmetry. An important feature of the CCM approach is that it not only computes the chirality content, but also provides the actual shape of the nearest achiral object, a feature that helps us understand the dependence of the chirality measures on the molecular geometry.

In brief, given the positions of the N atoms in the investigated molecule defined by vectors Q_k ($k = 1, 2, . . . N$), one searches for the nearest achiral molecule with coordinates P_k ($k = 1, 2, . . . N$) and the sum of the squared distance between the two sets of coordinates is the chirality measure of the molecule under study, given by eqn. 1, where the denominator provides a size normalization factor (Q_0 is the coordinate vector of the center of mass of the investigated structure) that makes the chirality measure independent of size. The quotient takes values between 0 (achiral molecule) and 1, and the factor of 100 is introduced for convenience;[10] the larger S, the more chiral the molecule is.

$$S = \frac{\sum_{k=1}^{N} |Q_k - P_k|^2}{\sum_{k=1}^{N} |Q_k - Q_0|^2} \times 100 \qquad (1)$$

The application of the CCM approach to hexacoordinate transition metal complexes has resulted in some interesting findings. For instance, we have shown how a variety of homoleptic ML_6 complexes with monodentate ligands present dissymmetric metaprismatic structures[11] (intermediate between octahedral and trigonal prismatic), and have provided computational evidence that in one such family of complexes the racemization reaction should be slow at room temperature.[12] A study of the chirality measures of tris(chelate) complexes[13] has revealed the interesting feature that the first atomic shell (*i.e.*, the metal and donor atoms) and the second shell (comprising the spacers between two donor atoms of a bidentate ligand) present contributions that may be either commensurate or incommensurate to the chirality of the full complex. Furthermore, it was found that the chirality measure of the first two shells provides a semiquantitative estimate of that of the full molecule and the chirality of the inner shell is either amplified or attenuated depending on the type of bidentate ligand used.

A detailed analysis of how several distortions affect the symmetry measures of tetracoordinate complexes relative to the square and the tetrahedron, $S(D_{4h})$ and $S(T_d)$, respectively, has been carried out by us recently[14,15] without specifically considering chirality measures. On the other hand, we have focused on a small group of copper bisoxazolines and found an interesting correlation between their chirality measures and the

1

2
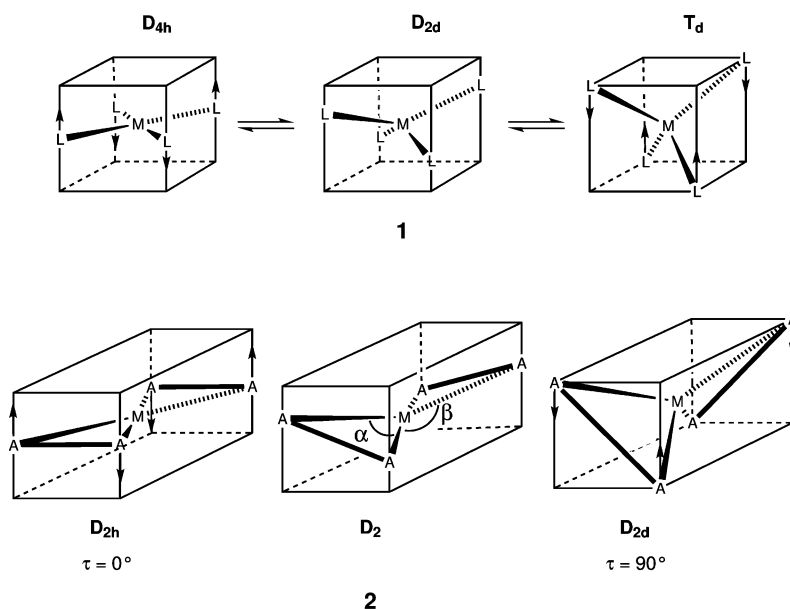
enantiomeric excess in cycloaddition reactions catalyzed by them.[16]

In the present paper we report a continuous chirality analysis of bis(chelate) tetracoordinate complexes. One of the aims of the present work, therefore, will be to show by a symmetry analysis how and when tetracoordinate complexes with symmetric chelating ligands can be chiral. Our study will show that chirality is a rather common property among that family of compounds, even in the absence of asymmetric ligands, and will also stress the importance of the first coordination sphere in the chiral nature of di- and polynuclear double-stranded helicates.

Tetrahedral to square planar interconversion pathways

When analyzing the chirality of the bis-chelated tetra-coordinate complexes it is important first to stress their differences compared to the monodentate homoleptic analogues. In the case of monodentate ligands, ML_4, the two highest-symmetry ideal geometries are the square and the tetrahedron belonging to the achiral symmetry point groups D_{4h} and T_d, respectively. These structures can be interconverted through the *spread* or *twist* pathways,[14,15] which can both be described by a B_{2u} (or E) distortion mode in the D_{4h} (or T_d) point group[17] and are schematically represented in **1**. In the spread distortion mode, the ligands are described as ideally displacing along the edges of a cube at any point along the path (although the size of the cube gradually changes if the M–L distances are kept constant). Along such a pathway, the four *cis* L–M–L bond angles (and the four *trans* angles) of the square planar geometry remain equivalent, all intermediate geometries belong to the D_{2d} symmetry point group and are therefore achiral. This is essentially what is found for complexes with monodentate ligands, such as the tetrahalocuprates, which appear scattered through the spread pathway:[15] as we move from the square planar ($\tau = 0°$) to the tetrahedral ($\tau = 90°$) geometry, the X–Cu–X bond angles smoothly change from 90 to 109° and retain their achiral character, as indicated by chirality measures smaller than 0.05 (92 structural data set, only structures with $R \le 5\%$ considered), as shown in Fig. 1.

In the twist distortion pathway, we assume that the two opposite *cis* L–M–L bond angles remain constant throughout the distortion, as would happen in bis-chelated complexes with relatively rigid bidentate ligands. The main constraint imposed by the bidentate ligand is that the bite angle α is practically constant and is therefore unable to adapt to the values required
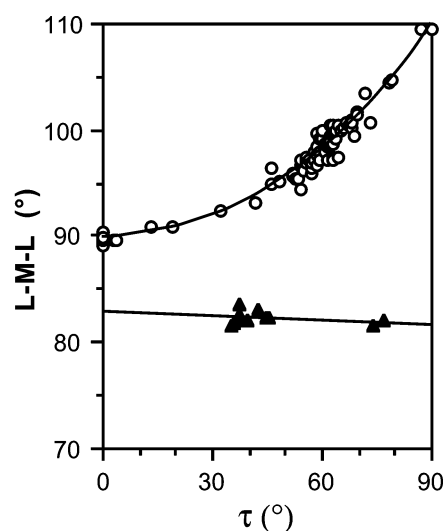

Fig. 1 Relationship between the torsion and bond angles for the families of tetrahalocuprates(II) (circles) and bis(bipyridine)copper(II) complexes (triangles). Least squares fitting lines given only as visual aid.

along the achiral path **1** (between 90 and 109°). In this case, there are two sets of different *cis* bond angles, the bite angle α and the angle between two different bidentate ligands β. The distortion pathway can be now ideally described by a displacement of the donor atoms along the edges of a square prism **2**, even if the size of the prism changes along the path if the M–L distances are kept constant. The end structures are of D_{2h} and D_{2d} symmetries and thus achiral, while all intermediate geometries are of D_2 symmetry and therefore chiral (**2**). Thus, *two enantiomers* are expected for all bis(chelate) tetracoordinate complexes, except for the two extreme cases in which the LML planes defined by the two bidentate ligands are coplanar (pseudo square planar, torsion angle $\tau = 0°$, D_{2h} symmetry) or perpendicular (pseudo tetrahedral, torsion angle $\tau = 90°$, D_{2d} symmetry). This can be illustrated by the behavior of the family of bis(bipyridine) copper(II) complexes: as we move from the square planar ($\tau = 0°$) to the tetrahedral ($\tau = 90°$) geometry, the N–Cu–N bond angles subtended by the bipyridine ligands remain practically constant (Fig. 1) and their chirality measures can be as high as 1.0 as will be discussed below, to be compared with chirality measures smaller than 0.05 found for the tetrahalocuprates that follow the achiral spread pathway.

It is important to stress that the chirality induced by the presence of bidentate ligands is independent of the nature and geometry of the spacers that link the two donor atoms, except that some degree of rigidity of the chelate ring is assumed. Chirality is imprinted in the first coordination sphere because the bond angles subtended by each bidentate ligand (a in **2**) are different from the inter-ligand bond angles (β in **2**).

The family of tetracoordinate bipyridine and phenanthroline complexes presents structures through all the range of coordination geometries between tetrahedral and square planar, as illustrated in the symmetry map (Fig. 2). There we plot the
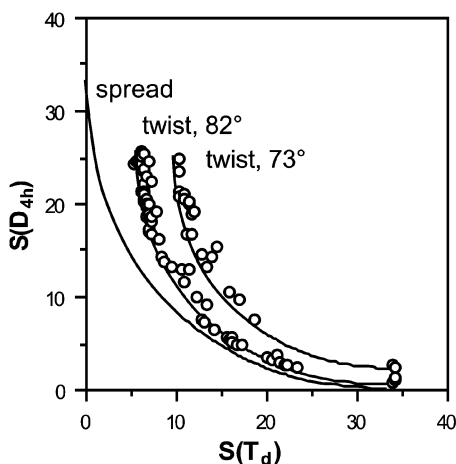

Fig. 2 Scatterplot of the tetrahedral and square planar symmetry measures of tetracoordinate complexes of the $[M(bipy)_2]$ family (circles). The ideal curves for several interconversion paths between square planar and tetrahedral geometries are shown: the spread path in which the L–M–L bond angles gradually change from 90° (in the square planar geometry) to 109.4° (in the tetrahedral one), and two twist pathways in which the bidentate nature of the ligands is introduced by keeping the two opposite L–M–L bond angles constant at typical values for the bipy complexes, 82 and 73°.

symmetry measure of each structure relative to the ideal square planar structure ($S(D_{4h}) = 0$ corresponds to a perfectly square planar molecule) as a function of the symmetry measure relative to the ideal tetrahedron ($S(T_d) = 0$ corresponds to a perfectly tetrahedral molecule). The position of the experimental data in such a graph clearly indicates that they appear along tetrahedron-square interconversion paths discussed in more detail elsewhere.[14] This family, therefore, constitutes an excellent reference set to illustrate the evolution of chirality along the spread pathway. Hence, we will first study chirality measures corresponding to idealized models of $[M(bipy)_2]$, and then will compare with the values corresponding to the experimental structures. In later sections we will briefly comment on the behavior of other families of bis(chelate) complexes. A related study on a family of mono(chelate) tetradentate molecules which are of importance in enantioselective catalysis, the bisoxazoline copper complexes, will be the subject of an independent paper.[18]

$[M(bipy)_2]$ models

For the study of the chirality of bis(chelate) complexes it is useful to consider the atoms in the molecule as pertaining to successive shells, as exemplified for the case of bis(bipyridine) complexes in **3**. The first shell comprises the metal and the coordinated donor atoms (MN_4 group) and the second shell is formed by the spacers that connect the two donor atoms of each ligand, *i.e.*, the two C_2 fragments. Thus, we shall refer to the chirality measures as S_1 (first shell only), S_2 (second shell only), S_{1+2} (first and second shells together), and S_f for that of the full molecule (devoid of the hydrogen atoms, *i.e.*, $M(N_2C_{12})_2$ for bipy and $M(N_2C_{14})_2$ for phen).
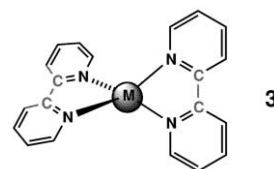
We calculate first the expected chirality values S_1, S_2 and S_{1+2} for molecular models as a function of the torsion angle between the planes of the two chelate rings ($\tau = 0°$ indicates a square, $\tau = 90°$ a tetrahedron) at different bite angles to sample the different geometries found in experimental structures (Fig. 3).
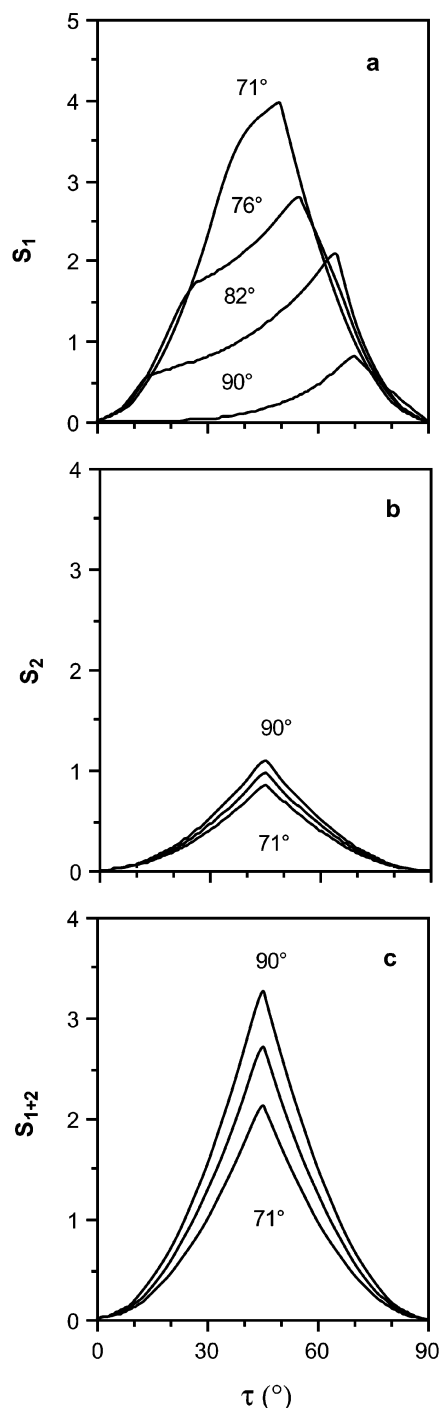
Fig. 3 Chirality measures along the square-planar to tetrahedral interconversion pathway for molecular models $M(N_2C_2)_2$ having N–M–N bite angles between 71 and 90°. (a) For the first shell, MN_4; (b) for the second shell, C_4; and (c) for the combination of the first two shells, $M(N_2C_2)_2$.

4a   **4b**   **4c**
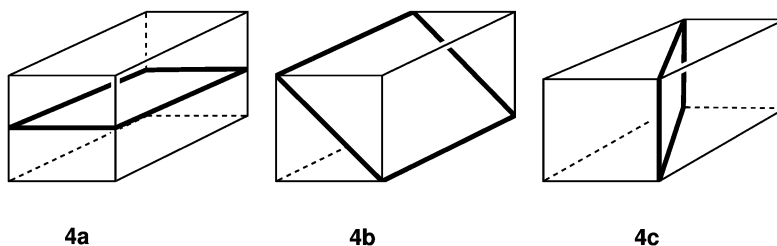
This model can apply to other bidentate ligands for the chirality measures of the first shell, but the second shell may behave differently depending on the number and geometry of the intervening atoms between the two donors. As expected, the two innermost shells are achiral at the two extremes of the spread pathway, *i.e.*, $S_1 = S_2 = S_{1+2} = 0$ at $\tau = 0$ and $\tau = 90°$, and increase for intermediate geometries. For twisted geometries, however, the chirality measures show some complexity that deserves a closer look. The chirality measures S_2 and S_{1+2} present maxima exactly halfway from the square to the tetrahedron, at $\tau = 45°$, and are little affected by the bite angle. The left branch corresponds to geometries whose nearest achiral structures are planar D_{2h} whereas for the right branch the nearest achiral structures are pseudotetrahedral D_{2d}.

The behavior of S_1 is quite different; comparison of the model curves calculated with different bite angles clearly shows that, for the same torsion angle τ, a smaller bite angle results in a much larger chirality measure S_1. In particular it is worthy of note that the first shell of complexes with bite angles of about 90° are nearly achiral except at twist angles larger than 40°. On the other hand, these curves present three different branches, indicative of three different nearest achiral reference geometries. At small and large angles (left and right branches), the nearest achiral structures are the same as for the two other chirality measures: the D_{2h} (left) and D_{2d} (right) geometries illustrated in **2**, symmetric with respect to planes **4a** and **4b**, respectively. Hence these two branches are symmetric with respect to the $\tau = 45°$ point. For the middle branch that appears at intermediate angles, the chirality measures refer to a symmetric structure that is contained in the plane depicted in **4c** that corresponds to both the $\sigma_v(D_{4h})$ and $\sigma_v(T_d)$ symmetry planes of the ideal square planar and tetrahedral structures **1**. Now we can understand why the shape of the S_1 curve is strongly affected by the N–M–N bond angle (Fig. 3a): As the N–M–N bond angle deviates from 90°, the reference polyhedron deviates from a cube (**2**) and the structure is less symmetric relative to the $\sigma_v(D_{4h})$ plane, giving larger values of the chirality measure at the middle branch.

A related finding is that no correlation is found between the chirality measure of the first shell and S_2 or S_{1+2}, whereas a nice linear correlation is found between S_2 and S_{1+2}, regardless of the bite angle (least-squares fitting: $S_{1+2} = -0.01 + 2.82\ S_2$; regression coefficient $r^2 = 0.99$). To understand such a behavior we must note that the nearest achiral structures for the second shell or for the first two shells combined are symmetric with respect to the same plane: **4a** for small values of τ and **4b** for large angles of τ. We say that the chirality measures of different parts of a molecule are *commensurate* when the symmetry plane (or improper symmetry element) of their nearest achiral structures is the same,[13] hence in the present case S_2 and S_{1+2} are commensurate throughout the tetrahedron to square planar interconversion pathway. In contrast, the nearest achiral geometry for the first shell has a different reference mirror plane at intermediate torsion angles (**4c**) and S_1 is therefore incommensurate with S_2 and S_{1+2}. An interesting outcome of these differences is that the chirality of the second shell is amplified by the presence of the first shell, as seen by a slope of 2.8 in the linear least-squares expression.
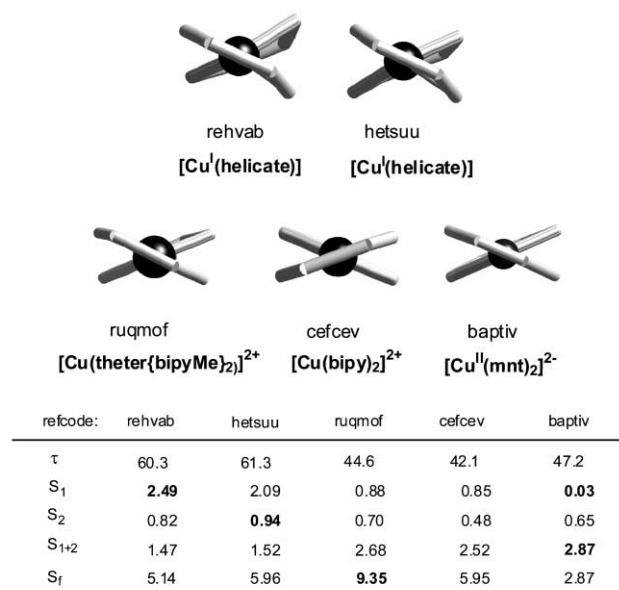
Our analysis of the dependence of the chirality measures on the torsion angle for the various fragments of the molecule

allows us to extract some conclusions of practical importance. What we are actually looking for is some rule of thumb that tells us when and how the chirality of the outer shells of a complex is correlated to that of the first or second shell. With such a rule, we should be able to design a molecule with given bite and torsion angles and predict whether chirality will increase or decrease (and by how much) when we add successive shells to the complex by incorporating ligands with the same coordination topology but with varying composition and complexity away from the central atom.

We have shown that the central branch in the S_1 curve (Fig. 3a) is the one that makes use of a different reflection plane than those in the right or left branches of S_1, S_2 and S_{1+2}. Consequently, we should expect incommensurability between S_1 and the other two chirality measures to appear only in those regions in which there is a central branch in the S_1 curve, given by the combination of large bite angles and intermediate torsion angles. For other combinations of these two angles, S_1 should be commensurate with S_2 and with S_{1+2}. This is actually what is found, as shown in Fig. 4a. There we see clearly the two kinds of behavior: for the commensurate region a nice
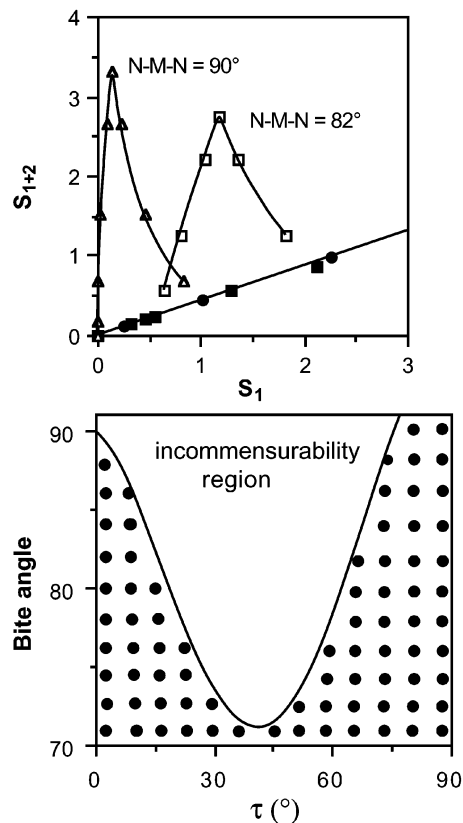
Fig. 4 (a) Chirality measures for the first two shells of a bis(bipyridine) model as a function of the chirality measure of the first shell. Open symbols correspond to the incommensurate region (intermediate torsion angles τ) for bite angles of 90 (triangles) and 82° (squares), filled symbols to the commensurate regions (small and large τ angles) for bite angles of 82 (squares) and 90° (circles). (b) Combinations of bite and torsion angles that result in commensurate (shaded region) and incommensurate (white region) S_1 and S_{1+2} values.

refcode:	rehvab	hetsuu	ruqmof	cefcev	baptiv
τ	60.3	61.3	44.6	42.1	47.2
S_1	**2.49**	2.09	0.88	0.85	**0.03**
S_2	0.82	**0.94**	0.70	0.48	0.65
S_{1+2}	1.47	1.52	2.68	2.52	**2.87**
S_f	5.14	5.96	**9.35**	5.95	2.87

Fig. 5 Helical structures of the two inner shells of bis(chelate) complexes showing the largest values for the chirality measures S_1, S_2 and S_{1+2}, together with their torsion angles τ and the chirality measure of the full molecules (S_f) devoid of their hydrogen atoms. The largest value found for each chirality measure is highlighted in boldface.

linear correlation is found between S_1 and S_{1+2}, regardless of the bite angle, given by the approximate expression $S_{1+2} = 0.42\, S_1 \pm 0.02$, indicating that the chirality of the central shell is attenuated when the second shell is incorporated. In contrast, for the incommensurate regime, no monotonous relationship between the two chirality measures exists, and the ratio between the two values is strongly affected by both the bite and torsion angles. The combination of bite and torsion angles that result in commensurability and incommensurability between S_1 and S_{1+2} are graphically represented in Fig. 4b by the shaded and white regions, respectively.

Experimental structures: bipyridine and phenanthroline complexes

We consider in this section 2,2′-bipyridine and topologically equivalent ligands, such as phenanthroline or cyclometalated phenylpyridine. Among the tetracoordinate complexes with two such ligands one finds a variety of geometries intermediate between the pseudo-square planar (D_{2h}) and pseudo-tetrahedral (D_{2d}) extremes. Those structures are seen to fall along the spread pathway not only from the torsion angle between the two chelate rings, but also from the analysis of their symmetry measures relative to the tetrahedron and the square,[14,15] as shown above in Fig. 2. Some representative structures, together with their chirality measures are given in Fig. 5, where the D_2 symmetry can be clearly appreciated. The chirality measures for the bipyridine and related complexes (Fig. 6) show how the theoretical models of Fig. 3 are fulfilled by the experimental data.[19] Moreover, we have separately plotted in Fig. 6 the chirality measures of double-stranded helicates (circles) and those of mononuclear complexes, and it can be seen that the two families present essentially the same behavior. In other words, if we focus on the inner shells, the chirality in the helicates is not different from that in the twisted mononuclear complexes. The only significant difference is that helicates appear concentrated at the right of the plots, which we think is just a result of the choice of d[10] ions such as Cu(I), Ag(I) or Zn(II) for building double-stranded helicates. The chirality of the full molecules will be discussed below.

It has been noted recently[4,20] that bis-cyclometallated Pt(II) compounds strongly distort from planarity and show a helical
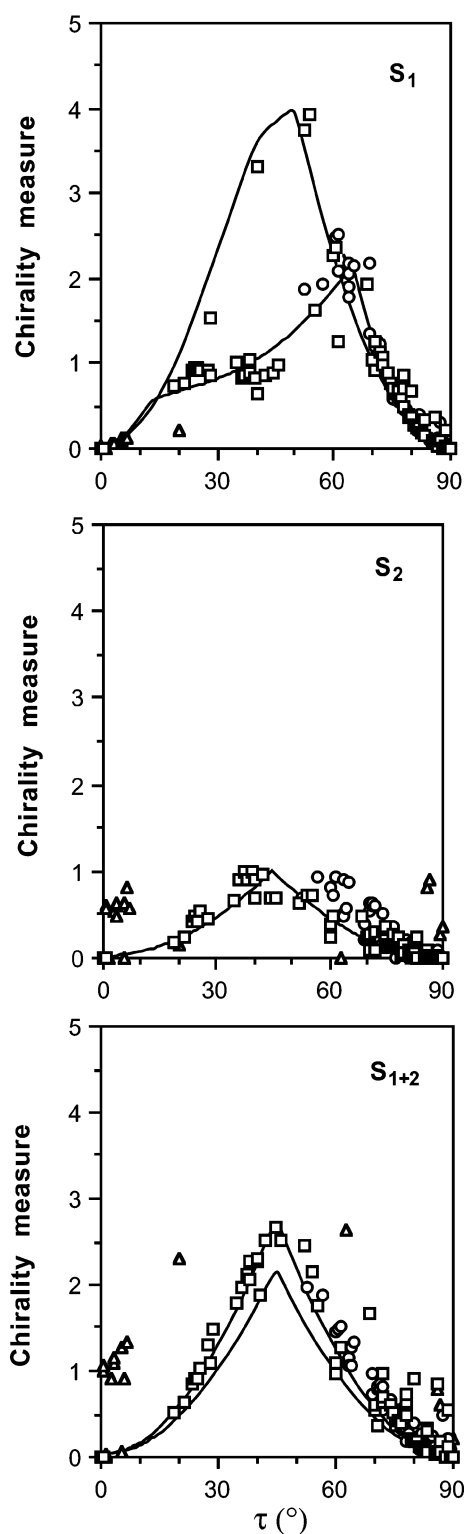
Fig. 6 Chirality measures along the square-planar to tetrahedral inter-conversion pathway for complexes of the [M(bipy)$_2$] and [M(phen)$_2$] families for the first shell MN_4 (S_1), second shell C_4 (S_2) and for the combination of these two shells (S_{1+2}). The corresponding curves obtained for molecular models also shown as reference (see Fig. 3). Squares correspond to mononuclear complexes, circles to double-stranded helicates, triangles to the related [M(en)$_2$] complexes.

arrangement of the two chelate rings. However, to the best of our knowledge, no attempts to obtain dinuclear helicates based on Pt(II) or Pd(II) have been reported.

The maximum chirality for the first shell (S_1) appears for mononuclear Hg(II)[21] and Ag(I)[22] bipyridine complexes with torsion angles between 40 and 55° (Fig. 6a), as expected from the theoretical curve (Fig. 3). Also in good agreement with

expectations, the chirality measures for the second shell (Fig. 6b) are smaller and a variety of structures present values near the maximum at around 45°. Finally, the two inner shells combined (S_{1+2}, Fig. 6c), present chirality measures intermediate between those of the first and second shells, with a maximum at $\tau = 45°$ found in the crystal structure of a Cu(II) complex in which two bipyridine units are joined by a *p*-diethylbenzene tether[23] (Fig. 5). It is remarkable that a similar chirality value is found for the much simpler [Cu(bipy)$_2$]$^{2+}$ cation.[24]

It is now time to ask what is the rationale for studying the chirality of molecular fragments as we are doing here. In other words, does the chirality measure of one or two inner shells correctly represent the chirality of the full molecule? Since the Cotton effect is associated with absorption bands in the visible spectrum, it is sensible to assume that what is relevant for such an effect is the chirality of the molecular fragment at which the corresponding electronic transitions are centered. In the case of coordination compounds the ligand field and charge transfer transitions usually dominate the visible spectrum, and this is one of the reasons why we study the chirality measures of metal centered fragments. For example, in a recent report of enantio-pure bis(chelate) Pt(II) complexes, von Zelewsky and co-workers have shown that the enantiomerically pure ligands are not circular dichroic between 250 and 800 nm, whereas the corresponding complexes present a strong Cotton effect at the MLCT wavelength.[25]

As for our chirality analysis, we note first that in the bis(chel-ate) complexes analyzed here there is some correlation between S_2 and S_{1+2} (least-squares fitting of the data: $S_{1+2} = 0.06 + 2.52$ S_2, $r^2 = 0.90$ for mononuclear complexes; $S_{1+2} = 0.10 + 1.62 S_2$, $r^2 = 0.86$ for helicates), as predicted by our model, and also that the chirality of the second shell is amplified by the presence of the first shell (slopes of about 2). Next we analyze the chirality measures of those molecules with the [M(bipy)$_2$] or [M(phen)$_2$] stoichiometry (*i.e.*, with no substituents), omitting only their hydrogen atoms. In contrast with what was earlier found for the tris(chelate) family,[13] the chirality measure of a full molecule (S_f) is nicely correlated with that of the second shell (S_2, squares in Fig. 7), with a remarkable amplification ratio of about 6. We can consequently conclude that the chirality of the [M(bipy)$_2$] or [M(phen)$_2$] molecules can be deduced from that of their (C$_2$)$_2$ fragments only.

Let us recall now that the above analysis of model molecules showed that there is a region of commensurability of S_1 and S_2 (*e.g.*, for bite angles of around 82° and $\tau < 15°$ or $\tau > 70°$). Given
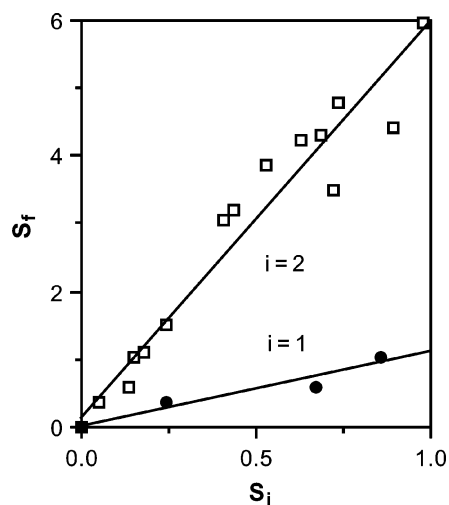
Fig. 7 Chirality measures of complete unsubstituted [M(bipy)$_2$] and [M(phen)$_2$] molecules (except for the hydrogen atoms) as a function of the chirality of the second shell (open squares) and as a function of the chirality measure of the first shell (filled circles, only structures in the commensurate region: $\tau < 15°$ and $\tau > 70°$; bite angles of 82 ± 2°) obtained from experimental structures.

Table 1 Tetracoordinate complexes with the M(chel)$_2$ core (chel = 2,2′-bipyridine or phenanthroline ligands) that crystallize in enantio-morphic space groups

	M	Chel	Refcode	Space group	τ	S_{1+2}	Ref.
A	Pt(II)	bipy	parzud	$P2_1$	0	0.00	27
B	Cu	phen	hocfio	$P2_12_12$	64	1.10	28
C	Cu(I)	bipy	nuyluo	$P2_12_12_1$	71	0.83	29
D	Cu(I)	bipy	nuyloi	$P2_12_12_1$	72	0.80	29
E	Cu(I)	bipy	tofpaf	$C2$	74	0.62	30
F	Cu(I)	bipy	fupcoi	$C222_1$	76	0.43	31
G	Cu(I)	bipy	yefsil	$C2$	77	0.43	32
H	Cu(I)	phen	nozcou	$P2_12_12_1$	87	0.18	33
i	Cu(I)	phen	bobcuq	$P2_1$	90	0.00	34
J	Ag(I)	bipy	loskin	$P2_12_12_1$	25	0.92	26
K	Pd(II)	bipy	loskot	$P2_12_12_1$	27	1.30	26
L	Pd(II)	bipy	loskuz	$P3_1$	28	1.48	26
M	Zn(II)	bipy	loslek	$P1$	38	2.05	26

the correlation between S_2 and S_f found here, we should expect also a good correlation between S_1 and S_f within that region. This is what is actually found (Fig. 7, circles), the relationship between the two chirality measures being approximately expressed as $S_f = 1.09 S_1$. In other words, for structures of this family within the commensurability region, the chirality measure of the full molecule is practically identical to that of the first shell.

Most compounds of these families crystallize in space groups having improper symmetry operations, and only a few of them (Table 1) crystallize in enantiomorphic space groups. In the former case the two mirror images of the molecule coexist in the unit cell and the crystal is thus racemic, whereas in the latter case only one enantiomer exists in each crystal which is then enantiopure. It is adequate to point out here that the chirality of a molecule is not reflected in its chiroptical proper-ties unless the two enantiomers are optically resolved. A successful approach applied by von Zelewsky and coworkers[4,6] consists of incorporating an enantiopure chiral organic substituent into a bidentate ligand, whereupon one of the enantiomeric forms of the metal coordination sphere is prefer-entially obtained. Among the compounds that crystallize in enantiomorphic space groups (Table 1), some present practic-ally the *square planar* (entry **A**) or *tetrahedral* (**H** and **I**) geom-etries and are achiral. But others present intermediate geom-etries and therefore the crystals must be enantiomerically pure (Table 1, **B**–**G**). In some cases (Table 1, **B**–**D** and **L**–**M**) the absolute configuration of one or the two enantiomeric crystals have been determined and their circular dichroism reported. In compounds **L**–**M** the two bipyridine groups belong to a chiral molecule of the *chiragen* family and it has been claimed that the chirality of the ligand allows for the isolation of one of the enantiomeric coordination spheres.[26] In other cases, the disymmetric nature of the compounds was not disclosed by the authors and their optical activities or circular dichroism spectra went unreported (Table 1, entries **E**–**G**).

It is worth mentioning that ligands containing bipyridine or phenanthroline units are commonly used to form chiral heli-cates,[35–38] or trefoil knots[28] (compound **B**, Table 1), in which the helical wrapping of the ligands is the most obvious manifest-ation of the chirality of such fascinating molecules. According to the present results, there is chirality associated not only with the overall topology of the di- or polynuclear molecule, but chirality is imprinted already at the core of the M(N$_2$C$_2$)$_2$ build-ing block (see Fig. 5). For a family of Ag helicates with chiral ligands, Constable and coworkers have found experimental evi-dence that the measurable chiroptical effects are associated with the helix, not with the chiral ligand.[39] If we put our results together we can therefore say that the chirality of the first and second shells of helicates behave in exactly the same way as that of the mononuclear complexes (at least for relatively rigid

Table 2 Chirality measures of the most chiral tetracoordinate bis(chelate) transition metal complexes of different analyzed families

M	τ	S_1	S_2	S_{1+2}	S_{1-3}	Bite angle	Refcode
Dithiolenes							
Cu	36.1	0.00	0.53	2.15	1.34	92.7	secbeh
Cu	47.2	0.03	0.65	2.87	1.84	92.9	baptiv
Cu	44.4	0.03	0.65	2.87	1.95	92.5	qqqdca01
Cu	48.3	0.00	0.72	3.18	1.61	95.8	sevnuc
Dithiocarbamates							
Hg	65.8	4.20	0.00		1.97	65.0	bhgetc
Acetylacetonates							
Ag	23.5	0.91	0.30		1.00	73.3	teybaa
	24.5	1.09	0.40		1.21	73.4	
Troponeiminates							
Ni	70.1	1.27	0.07	0.46		81.6	burcew
Ni	69.5	1.36	0.08	0.50		81.9	yunruu
Salicylenealdiminates							
Ni	21.7	0.03	1.07	1.24		93.0	zaxdil
Diphosphinoethanes							
Hg	68.0	1.61	0.01	1.98		82.9	tisfuw
Au	70.3	1.25	0.13	0.60		87.7	regjes
Au	70.7	1.34	0.17	0.59		86.2	fessax
Cu	73.5	1.22	0.64	1.49		90.0	rocgul

bidentate ligands), the chirality of the full molecules is most likely related to those of the inner shells and, as a consequence, the helicity and chirality of helicates is intimately linked to the chirality of their innermost shells.

Experimental structures: other bis(chelate) complexes

Since all the complexes analyzed so far contain bidentate ligands that form planar chelate rings, it seemed interesting to briefly analyze the changes that should be expected in the chirality measures when these are replaced by puckered rings as in the ethylenediamine complexes. With that purpose we have included also in Fig. 6 the chirality measures calculated for the bis(ethylenediamine) complexes (white triangles). In contrast to the bipyridine and phenanthroline compounds, these appear mostly at the two extremes of the spread pathway, i.e., $\tau \approx 0$ and 90°. The theoretical expectations of the model used above do not apply to these complexes because their chelate rings strongly deviate from planarity. At the two extreme geometries, the MN_4 core presents the full symmetry of the achiral point groups D_{2h} and D_{2d} (**2**), as reflected by $S_1 = 0$ (Fig. 3a), but the carbon atoms strongly deviate from those planes, resulting in relatively high chirality measures for the second shell (Fig. 3b) and for the combination of first and second shells (S_{1+2}, Fig. 3c). Even if scarce data have been found for intermediate situations, these suggest that the chiralities of the chelate rings and of the coordination sphere are synergistically enhanced, resulting in chirality measures significantly larger than for the bipyridine and phenanthroline complexes.

We have also studied the chirality measures of other families of bis(chelate) complexes and those compounds that were found to present significantly twisted geometries and correspondingly large chirality measures are presented in Table 2. The bis(dithiolene) complexes present bite angles between 87 and 96°. According to the discussion above (Fig. 3a), one should expect complexes with bite angles around 90° to have nearly achiral first shells, and this is what is found in the experimental structures analyzed ($S_1 < 0.3$ for 157 data sets). Also following the expectations from our model studies,

significant chirality measures are found for S_2 and still larger values for S_{1+2} (up to 3.2), showing a nice linear correlation between these two chirality measures. Finally, the chirality measure of the three first shells, S_{1-3}, is nicely correlated with S_2, which is significantly amplified by the incorporation of the third shell.

In the bis(dithiocarbamate) family the experimental structures are concentrated around the square planar and tetrahedral geometries and only one compound is found to be significantly twisted ($\tau = 65.8°$), thus being highly chiral, while all other structures have $S_1 < 0.60$. However, this Hg compound[40] should be considered as linear di- rather than as tetracoordinate, since each dithiocarbamate has a sulfur atom within bonding distance of the Hg atom (2.36 Å) and the second one at a quite long (3.1 Å) distance. We notice that in dithiocarbamates the second shell is formed by one C atom from each ligand, and the set of two carbon atoms is per force achiral, therefore S_2 for dithiocarbamates has not been considered in this study. In spite of the low chirality measures, a correlation between S_{1-3} and S_1 can be detected (least squares regression gives $S_{1-3} = 0.476 \, S_1 + 0.008$, regression coefficient $r^2 = 0.99$ for 71 data sets), with significant attenuation (i.e., the chirality of the first three shells combined is smaller than that of the first shell by a factor of about 0.5).

Most of the bis(diketonato) complexes are approximately square planar, and only one tetrahedral Zn complex was found in our structural database search. The most chiral example in this family[41] is an Ag complex (Table 2). We explored also the families of nickel troponeiminates and aldiminates. Again, most structures cluster around the tetrahedral and square planar geometries, but a few twisted, significantly chiral complexes were found (Table 2). Finally, small degrees of twisting from square planar geometry ($\tau < 23°$) and similar twisting from tetrahedral structures ($\tau > 68°$) were found for bis(diphosphinoethane) complexes. However, given the asymmetry of the S_1 curve (Fig. 3), the first shells of the latter are significantly more chiral than the distorted square planar ones. There is no correlation between the torsion angle and the chirality of the second shell, due to the different degree of puckering of the chelate rings, as found previously for tris(ethylenediamine) complexes,[13] and in this case the chirality of the bis(chelate) unit cannot be guessed from that of one shell only. Only five tetracoordinate compounds were found with the related bis(diphosphinometane) bidentate ligand and small chirality measures were found for them.

An interesting related family of tetracoordinate complexes with only one bidentate ligand is that of the bis(oxazoline) copper(II) catalysts which have found applications in enantioselective catalysis. Lipkowitz et al. theoretically optimized the structures of a series of bisoxazolines and found an excellent correlation between the chirality measures of the full molecules and the enantiomeric excess obtained in a Diels–Alder reaction between acrylimide and cyclopentadiene which they catalyse.[16] An analysis of the contribution of the different shells to the molecular chirality, similar to that presented here, has shown that relevant chirality is not associated with the chirality of the bisoxazoline group.[18]

Conclusions

Tetracoordinate bis-chelated metal complexes are found along the distortion path that interconverts the tetrahedron and the square. Although the two extremes of such pathway are achiral, the degree of chirality as calculated by the Continuous Chirality Measures methodology increases for intermediate structures. The chirality of the double stranded helicates with bipyridine or phenanthroline ligands shows the same behavior as that of mononuclear analogues, indicating that the chiral nature of such compounds may be imprinted in the metal coordination sphere and is not exclusively imposed by the

helical wrapping of the ligands. Double-stranded helicates are commonly built with d^{10} metal ions, since tetrahedral coordination is assumed to favor the helical supramolecular arrangement, the present results suggest that helicates can also be constructed by using twisted square planar metal centers which are as chiral and as common as the distorted tetrahedral ones.

The correlation between the chirality measures of the inner atomic shells and the torsion angle τ depends on the bite angle, the planar or puckered nature of the chelate rings and the number of intervening atoms between the two donors of the bidentate ligand. The analysis of the chirality measures of molecular fragments shows that the chirality of a full molecule with planar chelate rings is correlated to that of the second atomic shell around the metal atom, *i.e.*, the linkers between the donor atoms of each bidentate ligand. The chirality of the first atomic shell is also correlated to that of the full molecule but only within the commensurability region of the bite and torsion angles, mostly for small bite angles and either small or large torsion angles.

The complexes with most chiral inner shells of other families of bis-chelated compounds have been identified, including those with dithiolene, dithiocarbamate, β-diketonates and diphosphines as chelating ligands, as well as nickel troponeiminates and amidinates.

Methodology

The X-ray structural data used to calculate the symmetry measures were retrieved from the Cambridge Structural Database [42] (CSD, version 5.18), restricted to crystal structures with no disorder and $R < 10\%$. In addition, structures that significantly deviate from the spread pathway according to their tetrahedral and square planar symmetry measures [14,15] have been excluded. It has been verified that all such cases correspond to Cu(II) or Ag(II) complexes with contacts from the metal to oxygen or halogen atoms at distances of less than 3 Å, indicative of Jahn–Teller distorted hexacoordination. The chirality measures were calculated with the computer program *symm* developed by the Jerusalem group. For the analysis of a large number of structural data from the CSD, the interface program *csm_ctrl* developed by M. Llunell was used.

Acknowledgements

References and notes

1 R. H. Holm and M. J. O'Connor, *Prog. Inorg. Chem.*, 1971, **14**, 241.
2 A. von Zelewsky, *Stereochemistry of Coordination Compounds*, John Wiley, Chichester, UK, 1996.
3 J. E. Huheey, E. A. Keiter, and R. L. Keiter, *Inorganic Chemistry*, 4th edn., Harper Collins, New York, 1993.
4 A. von Zelewsky, *Coord. Chem. Rev.*, 1999, **190–192**, 811.
5 M. Albrecht, *Chem. Rev.*, 2001, **101**, 3457.
6 U. Knof and A. von Zelewsky, *Angew. Chem., Int. Ed.*, 1999, **38**, 303.
7 D. Avnir, O. Katzenelson, S. Keinan, M. Pinsky, Y. Pinto, Y. Salomon, and H. Zabrodsky Hel-Or, in *Concepts in Chemistry:*
A Contemporary Challenge, ed. D. H. Rouvray, Research Studies Press, Taunton, England, 1997, pp. 283–324.
8 H. Zabrodsky and D. Avnir, *J. Am. Chem. Soc.*, 1995, **117**, 462.
9 H. Zabrodsky, S. Peleg and D. Avnir, *J. Am. Chem. Soc.*, 1992, **114**, 7843.
10 H. Zabrodsky, S. Peleg and D. Avnir, *J. Am. Chem. Soc.*, 1993, **115**, 8278; H. Zabrodsky, S. Peleg and D. Avnir (*Erratum*), *J. Am. Chem. Soc.*, 1994, **116**, 656.
11 S. Alvarez, M. Pinsky, M. Llunell and D. Avnir, *Cryst. Eng.*, 2001, **4**, 179.
12 P. Alemany, S. Alvarez and D. Avnir, *Chem. Eur. J.*, in press.
13 S. Alvarez, M. Pinsky, M. Llunell and D. Avnir, *Cryst. Eng.*, 2001, **4**, 179.
14 J. Cirera, P. Alemany and S. Alvarez, 2001, to be submitted.
15 S. Keinan and D. Avnir, *Inorg. Chem.*, 2000, **40**, 318.
16 K. B. Lipkowitz, S. Schefzick and D. Avnir, *J. Am. Chem. Soc.*, 2001, **123**, 6710.
17 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 5th edn., Wiley-Interscience, New York, 1997.
18 S. Alvarez, S. Schefzick, D. Avnir, and K. B. Lipkowitz, to be submitted.
19 Besides the usual requirement for structures with no disorder and $R < 0.10$, the only structures in these family of compounds that were disregarded are those whose tetrahedral and square planar symmetry measures do not correspond to the spread pathway and have been seen to present extra contacts to donor atoms. Such structures should then be rather considered as penta- or hexacoordinate with a Jahn–Teller distortion. CSD refcodes: BPYAGN, BPYCUP, BUWWOF, BEDTIN, BPCUDT, BPYAGN, JOBYAA, JOBTOJ, JURZEV, SICCOW, TEPFAV, and Cu1 in RUQMOF.
20 C. Deuschel-Cornioley, H. Stoeckli-Evans and A. von Zelewsky, *J. Chem. Soc., Chem. Commun.*, 1990, 121.
21 D. Grderic, B. Kamenar and A. Hergold-Brundic, *Croat. Chem. Acta*, 1979, **52**, 339.
22 H.-P. Wu, C. Janiak, G. Rheinwald and H. Lang, *J. Chem. Soc., Dalton Trans.*, 1999, 183.
23 Y.-J. Fu, H. Yang, D.-F. Wang, W.-X. Tang, B.-M. Wu and T. C. W. Mak, *Polyhedron*, 1997, **16**, 1505.
24 J. Foley, S. Tyagi and B. J. Hathaway, *J. Chem. Soc., Dalton Trans.*, 1984, 1.
25 M. Gianini, A. Forster, P. Haag, A. von Zelewsky and H. Stoeckli-Evans, *Inorg. Chem.*, 1996, **35**, 4889.
26 O. Mamula, A. von Zelewsky, T. Bark, H. Stoeckli-Evans, A. Neels and G. Bernardinelli, *Chem. Eur. J.*, 2000, **6**, 3575.
27 C.-W. Chan, C.-M. Che, M.-C. Cheng and Y. Wang, *Inorg. Chem.*, 1992, **31**, 4874.
28 C. Dietrich-Buchecker, G. Rapenne, J.-P. Sauvage, A. De Cian and J. Fischer, *Chem. Eur. J.*, 1999, **5**, 1432.
29 E. C. Constable, T. Kulke, G. Baum and D. Fenske, *Inorg. Chem. Commun.*, 1998, **1**, 80.
30 P. Ghosh, D. Shabat, S. Kumar, S. C. Sinha, F. Grynszpan, J. Li, L. Noodleman and E. Keinan, *Nature*, 1996, **382**, 339.
31 M. Munakata, S. Kitagawa, A. Asahara and H. Masuda, *Bull. Chem. Soc. Jpn.*, 1987, **60**, 1927.
32 J. S. Field, R. J. Haines, C. J. Parry and S. H. Sookraj, *Polyhedron*, 1993, **12**, 2425.
33 M. T. Miller, P. K. Gantzel and T. B. Karpishin, *Angew. Chem., Int. Ed.*, 1998, **37**, 1556.
34 M. T. Miller, P. K. Gantzel and T. B. Karpishin, *J. Am. Chem. Soc.*, 1999, **121**, 4292.
35 G. Baum, E. C. Constable, D. Fenske, C. E. Housecroft and T. Kulke, *Chem. Commun.*, 1999, 195.
36 G. Baum, E. C. Constable, D. Fenske and T. Kulke, *Chem. Commun.*, 1999, 2043.
37 J.-M. Lehn, *Supramolecular Chemistry*, VCH, Weinheim, Germany, 1995.
38 O. Mamula, A. von Zelewsky and G. Bernardinelli, *Angew. Chem., Int. Ed.*, 1998, **37**, 290.
39 G. Baum, E. C. Constable, D. Fenske, C. E. Housecroft, T. Kulke, M. Neuburger and M. Zehnder, *J. Chem. Soc., Dalton Trans.*, 2000, 945.
40 C. Chieh, *Can. J. Chem.*, 1978, **56**, 564.
41 K.-M. Chi, C.-T. Lin, S.-M. Peng and G.-H. Lee, *Organometallics*, 1996, **15**, 2660.
42 F. H. Allen and O. Kennard, *Chem. Des. Autom. News*, 1993, **8**, 31.