Keywords: charge transfer • density functional calculations • DNA structures • hydrogen bonds • resonance assistance

[1] a) G. Gilli, F. Bellucci, V. Ferretti, V. Bertolasi, *J. Am. Chem. Soc.* **1989**, *111*, 1023; b) H. Umeyama, K. Morokuma, *J. Am. Chem. Soc.* **1977**, *99*, 1316. See also, for example, c) G. A. Jeffrey, W. Saenger, *Hydrogen Bonding in Biological Structures*, Springer, Berlin, **1991**, p. 37; d) G. A. Jeffrey, *An Introduction to Hydrogen Bonding*, Oxford University Press, New York, **1997**, p. 103.

[2] a) W. Saenger, *Principles of Nucleic Acid Structure*, Springer, New York, **1984**; b) N. C. Seeman, J. M. Rosenberg, F. L. Suddath, J. J. P. Kim, A. Rich, *J. Mol. Biol.* **1976**, *104*, 109; c) J. M. Rosenberg, N. C. Seeman, R. O. Day, A. Rich, *J. Mol. Biol.* **1976**, *104*, 145.

[3] a) J. Sponer, J. Leszczynski, P. Hobza, *J. Phys. Chem.* **1996**, *100*, 1965; b) K. Brameld, S. Dasgupta, W. A. Goddard III, *J. Phys. Chem. B* **1997**, *101*, 4851; c) J. Bertran, A. Oliva, L. Rodríguez-Santiago, M. Sodupe, *J. Am. Chem. Soc.* **1998**, *120*, 8159.

[4] a) C. Fonseca Guerra, O. Visser, J. G. Snijders, G. te Velde, E. J. Baerends in *Methods and Techniques for Computational Chemistry* (Eds.: E. Clementi, G. Corongiu), STEF, Cagliari, **1995**, p. 305; b) A. Becke, *Phys. Rev. A* **1988**, *38*, 3098; c) J. P. Perdew, *Phys. Rev. B* **1986**, *33*, 8822 (erratum: *Phys. Rev. B* **1986**, *34*, 7406).

[5] a) F. M. Bickelhaupt, N. M. M. Nibbering, E. M. van Wezenbeek, E. J. Baerends, *J. Phys. Chem.* **1992**, *96*, 4864; b) T. Ziegler, A. Rauk, *Theor. Chim. Acta* **1977**, *46*, 1.

[6] Mass spectrometric data from I. K. Yanson, A. B. Teplitsky, L. F. Sukhodub, *Biopolymers* **1979**, *18*, 1149, with corrections proposed in ref. [3b].

[7] F. M. Bickelhaupt, N. J. R. van Eikema Hommes, C. Fonseca Guerra, E. J. Baerends, *Organometallics* **1996**, *15*, 2923.

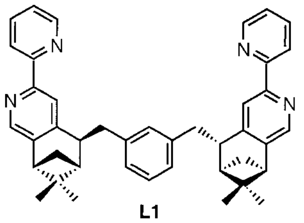
Stereoselective Synthesis of Coordination Compounds: Self-Assembly of a Polymeric Double Helix with Controlled Chirality**

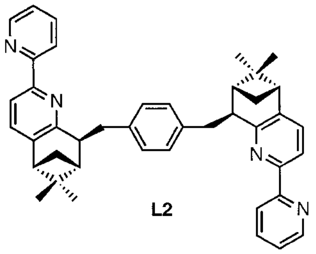
Olimpia Mamula, Alex von Zelewsky,* Thomas Bark, and Gérald Bernardinelli

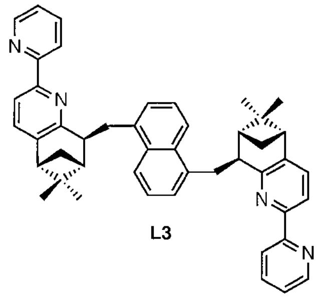
The formation of helical structures by the assembly of metal coordination species has received a great deal of attention in recent years. The field of helicates has recently been reviewed by Piguet et al.,[1] and several observations of infinite coordination helices have been reported.[2–13] Most of these infinite helices are formed from achiral ligands,[2–9] consequently yielding racemates of *P* and *M* helices. In a few cases chiral predetermination is achieved by the use of enantiopure ligands.[10–13]

Here we describe a self-assembled coordination polymer that is chirally predetermined and represents, to the best of our knowledge, the first example for intertwining of two single-stranded helicates to form an infinite, highly symmetric double helix. The two strands of this double helix are connected neither by chemical bonds nor through attractive intermolecular forces, except unspecific van der Waals interactions.

We have shown recently that CHIRAGEN-type ligands[14] can give rise to the formation of self-assembled helicates that are predetermined in their chirality. With metals that give octahedral coordination, 4,5-CHIRAGEN[*m*-xylyl] (**L1**) yields dinuclear species of M_2L_3 stoichiometry.[15] This 2:3 stoichiometry seems to be fairly common, since several other ligands in which two bidentate units are connected through a bridge provide such assemblies.[1, 16–19] The use of the 5,6-CHIRAGEN **L2** containing a *para*-xylylidene bridge with metals that form tetrahedral coordination species, such as Ag^+ and Cu^+, yielded highly symmetric, circular, hexanuclear single-stranded helicates; the chirality is again totally predetermined by the chiral pinene groups present in these ligands.[20] To investigate further the influence of the ligand geometry on the molecular assembly, we varied the bridge in the 5,6-CHIRAGEN ligand. Here we report the structural properties of the species obtained with the ligand **L3**, in which the bridge has been derived from 1,5-dimethylnaphthalene.


L1


L2


L3

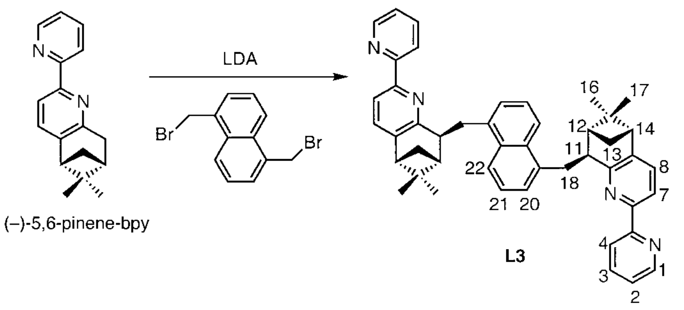
The ligand **L3** was synthesized following the general procedure (Scheme 1) that has been applied for several other ligands of the CHIRAGEN family.[14, 21, 22] The ligand was completely characterized, and its NMR spectra show the symmetry expected owing to the C_2 axis perpendicular to the naphthalene plane and passing through its center. As a consequence of the high stereoselectivity in its synthesis, the ligand is isomerically pure within NMR analytical accuracy. According to the NMR spectra, a self-assembled species with high symmetry is formed upon addition of Ag^+, as in the case of **L2**.[20] Figure 1 shows the aromatic part of the ^1H NMR spectra of the free ligand **L3** (b) and of the silver complex (a).

---

[*] Prof. Dr. A. von Zelewsky, O. Mamula, T. Bark
Institute of Inorganic Chemistry
University of Fribourg
Perolles, CH-1700, Fribourg (Switzerland)
Fax: (+41) 26-300-97-38
E-mail: alexander.vonzelewsky@unifr.ch

Dr. G. Bernardinelli
Laboratory of X-Ray Crystallography
University of Geneva (Switzerland)

[**] This work was supported by the Swiss National Science Foundation. We thank M. Düggeli for preparing (−)-5,6-pinene-bpy.



Scheme 1. Synthesis of the ligand **L3** and numbering of the atoms. bpy = 2,2′-bipyridine, LDA = lithium diisopropylamide.

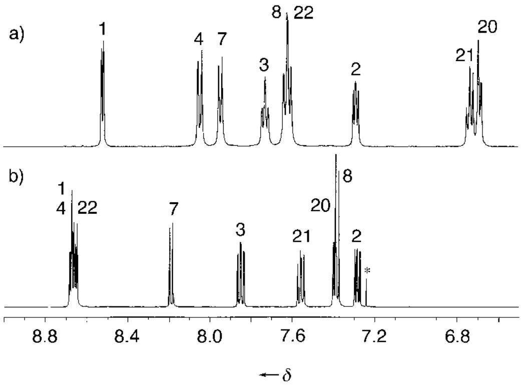


Figure 1. Aromatic part of the ^{1}H NMR spectra (500 MHz) of a) the Ag^{I} compound in CD_3CN and b) **L3** in chloroform (*). The spectrum of **L3** in CD_3CN is almost identical, but much less intense owing to very low solubility.

The preservation of C_2 symmetry for the ligand in the complex on the NMR time scale, combined with the observation of oligonuclear species in the electrospray (ES) mass spectrum, can be explained either by the formation of circular helicates, similar to those observed with **L2**, or by rapid dynamic equilibria between fragments. Redissolution of the crystals does not result in a change in the NMR spectra, indicating a completely reversible behavior of the compound upon the solid/solution transition.

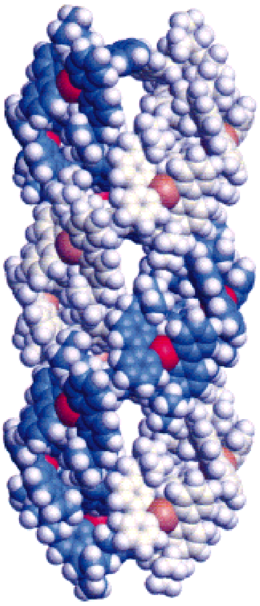


Figure 2. Side view of the cationic polymer (one and a half turns).

Crystals suitable for X-ray analysis were obtained by slow diffusion of diethyl ether into a solution of the 1:1 complex, with PF_6^- as anion, in acetonitrile. The analysis of the diffraction data shows an infinite double helix. The helical pitch, given by the distance between equivalent atoms generated by one full rotation of the sixfold screw axis, is 3.417 nm (two times the crystallographic *c* axis).

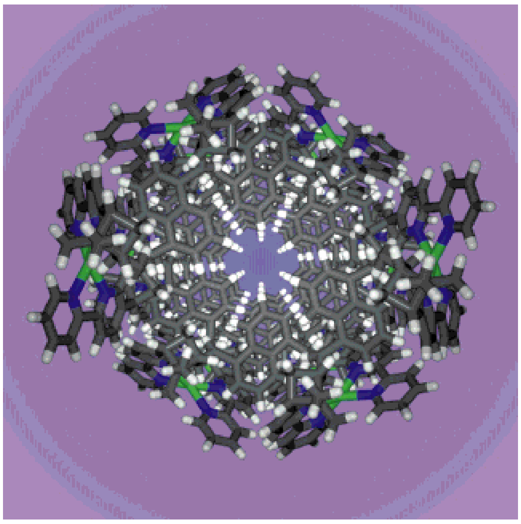


Figure 3. Perspective view of the double-stranded helix along the C_6^4 screw axis.

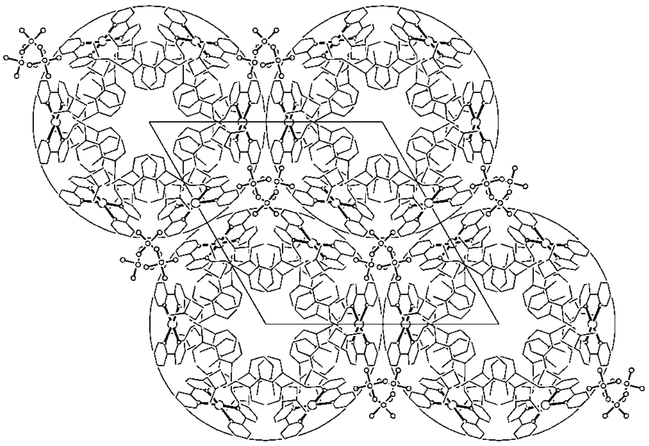


Figure 4. Molecular packing as seen along the crystallographic *c* axis. The PF_6^- anions occupy the channels between three adjacent double helices.

Figure 2 presents a side view of the cationic polymer, Figure 3 a projection in the direction of the sixfold screw axis, and Figure 4 the packing as seen along the crystallographic *c* axis. In the following, the various, quite unusual features of this structure will be discussed. All metal centers have a strongly distorted tetrahedral coordination geometry, and their chirality is predetermined by the pinene groups in the ligands. Thus, the metal centers show homochiral coordination with absolute configuration Λ.[23] The nitrogen–silver distance of 2.28(3) Å is quite normal. The local coordination geometry is therewith very similar in the circular helicate with **L2** and in the double-stranded helix with **L3**. The angle between the planes defined by the two N-Ag-N chelate rings at one metal center is 67.5(4)°, and the bite angle of each bipyridine unit is 71.3(9)°. The chirality of the double helix is *P*. *P* helicity combined with local Λ configuration at each tetrahedral metal center was already observed in related structures.[20, 24]

An exceptional feature of this cationic polymer is the high degree of symmetry (D_6^4) of its double-helical arrangement. In addition to the C_6^4 axis parallel to the main direction of the helix, the Ag$^+$ ions and the naphthalenes are located on twofold axes. These C_2 axes are perpendicular to the direction

1433-7851/99/3819-2946 $ 17.50+.50/0

of the helix, and, on account of the conformation of the ligand in the helical structure, such an arrangement is in contradiction to the intrinsic molecular symmetry of the 1,5-disubstituted naphthalene moiety. Indeed, the crystal structure shows a disorder of the naphthalene bridge. This disorder has been resolved by two distinct orientations of the 1,5-substituted naphthalene (Figure 5a).

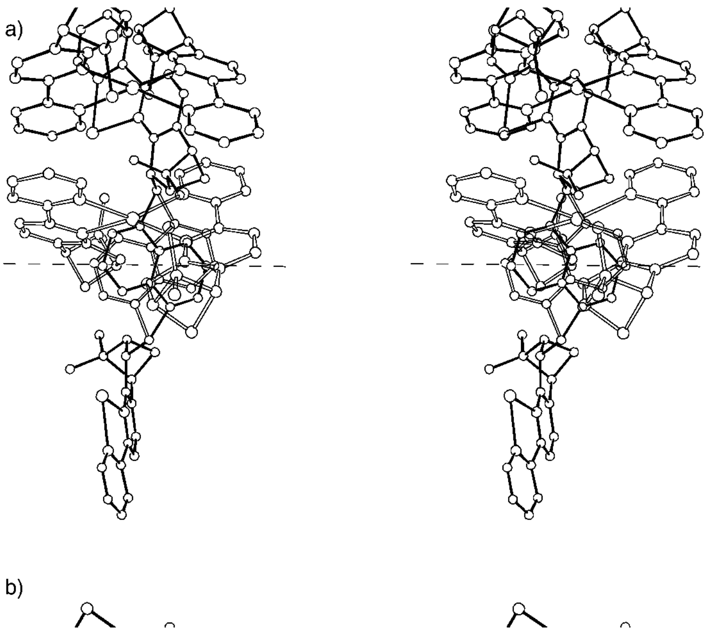


Figure 5. a) Stereoview of the two distinct orientations of the disordered naphthalene bridge. b) Stereoview emphasizing the π-stacking interactions between the bpy moieties of neighboring double helices.

If an isolated double-stranded helix is considered, no obvious reason for the intertwining can be recognized. A detailed analysis shows that there is no π stacking between the aromatic parts of the complexes. Moreover, the nature of the ligand precludes hydrogen-bond interactions between the strands, as observed in the DNA double helix. Nevertheless, the two intertwined strands are topologically inseparable (except by an "unscrewing" along the axis of the helix).

An analysis of the molecular packing reveals almost perfect π-stacking interactions involving four bipyridine moieties between neighboring double helices (parallel mean planes separated by 3.68 Å, Figure 5b). Thus, 12 π–π interactions per one full turn of the double helix, as well as the electrostatic attraction between the cationic polymer and the anions, are undoubtedly responsible for the cohesion of the crystal. They consequently contribute to the driving force for the formation of the double helix itself. These π-stacking interactions lead to a closest approach of 4.694(4) Å for two silver centers from neighboring double helices, which is much closer than the silver–silver distances within one strand (11.003(9) Å). The channels between the infinite double helices are filled with the counterions PF_6^-, which are located on twofold crystallographic axes. The low calculated density for the crystal ($\rho_{calcd} = 1.102\ g\,cm^{-3}$) is significant of a loosely packed structure (probably due to the nonexistence of specific attractive interactions between the two strands), yet there are no cavities that are large enough to accommodate guest molecules. This is in agreement with the thermochemical investigations, which show no weight loss and no DSC signal (DSC = differential scanning calorimetry) for a sample up to 250 °C, and also with the fact that no solvent molecules have been detected in the crystallographic analysis.

In conclusion, the highly symmetrical solid-state structure reported here is another example for the versatility of the CHIRAGEN ligands in forming configurationally predetermined self-assembled structures. The relatively small variation of the bridging group leads from a highly fragile solid containing discrete molecular ions (**L2** as ligand) to a thermally remarkably stable crystalline material with linear double helices of nanometer-sized diameter (2.46 nm) and "infinite" length (**L3** as ligand). The absolute configuration of the natural product (−)-α-pinene used in ligand synthesis determines the chirality of the final structure. Thus, this class of ligands seems to be highly appropriate for applications in molecular and crystal engineering.[25, 26]

Experimental Section

1,5-Bis(bromomethyl)naphthalene (BBMN) was prepared by standard methods.

Ligand **L3** was synthesized according to published procedures.[27] Starting from (−)-5,6-pinene-bpy (1107 mg, 4.42 mmol) and BBMN (694 mg, 2.21 mmol), pure **L3** (826 mg, 1.27 mmol, yield 57%) was obtained after column chromatography (SiO_2; hexanes/Et_2O/NEt_3 16/4/1) and recrystallization from hot MeCN. The product was characterized by NMR spectroscopy (the ^1H and ^{13}C signals were fully assigned), FAB-MS, UV/Vis, and elemental analysis. All data confirm the structure of the enantiomerically pure ligand **L3**.

$\{[Ag(\mathbf{L3})]PF_6\}_{2\infty}$: Ligand **L3** (80.0 mg, 122.5 μmol) and $AgOSO_2CF_3$ (31.5 mg, 122.5 μmol) were placed in MeOH (5 mL). The mixture was stirred for 3 h, when all solids had dissolved, and than concentrated to about 2 mL. NH_4PF_6 (300 mg) in MeOH (2 mL) was then added dropwise. The precipitate obtained was filtered off and washed with MeOH and Et_2O. It was dissolved in a few milliliters of MeCN, and traces of unchanged ligand were filtered off. The solvent was removed, and the resulting yellow powder dried under high vacuum. Yield: 98%. ^1H NMR (500 MHz, 25 °C, $CDCl_3$, TMS): $\delta = 8.52$ (dm, 2H, H(1), $^3J_{1,2} = 4.9$ Hz), 8.04 (d, 2H, H(4), $^3J_{4,3} = 8.2$ Hz), 7.94 (d, 2H, H(7), $^3J_{7,8} = 8.1$ Hz), 7.73 (dd, br, 2H, H(3), $^3J_{3,4} \approx 7.5$ Hz, $^3J_{3,2} \approx 7.2$ Hz), 7.64–7.60 (m, 4H, H(8), H(22)), 7.29 (dd, 2H, H(2), $^3J_{2,1} = 5.0$ Hz, $^3J_{2,3} = 7.1$ Hz), 6.75–6.68 (m, 4H, H(20), H(21)), 4.22 (dm, 2H, H(18a), $^2J_{18a,18b} = 14.8$ Hz), 3.47 (dm, 2H, H(11), $^3J_{11,18b} = 11.5$ Hz), 3.23 (dd, 2H, H(18b), $^2J_{18b,18a} = 14.8$ Hz, $^3J_{11,18b} = 11.4$ Hz), 2.95 (dd, 2H, H(14), $^3J_{14,13a} = 5.6$ Hz, $^4J_{14,12} = 5.6$ Hz), 2.56 (ddd, 2H, H(13a), $^2J_{13a,13b} = 10.3$ Hz, $^3J_{13a,14} = 5.6$ Hz, $^3J_{13a,12} = 5.5$ Hz), 1.83 (dd, broad, 2H, H(12)), 1.54 (d, 2H, H(13b), $^2J_{13b,13a} = 10.0$ Hz), 1.27 (s, 6H, H(17)), 0.60 (s, 6H, H(16)); the ^{13}C NMR signals were fully assigned; elemental analysis calcd for $C_{46}H_{44}AgN_4F_6P$: C 61.00, H 4.90, N 6.19; found: C 60.57, H 4.89, N 6.51.

Crystal structure determination of $\{[\mathrm{Ag}(\mathbf{L3})](\mathrm{PF_6})\}_\infty$; $M_r = 905.7$ (for one unit of Ag(**L3**)$\mathrm{PF_6}$ in two asymmetric units); $\mu = 3.658\ \mathrm{mm^{-1}}$, $F(000) = 2784$, $\rho_\mathrm{calcd} = 1.102\ \mathrm{g\,cm^{-3}}$, hexagonal, space group $P6_222$ (no. 180), $Z = 6$, $a = 23.524(2)$, $c = 17.086(2)$ Å, $V = 8188(2)$ Å^3, from 25 reflections ($22 < 2\theta < 33°$); colorless prism, $0.26 \times 0.34 \times 0.40$ mm, mounted on a quartz fiber with RS3000 oil. Cell dimensions and intensities were measured at 200 K on a Stoe Stadi4 diffractometer with graphite-monochromated $\mathrm{Cu_{K\alpha}}$ radiation ($\lambda = 1.5418$ Å), ω-2θ scans, scan width $1.05° + 0.35\ \mathrm{tg}\,\theta$, scan speed $0.06°\ \mathrm{s^{-1}}$. Two reference reflections measured every 45 min showed no variation. $-23 < h < 23$, $0 < k < 23$, $0 < l < 16$, and all antireflections of these; of 11176 measured reflections, 2812 were unique and of these 1957 were observed ($|F_o| > 4\sigma > (F_o)$); $R_\mathrm{int} = 0.17$ for 8364 equivalent reflections. Data were corrected for Lorentz and polarization effects and for absorption[28] (min./max. absorption 2.121/3.641). The structure was solved by direct methods using MULTAN 8,[29] and the XTAL[30] system was used for all other calculations. The chirality of the structure was refined, and the Flack parameter[31] converged to $x = 0.13(6)$. Full-matrix least-squares refinement based on F using a weighting of $1/(\sigma^2(F_o) + 0.0001(F_o^2))$ gave final values of $R = 0.095$, $\omega R = 0.094$, and $S = 3.14(9)$ for 255 variables and 1957 contributing reflections. Hydrogen atoms were placed in calculated positions. All atoms of the ligand, except for the methylene bridge (C18) between the disordered naphthalene and the pinene moieties, were refined with soft restraints (99) on bond lengths, bond angles, and, for the aromatic fragments, torsional angles; max./min. residual electron density $+0.74/-0.49\ \mathrm{e\,Å^{-3}}$. The Ag and P atoms are located on special positions 6h and 6j, respectively, and the two positions of the disordered naphthalene unit are related by the symmetry operation $x, x-y-1, 4/3-z$ (around the C_2 axis in the special position 6i). A majority of the crystals showed significant disorders or cleavages, leading to poor diffraction, very large overall displacement parameters, and enlarged or split diffraction profiles. A refinement of the structure in the less symmetric space group $P6_2$ (loss of the twofold axes perpendicular to the c axis) leads to the observation of the same disorder and suggests the presence of C_2 (pseudo)merohedral twinning. The quality of the data does not allow a differentiation between a twinned crystal in $P6_2$ and a disordered structure in $P6_222$, but the overall results could be considered as identical. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-119096. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+49)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Received: April 30, 1999 [Z13348IE]
German version: *Angew. Chem.* **1999**, *111*, 3129–3133

Keywords: bipyridine ligands · chirality · helical structures · silver · supramolecular chemistry

[1] C. Piguet, G. Bernardinelli, G. Hopfgartner, *Chem. Rev.* **1997**, *97*, 2005–2062.
[2] C. Kaes, M. W. Hosseini, C. E. F. Rickard, B. W. Skelton, A. H. White, *Angew. Chem.* **1998**, *110*, 970–973; *Angew. Chem. Int. Ed.* **1998**, *37*, 920–922.
[3] H.-P. Wu, C. Janiak, L. Uehlin, P. Klüfers, P. Mayer, *Chem. Commun.* **1998**, 2637–2638.
[4] O. J. Gelling, F. van Bolhuis, B. L. Feringa, *Chem. Commun.* **1991**, 917–919.
[5] K. Biradha, C. Seward, M. J. Zaworotko, *Angew. Chem.* **1999**, *111*, 584–587; *Angew. Chem. Int. Ed.* **1999**, *38*, 492–495.
[6] S. R. Batten, B. F. Hoskins, R. Robson, *Angew. Chem.* **1997**, *109*, 652–653; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 636–637.
[7] M. A. Withersby, A. J. Blake, N. R. Champness, P. Hubberstey, W.-S. Li, M. Schröder, *Angew. Chem.* **1997**, *109*, 2421–2423; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2327–2329.
[8] K. A. Hirsch, S. R. Wilson, J. S. Moore, *Chem. Commun.* **1998**, 13–14.
[9] N. Masciocchi, G. A. Ardizzoia, G. LaMonica, A. Maspero, A. Sironi, *Angew. Chem.* **1998**, *110*, 3561–3564; *Angew. Chem. Int. Ed.* **1998**, *37*, 3366–3369.
[10] D. A. Evans, K. A. Woerpel, M. J. Scott, *Angew. Chem.* **1992**, *104*, 439–441; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 430–432.
[11] R. W. Saalfrank, M. Decker, F. Hampel, K. Peters, H. G. von Schnering, *Chem. Ber.* **1997**, *130*, 1309–1313.
[12] P. K. Bowyer, K. A. Porter, A. D. Rae, A. C. Willis, S. B. Wild, *Chem. Commun.* **1998**, 1153–1154.
[13] J. F. Modder, G. van Koten, K. Vrieze, A. L. Spek, *Angew. Chem.* **1989**, *101*, 1723–1725; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1698–1700.
[14] P. Hayoz, A. von Zelewsky, H. Stoeckli-Evans, *J. Am. Chem. Soc.* **1993**, *115*, 5111–5114.
[15] H. Muerner, A. von Zelewsky, G. Hopfgartner, *Inorg. Chim. Acta* **1998**, *271*, 36–39.
[16] J.-M. Lehn, *Supramolecular Chemistry—Concepts and Perspectives*, VCH, Weinheim, **1995**.
[17] M. Albrecht, *Chem. Soc. Rev.* **1998**, *27*, 281–287.
[18] D. L. Caulder, K. N. Raymond, *Angew. Chem.* **1997**, *109*, 1508–1510; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1439–1442.
[19] P. Baret, D. Gaude, G. Gellon, J.-L. Pierre, *New J. Chem.* **1997**, *21* , 1255–1257.
[20] O. Mamula, A. von Zelewsky, G. Bernadinelli, *Angew. Chem.* **1998**, *110*, 301–305; *Angew. Chem. Int. Ed.* **1998**, *37*, 289–293.
[21] P. Hayoz, A. von Zelewsky, *Tetrahedron Lett.* **1992**, *33*, 5165–5168.
[22] H. Muerner, A. von Zelewsky, H. Stoeckli-Evans, *Inorg. Chem.* **1996**, *35*, 3931–3935.
[23] A. von Zelewsky, *Stereochemistry of Coordination Compounds*, Wiley, Chichester, **1996**.
[24] G. Baum, E. C. Constable, D. Fenske, T. Kulke, *Chem. Commun.* **1997**, 2043–2044.
[25] M. J. Zaworotko, *Angew. Chem.* **1998**, *110*, 1269–1271; *Angew. Chem. Int. Ed.* **1998**, *37*, 1211–1212.
[26] A. J. Blake, N. R. Champness, P. Hubberstey, W.-S. Li, M. A. Withersby, M. Schröder, *Coord. Chem. Rev.* **1999**, *183*, 117–138.
[27] H. Muerner, P. Belser, A. von Zelewsky, *J. Am. Chem. Soc.* **1996**, *118*, 7989–7994.
[28] E. Blanc, D. Schwarzenbach, H. D. Flack, *J. Appl. Crystallogr.* **1991**, *24*, 1035–1041.
[29] P. Main, S. J. Fiske, S. E. Hull, L. Lessinger, G. Germain, J.-P. Declercq, M. M. Woolfson, *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-Ray Diffraction Data*, Universities of York, England, and Louvain-la-Neuve, Belgium, **1987**.
[30] *XTAL 3.2 User's Manual* (Eds.: S. R. Hall, H. D. Flack, J. M. Stewart), Universities of Western Australia and Maryland, **1992**.
[31] H. D. Flack, *Acta Crystallogr. Sect. A* **1983**, 39, 879–881.