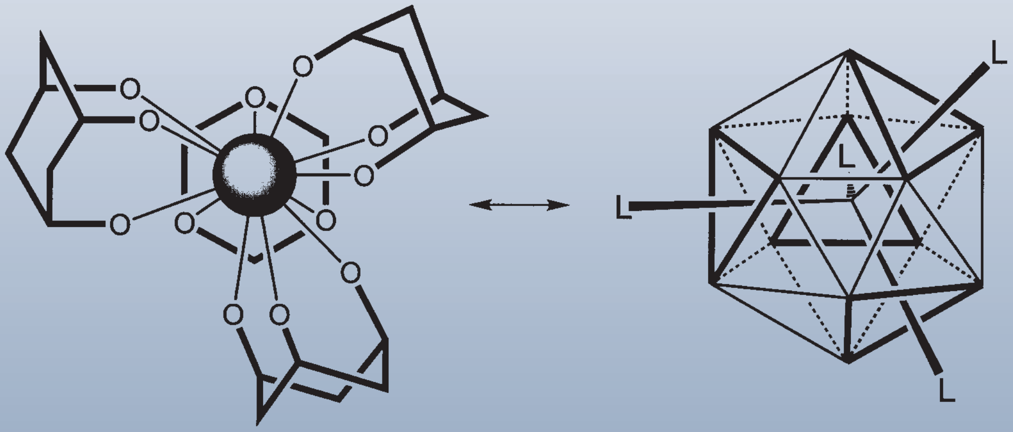
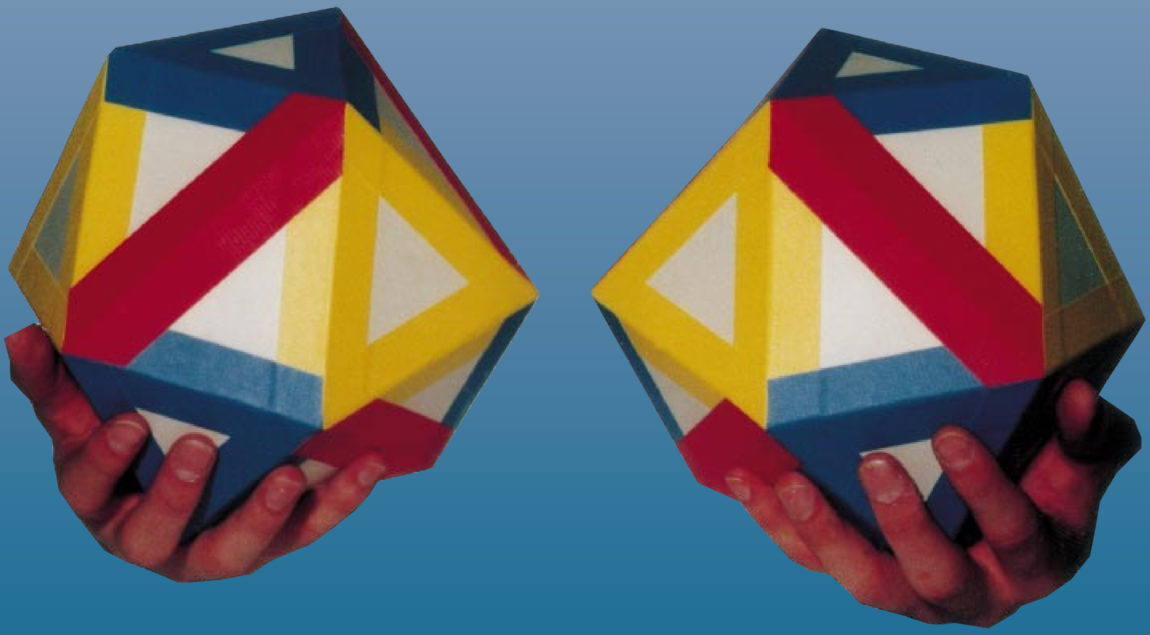


Four equal substituents placed at the vertices of a regular tetrahedron result in a highly symmetric, but chiral, structure if these substituents are tripodal, facedelineated ligands: The resulting icosahedral geometry retains the full rotational symmetry of the tetrahedron.



For more information see the following pages.

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T-Symmetrical Icosahedra: A New Type of Chirality in Metal Complexes[**]

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Thomas Weyhermüller, and Iris Müller

Dedicated to Professor Alan M. Sargeson
on the occasion of his 71th birthday

The preparation of metal complexes with a chiral structure has been one of the great challenges in synthetic coordination chemistry within the last 100 years. As early as 1911 Alfred Werner made use of the optical activity of chiral Co^{III} complexes to establish the octahedral geometry of this metal cation.[1] Since this pioneering work, interest in such materials has grown because a variety of important properties, such as enantioselective catalytic activity, specific binding of chiral guests, and optical behavior, depend on chirality.[2, 3] A uniform and undistorted coordination sphere of a metal complex is on its own not chiral, and specific strategies must be used to obtain chiral structures. These include the use of chiral ligands, heteroleptic complexes, or substitution of monodentate ligands L by multidentate analogues.[3] One may elucidate the individual isomers of a metal complex by visualizing with a particular color the corners, edges, or faces of the coordination polyhedron which are occupied by a ligand. A monodentate ligand would represent a colored corner,[4] a bidentate ligand L-L a colored edge,[5] while a C_3-symmetric, tridentate, tripodal ligand L–L–L would represent a colored triangular face. In an edge- or a face-delineated polyhedron containing bi- or tridentate ligands, isomers exist for each configuration in which the colored edges or faces do not meet at any of the vertices. This is rather trivial for coordination numbers up to eight, where only a limited number of solutions exists. The well known octahedral D_3-symmetric tris-chelates [M(L-L)$_3$] represent one of the few chiral examples. It would be of particular interest to know whether this concept would allow for the generation of *isometric* chiral structures. Such species would be unique because they are optically active but would not adopt any preferred orientation in space, for example, in an external magnetic or electric field. Only three possible point groups, *T*, *O*, and *I*, account for chiral isometric structures, and corresponding polyhedra would have a minimum of 12, 24, and 60 vertices, respectively.[6] The latter two are outside the range accessible to mononuclear complexes; however, metal complexes with a coordination number of 12 and icosahedral geometry are known.[7, 8] Since the chiral point group *T* is a subgroup of I_h, this strategy should allow for the generation of chiral *T*-symmetric complexes. We performed an exhaustive search for such solutions,[9] and could demonstrate that a total of five isomers,[10] with T_h, D_{3d}, D_3, D_2, and C_2 symmetry, are possible for an icosahedral [M(L-L)$_6$] structure. Two of them, namely the T_h and the D_3 isomers have been observed in complexes with bidentate ligands having a sufficiently small bite angle (for example, with NO_3^-).[7, 8] A chiral isometric structure can thus not be achieved by using bidentate ligands. Such a structure is, however, possible by coloring four triangular faces of an icosahedron. If the restriction is applied that the colored faces cannot have common vertices, only one single solution exists (Figure 1); this structure is chiral and retains the full rotational symmetry of the tetrahedron.

A synthetic route to such a complex has been established in our laboratory by testing a series of substituted cyclohexane-1,3,5-triols as possible ligands for Ba^{2+} ions. Since additional binding of H_2O has been observed in the complex formed with the unsubstituted ligand 1,3,5-triamino-1,3,5-trideoxy-*cis*-inositol (taci), namely $[Ba(taci)_2(H_2O)_3]^{2+}$,[11] we used more lipophilic derivatives, such as the tris(benzylamino)- and tris[benzylmethyl)amino] compounds, tbci and tbmci, respectively, for coordination in a non-aqueous medium (Figure 1 d). The hexaalkylated derivative tbmci proved to be too bulky, and the mass spectrum established that only the 1:2 complex $[Ba(tbmci)_2]^{2+}$ formed. For the intermediate tbci, the mass spectrum established the formation of the 1:4 complex $[Ba(tbci)_4]^{2+}$. The NMR data (^1H and ^{13}C) indicated that all four ligand moieties were equivalent, and that the local C_3 symmetry within each ligand was preserved. If a reasonable potential is considered with attractive forces between the cation and the oxygen donors, and repulsion between the individual ligand moieties, the center of gravity of the four ligands should be located on the vertices of a regular tetrahedron (Figure 1 a). Rotation around the threefold axes would generate a variety of different polyhedra such as the truncated tetrahedron, the cuboctahedron, the anticuboctahedron, and the icosahedron (Figure 1 b), with the icosahedral structure being of lowest energy.[7] A crystal-structure analysis of $[Ba(tbci)_4]^{2+}$ did indeed exhibit an almost regular icosahedron for the BaO_{12} sphere (Figure 2).[12]

$[Ba(tbci)_4]Br_2 \cdot 2.5\,MeOH$ crystallizes as a racemate with the two enantiomers related through a center of inversion. The twelve peripheral benzyl moieties encapsulate the central BaO_{12} icosahedron completely, thus generating a lipophilic

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Supporting information for this article is available on the WWW under http://www.angewandte.com or from the author.

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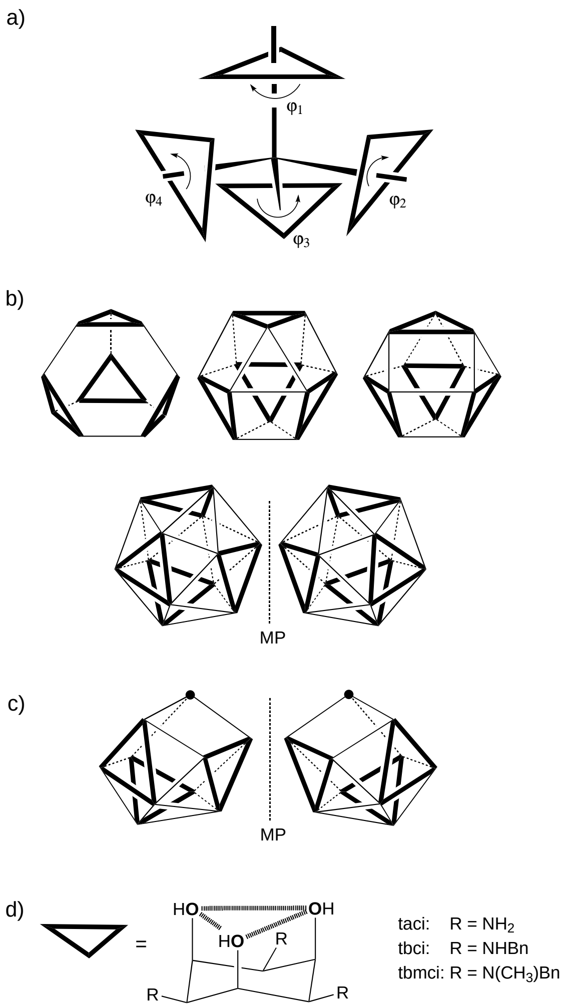

Figure 1. Coordination numbers of 10 and 12: Four tripodal tridentate ligands are arranged around a metal center with their centers of gravity placed on the vertices of a regular tetrahedron (a). Depending on the angles $\varphi_1 - \varphi_4$ different coordination polyhedra are obtained. Note that only one two-color solution is possible for each polyhedron and only the icosahedral structure is chiral (b; MP = mirror plane). The highlighted equilateral triangle at the top collapses to a single point (H_2O ligand) giving the chiral C_3-symmetric coordination polyhedron observed for the Sr complex (c). The scheme used for the ligands is shown in (d).

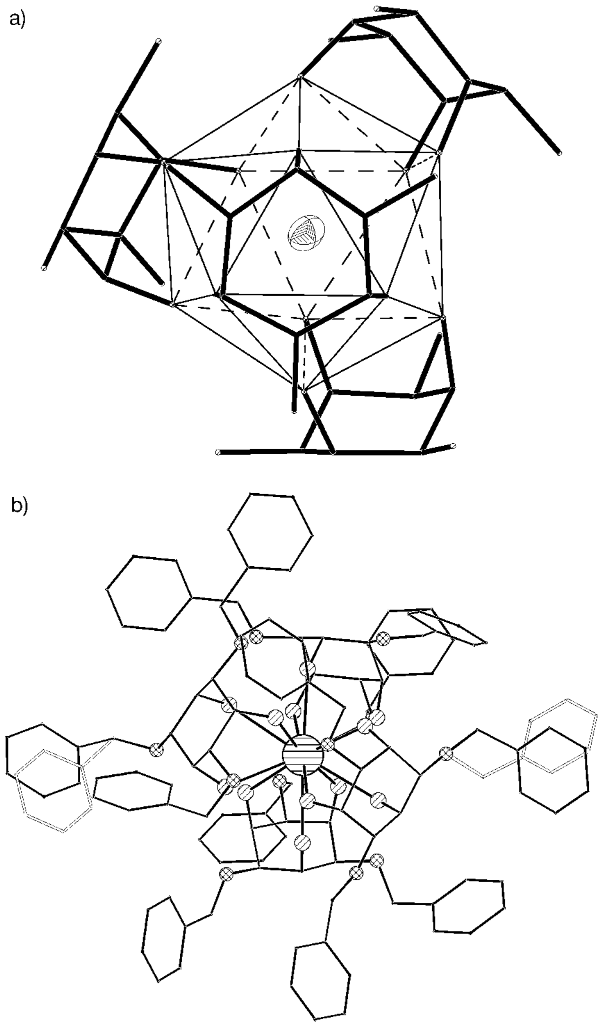

Figure 2. Structure of $[Ba(tbci)_4]^{2+}$ in the crystal. a) The BaO_{12} coordination sphere. b) Ball and stick model of the entire cation showing the disordered phenyl groups. (Ba–O bond lengths: 276(1) – 291(1) pm, mean value: 284 ± 5; O ··· O distances between adjacent oxygen donor atoms: 285(2) – 340(2) pm, average: 300 ± 12 pm).

molecular surface for the entire cation. The benzyl groups have an asymmetric orientation and the BaO_{12} icosahedron exhibited some minor distortions from full tetrahedral symmetry. However, as shown by the NMR data, the four ligand moieties as well as all the Ba–O bonds are equivalent in solution, and the deviation from true *T* symmetry is clearly the result of crystal packing effects in this particular structure.

Three different types of triangles can be specified in the *T*-symmetric coordination sphere: a) four equilateral triangles defined by the donor set of each ligand, b) twelve irregular triangles with one side derived from the two donors of one ligand and the additional vertex from another ligand, c) four additional equilateral triangles with all three vertices belonging to different ligand entities. Triangles of type a and c lie opposite to each other and are surrounded entirely by triangles of type b. The four threefold axes run through the mid-points of a type a and type c triangle, while the three twofold axes run through the mid-points of the common edges of two adjacent type b triangles.

The high coordination number (12) of $[Ba(tbci)_4]^{2+}$ is clearly a consequence of the large ionic radius of the Ba^{2+} ion. The use of Sr^{2+} and Mg^{2+} result in the formation of $[Sr(tbci)_3(H_2O)]^{2+}$ and $[Mg(tbci)_2]^{2+}$ with coordination numbers of 10 and 6, respectively.[13] The coordination sphere of the Sr complex is closely related to that of the Ba complex: It is obtained if one of the equilateral triangles of the MO_{12} icosahedron collapses to a single point. This point in the Sr complex is occupied by the water ligand. The resulting idealized SrO_{10} polyhedron has chiral C_3 symmetry (Figure 1c). It consists of 10 triangles with an *arachno* structure and three quadrilateral faces (rhombi) having the water oxygen atom as a common vertex. To the best of our knowledge, such a C_3 geometry with a coordination number of 10 is unprecedented. The Mg complex has a simple trigonal antiprismatic (octahedral) coordination.

Molecules with chiral *T* symmetry are scarce, and only a few examples of metal complexes have been reported. In general they have an oligonuclear structure.[14] A mononuclear complex with T symmetry and achiral ligands was hitherto unknown. The structure of $[Ba(tbci)_4]^{2+}$ is further unique in that it represents one of the very few examples of a 12-coordinate complex with exclusive formation of six-membered chelate rings. The facile formation of this complex in non-aqueous media may indicate that lipophilic derivatives of symmetrically substituted *cis*-cyclohexane-1,3,5-triols could serve as building blocks for such complexes if sufficiently large metal centers are used.

Experimental Section

tbci[15] was prepared by the reaction of taci[11] and an excess of benzaldehyde in MeOH, followed by $NaBH_4$ reduction. tbmci was obtained from tbci by an Eschweiler–Clarke-type methylation with formaldehyde and formic acid. Both ligands were characterized by ^1H and ^{13}C NMR spectroscopy as well as positive-ion fast-atom bombardment (FAB^+) MS, and gave correct C,H,N analyses (see Supporting Information).

$[Ba(tbci)_4]Br_2 \cdot 2CH_3OH$: A solution of $BaBr_2 \cdot 2H_2O$ (41 mg) in MeOH (5 mL) was added to a suspension of tbci (220 mg) in MeOH (5 mL). A clear solution was formed from which a crop of colorless crystals deposited within several minutes. Yield: 61 % of the air-dried product. Elemental analysis calcd (%) for $C_{110}H_{140}BaBr_2N_{12}O_{14}$ (2151.57): C 61.41, H 6.56, N 7.81; found: C 61.48, H 6.66, N 7.65; ^1H NMR ($CDCl_3$): $\delta = 2.15$ (3H), 3.70 (6H), 3.80 (3H), 7.23–7.36 (15H); ^{13}C NMR: $\delta = 50.7$, 58.4, 66.7, 125.9, 127.1, 128.5, 140.0; MS (FAB^+, 3-nitrobenzylalcohol) m/z (%): 2007.8 (55) $[Ba(tbci)_4Br]^+$, 2005.8 (45) $[Ba(tbci)_3(tbci-H_2)Br]^+$, 1926.3 (7) $[Ba(tbci)_4-H^+]^+$.

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[8] A search of the Cambridge Structural Database revealed a total of 31 hexanitrato complexes with bidentate NO_3^- ligands. A compilation is given in the Supporting Information.

[9] A derivation, based on geometrical and group theory considerations, together with a figure of the five isomers is given in the Supporting Information.

[10] Three of the five possible isomers (T_h, D_3, and D_{3d}) are discussed in ref. [7]; in ref. [5] the total number of possible solutions is erroneously given as six, without specifying the geometry of the individual isomers.

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[12] Crystals of composition $[Ba(tbci)_4]Br_2 \cdot 2.5MeOH$ disintegrate rapidly upon exposure to air. A crystal of dimensions $0.30 \times 0.18 \times 0.12$ mm was therefore embedded in a perfluoropolyether and cooled. Data collection was performed at 100(2) K on a SIEMENS SMART-CCD diffractometer, $Mo_{K\alpha}$-radiation ($\lambda = 71.073$ pm): space group $P2_1/n$, $a = 1910.1(5)$, $b = 2650.1(6)$, $c = 2050.1(5)$ pm, $\beta = 95.39(3)°$, $Z = 4$, $V = 10332(4) \times 10^6$ pm^3, $\rho_{calcd} = 1.393$ Mg m^{-3}, $\mu = 1.228$ mm^{-1}, graphite monochromator, numerical absorption correction ($T_{min} = 0.644$, $T_{max} = 0.862$), $2\theta_{max} = 42.0°$. Of 32396 measured reflections, 11083 independent reflections were used for the refinement of 576 parameters, and the structure was solved by direct methods (SHELXS-97). Ba, O, and N atoms were refined with anisotropic displacement parameters (SHELXL-97, full-matrix least-squares calculations on F^2). All other non-hydrogen atoms were refined isotropically. The phenyl groups were modeled as rigid bodies with fixed C–C bond lengths of 1.39 Å and fixed C-C-C angles of 120°. The phenyl groups appeared to be disordered. The disorder could only be partially resolved by using split positions. H(C) atoms were placed at calculated sites (riding model). $R = 0.112$ ($F_o^2 > 2\sigma(F_o^2)$), wR_2 (all data) = 0.267. Max/min residual electron density $+1.11/-1.18$ e Å^{-3}.[16]

[13] $[Sr(tbci)_3(OH_2)]Br_2 \cdot 4MeOH$ and $[Mg(tbci)_2]Cl_2 \cdot 10MeOH$ were prepared in an analogous way to the Ba^{2+} complex. Analytical and crystal data,[16] together with a figure showing the molecular structure are given in the Supporting Information.

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[16] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-164898–164900. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Coordinated B_2 Bridges in Porphyrins—Unexpected Formation of a Diborane(4)- from a Diborylporphyrin[**]

Andre Weiss, Hans Pritzkow, Penelope J. Brothers,[*] and Walter Siebert[*]

Dedicated to Professor Max Herberhold
on the occasion of his 65th birthday

Free-base porphyrins react with haloboranes to yield diborylporphyrins in which the porphyrin ligands show marked rectangular distortions.[1] The reaction of **1a**-H_2 with $F_3B \leftarrow OEt_2$ in the presence of trace water leads to green **1a**-

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