

One-step heterogeneous assembly of terbium(III) and silver(I) with thiacalix[4]arene ligands to form a cage including terbium(III) in an octa-oxygen cube

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Abstract A heterogeneous one-step self-assembly of Ag^+ , Tb^{3+} , and thiacalix[4]arene (TCAS), of which the donor atoms S and O showed high selectivity toward Ag^+ and Tb^{3+} ions, respectively, afforded a supramolecular cage compound, $\text{Ag}_4^+ \cdot \text{Tb}^{3+} \cdot \text{TCAS}_2$, at the center of which an octa-oxygen cube encapsulated the Tb^{3+} center to completely shield it from solvent molecules.

Keywords Heterometallic complexes · O,S ligands · Self-assembly · Supramolecular chemistry · Lanthanides

Introduction

Recent developments in supramolecular chemistry have proved that coordination linkages are effective for constructing molecular architectures because components can self-assemble via directional bond formation [1]. In order to include guest molecules, different types of molecular cages have been built by careful design of ditopic and/or tritopic ligands that coordinate to metal ions [2, 3]. For instance, Raymond et al., reported tetrahedral cage compounds, in which a hard Lewis acid such as Fe^{3+} , Ga^{3+} , or Ti^{4+} was linked to three catechol moieties from three

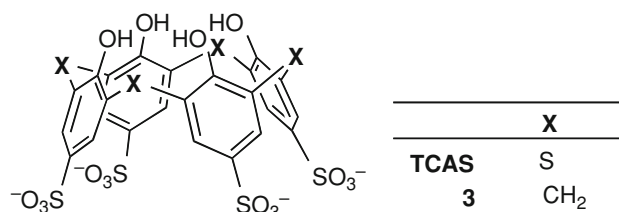
discrete bis- or tris(catechol) ligands at each apex [4]. Fujita et al. designed bis or tris(pyridyl) ligands that were joined by $-\text{Pd}^{2+}(\text{en})-$ groups (en = ethylenediamine) as rectangular connectors to produce various types of cage compounds [5, 6]. In all cases, a metal ion serves as a center providing directional bonds to the ligands. In the one-step preparation of a supramolecular assembly, a single metal species is usually used since hetero-metal species can produce mixtures of assemblies with statistically possible combinations of metal ions and ligands. However, there are a few exceptional cases where mixed-metal species have been used. For example, Shionoya et al., reported a heterogeneous assembly of Ag^+ and Ca^{2+} ions with a cyclic hexapeptide [7]. Bünzli et al., reported a one-step preparation of a supramolecular helix containing lanthanide(III) and 3d-transition metal ions having tunable luminescence properties [8, 9]. The key to achieving such heteronuclear assemblies is the selectivity of the binding sites of the ligands toward different metal species.

With the objective of creating supramolecular luminescent complexes [10–12], we have recently shown that by merely mixing the components: thiacalix[4]arene-*p*-tetrasulfonate (TCAS, Scheme 1), Tb^{3+} ions, and Ag^+ ions in aqueous solutions conveniently afforded the complex $\text{Ag}_2^+ \cdot \text{Tb}^{3+} \cdot \text{TCAS}_2$ (**1**) via self-assembly [13]. Interest in three-dimensional structure of the hetero-metal assembly has prompted us to attempt the isolation of single crystals of complex **1**, yielding the analogue $\text{Ag}_4^+ \cdot \text{Tb}^{3+} \cdot \text{TCAS}_2$ (**2**). In this paper, we report the crystallographic structure of complex **2** to reveal its supramolecular cage structure, highlighting the importance of the selectivity of the donor atoms of TCAS for soft and hard acids in a heterogeneous assembly to form the cage. At the center of the cage, a Tb^{3+} ion is accommodated in an O_8 -cube of phenolic oxygen.

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Scheme 1 Structure of TCAS and calix[4]arene-*p*-tetrasulfonate (**3**)

Experimental

Preparation of complex **2**

In a small beaker, 76 mg of TCAS (8.4×10^{-5} mol), 69 mg of 2-(*N*-cyclohexylamino)ethane sulfonic acid (CHES), and *ca.* 10 ml of water were mixed. The pH of the solution was adjusted to 10.0 by adding conc. NaOH solution. The solution was further mixed with 1 ml of an aqueous solution containing Ag_2SO_4 (21.5 mg, 6.9×10^{-5} mol) and $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (15.9 mg, 3.5×10^{-5} mol), and 1 ml aliquot of this mixture was transferred into a small cuvette. The cuvette was then placed in a large vial half-filled with DMF, and the vial was sealed. After standing the mixture for a few months, colorless blocks of $\text{Na}_9[\text{Ag}_4\text{Tb}(\text{tcas})_2\text{dmf}_2] \cdot 6\text{dmf} \cdot 6\text{H}_2\text{O}$ were obtained (3 mg, *ca.* 30% yield).

Crystal data for complex **2**

$\text{Na}_9 \cdot 2 \cdot 6\text{dmf} \cdot 6\text{H}_2\text{O}$ ($\text{C}_{72}\text{H}_{92}\text{Ag}_4\text{N}_8\text{Na}_9\text{O}_{50}\text{S}_{16}$ Tb; $M_r = 3179.81$): colorless prism, triclinic, space group $P-1$, $a = 11.817(5)$, $b = 13.705(5)$, $c = 17.539(7)$ Å, $\alpha = 72.374(8)$, $\beta = 85.490(9)$, $\gamma = 87.722(9)^\circ$, $V = 2698.4(18)$ Å³, $Z = 1$, $T = 100(2)$ K, $\rho_{\text{calcd}} = 1.957$ g/cm³, $F(000) = 1588$, $\mu(\text{MoK}\alpha) = 1.803$ mm⁻¹. The data were collected using a Bruker SMART CCD diffractometer ($\text{MoK}\alpha = 0.71073$ Å). The structures were elucidated by direct methods using SHELXS-97 [14, 15] and were further refined using least-squares on F^2 , SHELXL-97, with 756 parameters, $wR_2 = 0.1115$ (15387 unique reflections), $R_1 = 0.0425$ (11899 reflections with $I > 2\sigma$). CCDC-669273 contains the supplementary crystallographic data in support of the findings of this paper. These data can be obtained, free of charge, from The Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/data_request/cif.

Results and discussion

The slow diffusion of DMF vapors into an aqueous solution containing Ag^+ , Tb^{3+} , and TCAS ($\text{H}_4\text{tcas}^{4-}$) in 4:1:2 ratio at pH 10.0 yielded crystals of $\text{Na}_9 \cdot 2 \cdot 6\text{dmf} \cdot 6\text{H}_2\text{O}$, where **2** represents the complex anion $[\text{Ag}_4\text{Tb}(\text{tcas})_2\text{dmf}_2]^{9-}$.

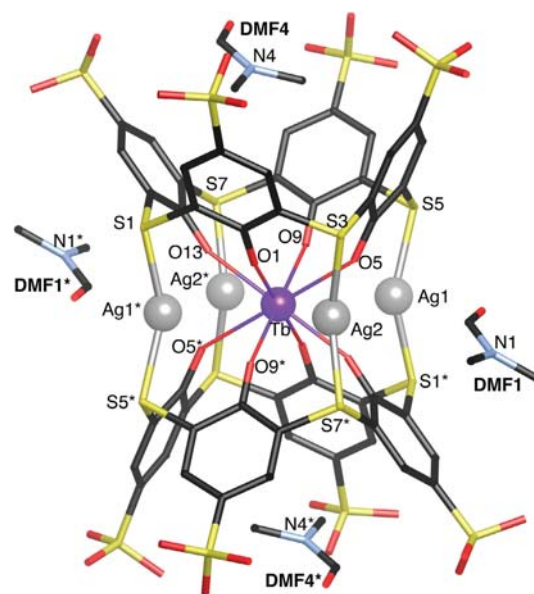


Fig. 1 Crystal structure of $[\text{Ag}_4\text{Tb}(\text{tcas})_2\text{dmf}_2]^{9-}$ (**2**) including two DMF molecules (DMF4) in the TCAS cavity. Tb^{3+} is located at the crystallographic inversion center and half of the molecule is independent

$\text{dmf}_2]^{9-}$. On irradiation of the crystals with UV light, they emitted green light, which was due to the $^5\text{D}_4 \rightarrow ^7\text{F}_5$ transition at the Tb^{3+} center (see supporting information). Complex **2** (Fig. 1) has a rectangular cage structure whose dimensions are $7.7 \times 6.9 \times 12.5$ Å³, as determined by the distances between SO_3^- groups. The wider rims of the cone-shaped TCAS ligands serve as the top and bottom faces of the cage, and the four S– Ag^+ –S linkages between the two TCAS ligands form the edges. The complex has a pseudo D_{4h} symmetry with a four-fold axis passing through Tb^{3+} ion and centers of the two TCAS ligands, however it indeed has a C_i symmetry with the inversion center at the Tb^{3+} ion due to a slight distortion in the TCAS ligands from the cone conformation to a pinched-cone conformation. By utilizing all the available coordinating sites, O_4S_4 , TCAS acts as an octadentate ligand to form the $\text{Ag}_4^+\text{Tb}^{3+}$ core, whose coordination environment is shown in Fig. 2. A close examination of the core reveals that the donor atoms are selective toward the metal ions based on the hardness and softness of the acids and bases: soft S coordinates to soft Ag^+ , while hard phenolic O^- coordinates to hard Tb^{3+} ion. Thus, the selectivity of the donor atoms plays an indispensable role in the heterogeneous self-assembly of metal ions to form complex **2** with a cage structure.

At the center of the complex, Tb^{3+} appears to be included in the cage; Tb^{3+} has an octa-oxygen cubic coordination environment provided by two TCAS ligands aligned in parallel. Thus the cube shields the Tb^{3+} ion from any coordinating solvent molecules. Previously, we

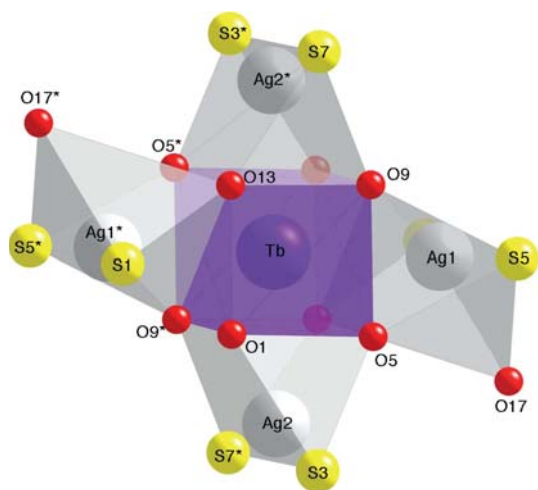


Fig. 2 Coordination environment of $\text{Ag}_4\text{Tb}^{\text{III}}$ core viewed along the pseudo C_4 axis. Selected bond length [Å]: Tb–O1 2.402(3), Tb–O5 2.515(3), Tb–O9 2.367(3), Tb–O13 2.364(3), Ag1–S1 2.4491(12), Ag1–S5* 2.4529(12), Ag2–S7* 2.4137(12), Ag2–S3 2.4401(12). Selected atomic distances [Å] and angles [°] for octa-oxygen cube: O1–O9* 2.703(4), O5–O13* 2.631(4), O1–O5 2.880(4), O5–O9 2.871(4), O9–O13 2.817(4), O13–O1 2.807(4); O13–O1–O5 92.59(11), O13–O1–O9* 87.20(11), O5–O1–O9* 90.03(11), O1–O5–O9 86.16(11), O1–O5–O13* 88.55(11), O9–O5–O13* 87.28(11), O5–O9–O13 92.59(12), O5–O9–O1* 91.26(10), O13–O9–O1* 88.47(11), O9–O13–O1 88.61(11), O9–O13–O5* 92.93(11), O1–O13–O5* 94.23(11)

revealed that $\text{Ag}_2^+ \cdot \text{Tb}^{3+} \cdot \text{TCAS}_2$ (**1**) has an extremely long luminescent lifetime ($\tau = 4.6$ ms) [13]. Structure of **2** at least suggests that complex **1** has two instead of four S– Ag^+ –S linkages to form a cage structure similar to **2** to provide Tb^{3+} a cubic coordination environment to expel coordinated water molecules responsible for quenching.

The O_8 -cube of complex **2** has two basal squares of O1/O5/O9/O13 and O1*/O5*/O9*/O13* with an average side of 2.844(4) Å, which is slightly greater than the distance between the squares (2.667(4) Å). At the same time, all the O–O–O angles are within the range of 86.16(11)°–94.23(11)°; thus the cubic structure is maintained. In coordination chemistry, it is common knowledge that cubic eight-coordination geometry is much less favorable than dodecahedron or square antiprism geometry because of the ligand–ligand repulsions [16, 17]. In the case of lanthanide(III) (Ln^{3+}) ions, only a few examples are known thus far: $[\text{LaL}_4^1](\text{ClO}_4)_3$ ($L^1 = 2,2'$ -bipyridine dioxide) was first revealed as a Ln^{3+} complex having cubic O_8 -coordination geometry, which was formed by the stacking of the aromatic rings of the ligand with those of neighboring complexes in the crystal packing [18]. More recently, $[\text{NdL}_4^2]^-$ ($\text{HL}^2 =$ dibenzoylmethane) with an almost perfect cubic O_8 -coordination geometry has been found in a crystal of $[\text{NdL}^3][\text{NdL}_4^2]$ ($L^3 =$ bis[3-(2-pyridyl)pyrazol-1-yl]dihydroborate) [19]. In this case, it was concluded that interpenetration of $[\text{NdL}_4^2]^-$ ions with counter cations

$[\text{NdL}^3]^+$ in the crystal lattice caused the formation of such sterically unfavorable coordination geometry. In both cases, the interactions of complexes with the neighboring entities in a crystal packing seemed to be responsible for the cubic eight-coordination geometry. In contrast, the self-assembly of TCAS, Tb^{3+} , and Ag^+ easily produces a unique cubic eight-coordination environment for Tb^{3+} . This is because of the presence of the S– Ag^+ –S bridges that align the two TCAS ligands in parallel such that there is no torsion around the pseudo C_4 axis. Each Ag^+ ion, which is attached to one of the four sides of the cube, shows deviation from an ideal linear bidentate coordination to a bent geometry with S– Ag^+ –S angles of 149.56(3)° and 145.48(3)° for Ag1 and Ag2, respectively. In addition, Ag1 is weakly coordinated by O17 of DMF1.

In a unit cell of a crystal of $\text{Na}_9 \cdot 2 \cdot 6\text{dmf} \cdot 6\text{H}_2\text{O}$, six DMF and six water molecules are included. Out of the three crystallographically independent DMF molecules, DMF4 is included in the cavity of TCAS (Fig. 1). The DMF4 is held in the TCAS cavity by weak interactions: hydrogen bonding between amide H and sulfo O^- ($\text{C34} \cdots \text{O15} = 3.309(5)$ Å) and CH/ π interaction between methyl H and phenyl rings ($\text{C35} \cdots \text{Ph3} = 3.395(5)$ Å) and ($\text{C36} \cdots \text{Ph1} = 3.445(5)$ Å) (Fig. 3). DMF2 and DMF3 are included in the crystal lattice. The crystal packing of $\text{Na}_9 \cdot 2 \cdot 6\text{dmf} \cdot 6\text{H}_2\text{O}$ (Fig. 4) shows a typical hydrophilic/hydrophobic bilayer structure in which complex **2** forms the hydrophobic part separated by the hydrophilic layers containing water molecules and Na^+ ions. Such a bilayer structure is similar to the reported

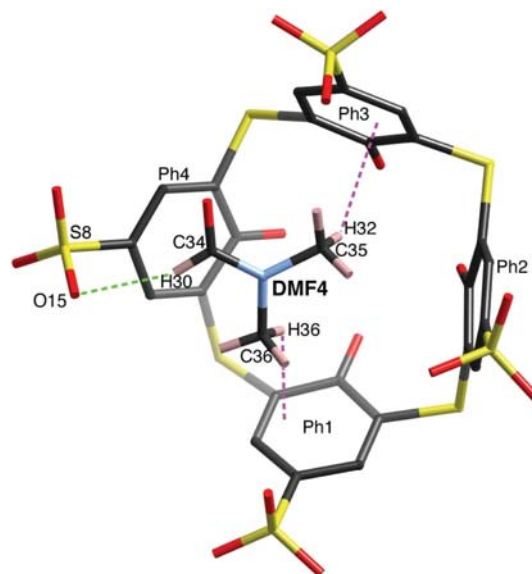


Fig. 3 Top view of $[\text{Ag}_4\text{Tb}(\text{tcas})_2\text{dmf}_2]^{9-}$ (**2**) showing the inclusion of DMF4 in the TCAS cavity. Dotted lines indicate hydrogen bonding (green) and CH/ π interaction (pink). To avoid ambiguity, only the TCAS ligand and a DMF molecule are shown. Ph1 and Ph3 denote the phenyl rings consisting of C1–6 and C13–18, respectively

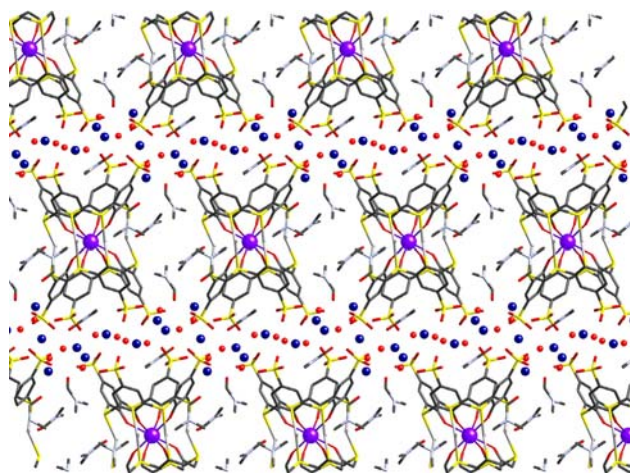


Fig. 4 Crystallographic packing of $\text{Na}_9 \cdot 2 \cdot 6\text{dmf} \cdot 6\text{H}_2\text{O}$ viewed from the x -axis, showing the hydrophobic/hydrophilic double layer. Blue and red spheres represent sodium(i) cation and water molecule, respectively

structures of the single crystals of calix[4]arene-*p*-tetrasulfonate (**3**) with various metal cations and guest molecules [20]. However, the major packing entities, i.e., the cone-shaped **3** or the double-cone **2** quadruply bridged by $\text{S}-\text{Ag}^+-\text{S}$, distinguish the two crystals. For instance, a single crystal of $\text{Na}_5 \cdot 3 \cdot 12\text{H}_2\text{O}$ contains the cones of penta-anionic **3** arranged in a head-to-tail manner to form the hydrophobic part. On the other hand, the $\text{Na}_9 \cdot 2 \cdot 6\text{dmf} \cdot 6\text{H}_2\text{O}$ crystal contains the double-cone **2** simply arrayed in the xy plane of the crystal. Since a double cone has a larger height than a single cone, the thickness of the bilayer of $\text{Na}_9 \cdot 2 \cdot 6\text{dmf} \cdot 6\text{H}_2\text{O}$ (16.7 Å) is larger than that of $\text{Na}_5 \cdot 3 \cdot 12\text{H}_2\text{O}$ (13.7 Å). It is interesting to note that the DMF and water molecules in $\text{Na}_9 \cdot 2 \cdot 6\text{dmf} \cdot 6\text{H}_2\text{O}$ appear to be separated into two “phases”: DMF2 and DMF3 exist in the hydrophobic layer, while the water molecules can be found only in the hydrophilic layer. In the hydrophilic layer, Na^+ ions are coordinated by the oxygen donors from the sulfo group, water, and DMF4 to form a coordination network of $\text{Na}-\text{O}$ bonds. Thus, in the crystal lattice, complex **2** is separated by DMF molecules in the xy plane and by water molecules and Na^+ ions in the z direction, such that there is no direct interaction among complexes **2** themselves. Hence, the four $\text{S}-\text{Ag}^+-\text{S}$ bridges between TCAS ligands, and not the crystal packing, are responsible for the Tb^{3+} ion to adopt a cubic coordination geometry.

Conclusions

In conclusion, we revealed the cage structure of a $\text{Ag}^+-\text{Tb}^{3+}$ -TCAS ternary complex, $[\text{Ag}_4 \text{Tb}(\text{tcas})_2\text{dmf}_2]^{9-}$ (**2**), which was formed by the one-step heterogeneous self-

assembly of Ag^+ and Tb^{3+} ions with the TCAS ligands containing donor atoms that have high selectivity toward the metal ions. Since the Tb^{3+} ion was encapsulated in an octa-oxygen cube, it was shielded from solvent molecules such as water and DMF, which is advantageous for construction of a highly luminescent environment for a lanthanide(III). The photophysical properties of complex **2** in the solid state are currently under investigation.

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References

1. Yeh, R.M., Davis, A.V., Raymond, K.N.: Comprehensive coordination chemistry II, Elsevier Ltd. Oxford **7**, 327–355 (2004)
2. Leininger, S., Olenyuk, B., Stang, P.J.: Self-assembly of discrete cyclic nanostructures mediated by transition metals. *Chem. Rev.* **100**, 853–908 (2000). doi:10.1021/cr9601324
3. Seidel, S.R., Stang, P.J.: High-symmetry coordination cages via self-assembly. *Acc. Chem. Res.* **35**, 972–983 (2002). doi:10.1021/ar010142d
4. Caulder, D.L., Raymond, K.N.: Supermolecules by design. *Acc. Chem. Res.* **32**, 975–982 (1999). doi:10.1021/ar970224v
5. Yoshizawa, M., Fujita, M.: A self-assembled coordination cage as a molecular flask. *Pure Appl. Chem.* **77**, 1107–1112 (2005). doi:10.1351/pac200577071107
6. Sun, W.Y., Yoshizawa, M., Kusukawa, T., Fujita, F.: Multi-component metal-ligand self-assembly. *Curr. Opin. Chem. Biol.* **6**, 757–764 (2002). doi:10.1016/S1367-5931(02)00358-7
7. Okada, T., Tanaka, K., Shiro, M., Shionoya, M.: Heterogeneous assembly of silver(I) and calcium(II) ions accompanying a dimer formation of cyclo(L-Ala-L-Met)₃. *Chem. Commun. (Camb.)* **2005**, 1484–1486 (2005). doi:10.1039/b415567j
8. Torelli, S., Imbert, D., Cantuel, M., Bernardinelli, G., Delahaye, S., Hauser, A., Bünzli, J.-C.G., Piguet, C.: Tuning the decay time of lanthanide-based near infrared luminescence from micro- to milliseconds through d-f energy transfer in discrete heterobimetallic complexes. *Chem. Eur. J.* **11**, 3228–3242 (2005). doi:10.1002/chem.200401158
9. Imbert, D., Cantuel, M., Bünzli, J.-C.G., Bernardinelli, G., Piguet, C.: Extending lifetimes of lanthanide-based near-infrared emitters (Nd, Yb) in the millisecond range through Cr(III) sensitization in discrete bimetallic edifices. *J. Am. Chem. Soc.* **125**, 15698–15699 (2003). doi:10.1021/ja0386501
10. Bünzli, J.-C.G., Piguet, C.: Taking advantage of luminescent lanthanide ions. *Chem. Soc. Rev.* **34**, 1048–1077 (2005). doi:10.1039/b406082m
11. Bünzli, J.-C.G.: Benefiting from the unique properties of lanthanide ions. *Acc. Chem. Res.* **39**, 53–61 (2006). doi:10.1021/ar0400894
12. Gunnlaugsson, T., Stomeo, F.: Recent advances in the formation of luminescent lanthanide architectures and self-assemblies from structurally defined ligands. *Org. Biomol. Chem.* **5**, 1999–2009 (2007). doi:10.1039/b700232g
13. Iki, N., Ohta, M., Horiuchi, T., Hoshino, H.: Exceptionally long-lived luminescence emitted from Tb^{III} ion caged in an $\text{Ag}^+-\text{Tb}^{\text{III}}$ -Thiacalix[4]arene supramolecular complex in water. *Chem. Asian J.* **3**, 849–853 (2008). doi:10.1002/asia.200700298
14. Package, SHELXTL/PC: Bruker. AXS Inc, Madison, Wisconsin, USA (1988)
15. Sheldrick, G.M.: A short history of SHELX. *Acta Crystallogr. A* **64**, 112–122 (2008). doi:10.1107/S0108767307043930

16. Cotton, F.A., Wilkinson, G.: *Advanced Inorganic Chemistry*, 5th edn, p. 15. Wiley, New York (1988)
17. Haigh, C.W.: Enumeration by Pólya's theorem of the isomerism in eight-coordinate complexes in square antiprismatic, triangular dodecahedral and hendecahedral (bicapped trigonal prismatic) geometries. *Polyhedron* **15**, 605–643 (1996). doi:[10.1016/0277-5387\(95\)00292-Z](https://doi.org/10.1016/0277-5387(95)00292-Z)
18. Al-Karaghoul, A.R., Day, R.O., Wood, J.S.: Crystal structure of tetrakis(2, 2'-bipyridine dioxide)lanthanum perchlorate: an example of cubic eight-coordination. *Inorg. Chem.* **17**, 3702–3706 (1978). doi:[10.1021/ic50190a076](https://doi.org/10.1021/ic50190a076)
19. Davies, G.M., Aarons, R.J., Motson, G.R., Jeffery, J.C., Adams, H., Faulkner, S., Ward, M.D.: Structural and near-IR photophysical studies on ternary lanthanide complexes containing poly(pyrazolyl)borate and 1, 3-diketonate ligands. *Dalton Trans.* **2004**, 1136–1144 (2004). doi:[10.1039/b400992d](https://doi.org/10.1039/b400992d)
20. Coleman, A.W., Bott, S.G., Morley, S.D., Means, C.M., Robinson, K.D., Zhang, H., Atwood, J.L.: Novel layer structure of sodium calix[4]arenesulfonate complexes—a class of organic clay mimics? *Angew. Chem. Int. Ed. Engl.* **27**, 1361–1362 (1988). doi:[10.1002/anie.198813611](https://doi.org/10.1002/anie.198813611)