Helical Structures

A Dinuclear, Triple-Stranded Helicate with a Diamide-Bridged Catechol/Benzenedithiol Ligand**

F. Ekkehardt Hahn,* Christian Schulze Isfort, and Tania Pape

The spontaneous self-organization of coordination compounds has been studied intensively over the last few years.^[1] One area of particular interest are the triple-stranded helicates with catecholato donor groups.^[2] Much less is known about helicates with thiolato donor groups, only bis(benzenedithiol) ligands^[3] and their dinuclear nickel complexes have been reported.^[4] Herein we present the synthesis of the first catechol/benzenedithiol (O–O/S–S) ligand H₄-1 and the molecular structure of the triple-stranded Λ , Λ -helicate Na(PNP)₃[Ti₂(1)₃] (PNP⁺=bis(triphenylphosphoranylidene)ammonium).



Triple-stranded helicates containing donor atoms from the second period (O, N) contain two metal centers coordinated in an octahedral fashion. However, under certain conditions, macrobicyclic tris(catecholato) ligands can enforce a trigonal-prismatic coordination environment in mononuclear complexes.^[5] In contrast, tris(benzenedithiolato) complexes can be pseudo-octahedral (e.g. $[W^V(bdt)_3]^-$, bdt = benzene-1,2-dithiolate)^[6] or trigonal-prismatic (e.g. $[W^{VI}(bdt)_3])$,^[7] depending on the oxidation state of the coordinated metal center. The connection of a catechol and an *o*-benzenedithiol donor group in the same ligand and the preparation of triple-stranded dinuclear complexes with such ligands was of interest to us. A parallel orientation of the ligands would

Angew. Chem. Int. Ed. 2004, 43, 4807–4810

DOI: 10.1002/anie.200460188

 ^[*] Prof. Dr. F. E. Hahn, Dipl.-Chem. C. Schulze Isfort, T. Pape Institut für Anorganische und Analytische Chemie Westfälische Wilhelms-Universität Münster Wilhelm-Klemm-Strasse 8, 48149 Münster (Germany) Fax: (+49) 251-833-3293 E-mail: fehahn@uni-muenster.de

^[**] Financial support for this work was provided by the Deutsche Forschungsgemeinschaft (GRK 673). We thank Dr. Klaus Bergander for recording of the NMR spectra.

Communications

allow the coordination geometry of the *o*-benzenedithiolatocoordinated metal center and thus the helicity of the complex to be switched by varying the oxidation state of this $\{MS_6\}$ metal center.

The preparation of ligand H_4 -1 starts from 2,3-di(isopropylsulfanyl) benzoic acid (2, Scheme 1).^[8] This acid was converted into the acid chloride, followed by the reaction with





Figure 1. ¹H NMR spectra (in $[D_7]DMF$, *=DMF resonances) of H₄-1 (top) and Na(PNP)₃[Ti₂(1)₃] (bottom).

Scheme 1. Synthesis of ligand H₄-4.

the single *tert*-butoxycarbonyl (Boc) protected diamine^[9] and subsequent removal of the Boc protecting group. The primary amine **4** reacts with 2,3-di(benzyloxy)benzoic acid chloride^[10] to give the ligand precursor **5**. All the protecting groups were simultaneously removed with Na/naphthalene in THF^[4,8] After protonation with H₂O/HCl ligand H₄-**1** was obtained in about 59% yield (relative to **2**) as a light yellow solid.

The ¹H NMR spectrum of H₄-1 (Figure 1, top) shows two resonance signals for the N–H protons (H_a, t, 9.10 ppm and H_e, s, 8.25 ppm), which based on their multiplicity were assigned to the catechol- and *o*-benzenedithiol-bound amide groups. In addition, six well resolved resonance signals were observed for the protons of the aromatic rings.

Only a few helical complexes with asymmetrical donor groups derived from functionalized benzene are known.^[11] Albrecht et al. reported a tetradentate, directional ligand containing an aminophenol and a catechol unit.^[12] In addition, directional ligands are known which have identical donor groups but an asymmetric spacer between them.^[13] The orientation of directional ligands in dinuclear complexes (parallel or antiparallel^[14]) is of special interest since not only complexes with stereoisomeric metal centers (Λ , Δ) but also as regioisomeric complexes can form.

The directional catechol/aminophenol ligand^[12] reacts with Ga^{III} or Ti^{IV} to give a dinuclear complex with parallel orientation of the ligands, while the reaction with a mixture of Ga^{III} and Ti^{IV} (1:1) gives a dinuclear complex with an antiparallel orientation of the ligands. The reaction of a directional phenylalanine-bridged di(catechol) ligand with Ti^{IV} gives a mixture of products containing a total of seven double-stranded dinuclear stereoisomeric (Λ , Δ) and regioisomeric (parallel and antiparallel) complexes.^[13b,c]

Ligand H₄-1 shows directionality based on the two different donor groups (O-O/S-S) and on the asymmetric CMe₂CH₂ spacer between them. The reaction of three equivalents of H_4 -1 with two equivalents of $[TiO(acac)_2]$ in the presence of Na₂CO₃ in methanol gives a red-brownish complex which dissolves well in methanol. Addition of PNPCl and diffusion of diethyl ether into a saturated methanol solution of the product gives the dinuclear complex $Na(PNP)_{3}[Ti_{2}[(1)_{3}]]$ as red-brown crystals. The NMR spectra of $Na(PNP)_3[Ti_2[(1)_3]$ show a surprisingly small number of signals (Figure 1, bottom). The aromatic protons of the benzenedithiolato and the catecholato groups are detected as one triplet ($\delta = 6.65 (H_{\sigma})$ and $6.32 (H_{c}) ppm$) and two doublets $(\delta = 7.08 (H_f), 6.98 (H_h) \text{ ppm}, \text{ and } \delta = 7.15 (H_h),$ $6.21 (H_d) ppm$) for each ring. This result demonstrates that the three ligands are oriented in an identical, parallel manner.

The downfield shift of the triplet H_a for the N–H proton of the catechol-bound amide ($\Delta \delta = 0.70$ ppm, Figure 1) is remarkable. This shift indicates the formation of a planar six-membered ring and a strong N–H…O hydrogen bond between the amide proton H_a and the *o*-catecholato oxygen atom (Figure 1). This type of hydrogen bond has been observed for helicates with amide-bridged catecholato donor groups^[15] and for other catechoylamide complexes and has often been shown to be structure determining.^[5,16] The chemical shift for the amide protons next to the benzenedithiolato group changes only marginally upon complex formation indicating the presence of no or only very weak $N-H\cdots$ S hydrogen bonds.

All the NMR data indicate the presence of the parallel regioisomer and only one pair of enantiomers in solution. However, the NMR data do not allow the determination which pair of enantiomers $\Lambda, \Delta/\Delta, \Lambda$ or $\Lambda, \Lambda/\Delta, \Delta$ is present.^[17] Slow diffusion of diethyl ether into a methanol solution of the complex gave single crystals of Na(PNP)₃[Ti₂(**1**)₃]·CH₃OH·H₂O·Et₂O suitable for an X-ray diffraction analysis.^[18]

The structure analysis revealed, that indeed the triplestranded helicate $[Ti_2(1)_3]^{4-}$ had formed (Figure 2). The three ligands are oriented in a parallel manner, as expected. One



Figure 2. Molecular structure of the tetraanion $[Ti_2(1)_3]^{4-}$ in a sideview (left) and along the Ti–Ti axis (right). Selected bond lengths [Å] and angles [°]: Ti-S 2.381(3)–2.436(3), Ti-O 1.904(6)–2.010(6), in one donor group S-Ti-S 81.64(9)–81.94(9), O-Ti-O 78.9(2)–80.9(3); the Ti–S or Ti–O bonds to the donor atoms in 2-position at the aromatic ring are always slightly longer than the bonds to donor atoms at the 3-positions at the aromatic rings.

titanium atom is coordinated in a distorted octahedral fashion by the six oxygen atoms of three catechoylamide groups. The Ti–O bond lengths fall in the range reported for other Ti^{IV} tris(catecholato) complexes.^[19] The second titanium atom is surrounded by six sulfur atoms from three benzenedithiolato groups in a strongly distorted octahedral fashion. The Ti–S bond lengths vary only slightly and are comparable to bond lengths reported for tris(*o*-benzenedtihiolato) Ti^{IV} complexes.^[20] The helical twist between two titanium centers measures 65.6°.

The unit cell contains one $[Ti_2(1)_3]^{4-}$ ion, three PNP cations, one sodium cation, and one molecule each of water, methanol, and (disordered) diethyl ether. The PNP cations maintain no contacts to the $[Ti_2(1)_3]^{4-}$ ion whereas the Na⁺ ion acts as a bridge between the $[Ti_2(1)_3]^{4-}$ ions and this leads to indefinite chains in the crystal lattice. The Na⁺ ion completes its coordination sphere by the coordination of one molecule each of methanol and water (Figure 3).

Both metal centers in $[Ti_2(1)_3]^{4-}$ in the crystal under investigation assume the same configuration, namely Λ . Since the complex crystallized in the acentric space group P1 and the CD spectrum of the reaction product shows no Cotton effect, crystals of the Δ , Δ enantiomer must also have formed.



Figure 3. Section of the crystal structure of Na(PNP)₃[Ti₂(1)₃]-CH₃OH-H₂O-Et₂O, for clarity the PNP cations and the diethyl ether molecule are not shown.

A similar spontaneous resolution of stereoisomers upon crystallization was first described for triple-stranded Ni^{II} complexes with oligobipyridine ligands.^[21] Since the NMR spectra show the formation of only one pair of enantiomers, the formation of helicates of the Λ , Δ and Δ , Λ type, can be excluded.

Currently we can only speculate about the driving force for the formation of the parallel triple-stranded helical complex $[Ti_2(1)_3]^{4-}$. With the related directional ligand containing catechol/aminophenol donor groups reported by Albrecht et al. only the antiparallel ligand orientation was observed for homobinuclear complexes,^[12] which leads to the smallest possible charge separation in the complex.^[22] Ligand H_4-1 was expected to behave similarly. However, H_4-1 is directional with respect the donor groups and with respect the spacer between them. Upon formation of the triple-stranded helicate a distorted ${TiS_6}$ octahedron and a smaller ${TiO_6}$ octahedron are obtained. It is reasonable to expect, that the sterically more demanding (CMe₂) part of the spacer CMe₂CH₂ is oriented towards the larger {TiS₆} octahedron thereby causing the parallel orientation of the ligands. This orientation allows the formation of three stable N-H-O hydrogen bridges (length H…O 1.824-2.039 Å) and of three almost planar N-H-O-C-C-C(O) rings within the catechoylamide groups at the ${TiO_6}$ octahedron (Figure 2). Similarly strong N-H...S hydrogen bonds were not observed (distance H...S 2.444–2.701 Å) and the benzenedithiolato groups are not coplanar with their amide groups. We therefore propose a structure-determining influence of the sterically unsymmetrical CMe₂CH₂ spacer for the formation of the parallel regioisomer. This postulate is corroborated by the observation that a ligand isomeric to H₄-1 with a symmetrical CH2CH2 spacer forms dinuclear TiIV complexes of the known structural type^[13b,c] $[Ti_2(L)_2(OMe)_2]^{2-}$ with an antiparallel orientation of the ligands.^[23]

The structure-determining influence of the unsymmetrical spacer in ligand H₄-1 will be more prominent in the synthesis of heterobimetallic triple-stranded helicates, where the preferences of the donor groups for different metal ions will be a factor. We expect that the reaction of H₄-1 with a mixture (1:1) of Ti^{IV} and W^V will yield a triple-stranded helicate with parallel ligand orientation containing {TiO₆} and {WS₆} octahedra. Such investigations are currently underway as well as attempts to remove the helicity in such heterobimetallic complexes by oxidation of the {W^VS₆} octahedron to give the trigonal-prismatic {W^{VI}S₆} coordination polyhedron.

Communications

Experimental Section

All synthetic manipulations were carried out under argon in Schlenk flasks. Solvents were dried, distilled, and stored under argon. Correct elemental analyses (C, H, N, S) were obtained for all compounds.

H₄-1: Yield 59% relative to 2. ¹H NMR (300 MHz, [D₇]DMF, assignment of signals given in Figure 1): δ = 10.44 (s, br, 2 H, OH), 9.10 (t, 1 H, H_a), 8.25 (s, 1 H, H_c), 7.60 (d, ³J = 7.8 Hz, 1 H, H_b), 7.49 (d, ³J = 8.2 Hz, 1 H, H_f), 7.35 (d, ³J = 7.8 Hz, 1 H, H_d), 7.12 (t, ³J = 7.8 Hz, 1 H, H_c), 7.05 (d, ³J = 8.2 Hz, 1 H, H_b), 6.78 (t, ³J = 8.2 Hz, 1 H, H_g), 5.59 (s, br, 2 H, SH), 3.82 (d, 2 H, CH₂), 1.56 ppm (s, 6 H, CH₃); ¹³C NMR (75 MHz, [D₇]DMF): δ = 171.40 (C=O), 169.93 (C=O), 150.58, 147.51, 137.56, 133.98, 131.59, 130.63, 126.09, 125.63, 119.55, 118.83, 118.03, 116.07 (C_{Ar}), 56.12 (CH₂C(CH₃)₂), 48.39 (CH₂C(CH₃)₂), 24.87 ppm (CH₂C(CH₃)₂); MALDI-MS (positive ions): *m*/z (%): 393 (100) [M+H]⁺.

 $Na(PNP)_3[Ti_2[(1)_3]]$ was prepared by stirring ligand H₄-1 (104 mg, 0.26 mmol), [TiO(acac)₂] (45 mg, 0.17 mmol), and Na₂CO₃ (18 mg, 0.17 mol) in methanol at room temperature for 72 h. Subsequently, the solvent was removed and the solid obtained was redissolved in methanol. After addition of bis(triphenylphosphoranylidene)ammonium chloride (PNPCl) (98 mg, 0.17 mmol) of the reaction mixture was filtered. Slow diffusion of diethyl ether into the filtrate yielded 60 mg (0.06 mmol, 23%) of red-brown crystals of $(PNP)_3Na[Ti_2(1)_3]$. CH₃OH·H₂O·Et₂O. ¹H NMR (500 MHz, [D₇]DMF, solvent-free compound, assignment of signals given in Figure 1): $\delta = 9.80$ (t, br, 3H, H_a), 8.14 (s, br, 3H, H_e), 7.80–7.60 (m, 90H, H_{Ar} , PNP), 7.15 (d, ${}^{3}J =$ 7.8 Hz, 3 H, H_b), 7.08 (d, ${}^{3}J = 7.5$ Hz, 3 H, H_f), 6.98 (d, ${}^{3}J = 7.5$ Hz, 3 H, $H_{\rm h}$), 6.65 (t, ${}^{3}J = 7.5$ Hz, 3H, $H_{\rm g}$), 6.32 (t, ${}^{3}J = 7.8$ Hz, 3H, $H_{\rm c}$), 6.21 (d, ${}^{3}J = 7.8 \text{ Hz}, 3 \text{ H}, \text{H}_{d}$, 4.81 (s, br, 6 H, CH₂), 1.38 ppm (s, br, 18 H, CH₃); $^{13}\mathrm{C}\,\mathrm{NMR}$ (125 MHz, [D7]DMF, solvent-free compound): $\delta\!=\!169.41$ (C=O), 167.44 (C=O), 161.81, 161.40, 155.24, 152.05, 135.63 (C_{Ar}, 1), 134.34, 133.08, 133.03, 132.98, 130.24, 130.19, 130.11, 128.48, 128.46, 127.62 (C_{Ar} , PNP), 128.22, 123.03, 121.85, 117.86, 116.47, 115.56, 112.29 (C_{Ar}, 1), 54.98 (CH₂C(CH₃)₂), 49.46 (CH₂C(CH₃)₂), 25.16 ppm (br, CH₂C(CH₃)₂); MS (ESI, negative ions): m/z (%): 630.7 (100) $[Ti_2(1)_3 + 2H]^{2-}$.

Received: April 1, 2004

Keywords: chirality · helical structures · O,S ligands · supramolecular chemistry · titanium

- a) J. M. Lehn, Supramolecular Chemistry: Concepts and Perspectives, VCH, Weinheim, 1995, Chapter 9; b) C. Piguet, G. Bernardinelli, G. Hopfgarten, Chem. Rev. 1997, 97, 2005–2062;
 c) C. A. Schalley, A. Lützen, M. Albrecht, Chem. Eur. J. 2004, 10, 1072–1080.
- [2] M. Albrecht, Chem. Soc. Rev. 1998, 27, 281-287.
- [3] a) F. E. Hahn, W. W. Seidel, Angew. Chem. 1995, 107, 2938–2941; Angew. Chem. Int. Ed. Engl. 1995, 34, 2700–2703;
 b) W. W. Seidel, F. E. Hahn, T. Lügger, Inorg. Chem. 1998, 37, 6587–6596;
 c) W. W. Seidel, F. E. Hahn, J. Chem. Soc. Dalton Trans. 1999, 2237–2241.
- [4] H. V. Huynh, C. Schulze Isfort, W. W. Seidel, T. Lügger, R. Fröhlich, O. Kataeva, F. E. Hahn, *Chem. Eur. J.* 2002, 8, 1327– 1335.
- [5] a) T. J. McMurry, M. W. Hosseini, T. M. Garrett, F. E. Hahn, Z. E. Reyes, K. N. Raymond, *J. Am. Chem. Soc.* **1987**, *109*, 7196 – 7198; b) T. M. Garrett, T. J. McMurry, M. W. Hossaini, Z. E. Reyes, F. E. Hahn, K. N. Raymond, *J. Am. Chem. Soc.* **1991**, *113*, 2965–2977.
- [6] T. E. Burrow, R. H. Moras, A. Hills, D. L. Hughes, R. L. Richards, Acta Crystallogr. 1993, C49, 1591–1594.

- [7] H. V. Huynh, T. Lügger, F. E. Hahn, Eur. J. Inorg. Chem. 2002, 3007–3009.
- [8] H. V. Huynh, W. W. Seidel, T. Lügger, R. Fröhlich, B. Wibbeling, F. E. Hahn, Z. Naturforsch. B 2002, 57, 1401–1408.
- [9] J.-F. Pons, J.-L. Fauchère, F. Lamaty, A. Molla, R. Lazaro, *Eur. J. Org. Chem.* **1998**, 853–859.
- [10] W. H. Rastetter, T. J. Erickson, M. C. Venuti, J. Org. Chem. 1981, 46, 3579–3590.
- [11] M. Albrecht, Chem. Rev. 2001, 101, 3457-3497.
- [12] M. Albrecht, R. Fröhlich, J. Am. Chem. Soc. 1997, 119, 1659– 1661.
- [13] a) M. J. Hannon, S. Bunce, A. J. Clarke, N. W. Alcock, Angew. Chem. 1999, 111, 1353-1355; Angew. Chem. Int. Ed. 1999, 38, 1277-1278; b) M. Albrecht, M. Napp, M. Schneider, P. Weis, R. Fröhlich, J. Chem. Soc. Chem. Commun. 2001, 409-410; c) M. Albrecht, M. Napp, M. Schneider, P. Weis, R. Fröhlich, Chem. Eur. J. 2001, 7, 3966-3975.
- [14] E. C. Constable, F. Heirtzler, M. Neuburger, Z. Zehnder, J. Am. Chem. Soc. 1997, 119, 5606-5617.
- [15] a) E. J. Enemark, T. D. P. Stack, Angew. Chem. 1995, 107, 1082–1084; Angew. Chem. Int. Ed. Engl. 1995, 34, 996–998; b) B. Kersting, M. Meyer, R. E. Powers, K. N. Raymond, J. Am. Chem. Soc. 1996, 118, 7221–7222; c) C. Brückner, R. E. Powers, K. N. Raymond, Angew. Chem. 1998, 110, 1937–1940; Angew. Chem. Int. Ed. 1998, 37, 1837–1839.
- [16] a) T. D. P. Stack, T. B. Karpishin, K. N. Raymond, J. Am. Chem. Soc. 1992, 114, 1512-1514; b) T. B. Karpishin, T. D. P. Stack, K. N. Raymond, J. Am. Chem. Soc. 1993, 115, 182-192; c) T. B. Karpishin, T. D. P. Stack, K. N. Raymond, J. Am. Chem. Soc. 1993, 115, 6115-6125; d) T. B. Karpishin, T. M. Dewey, K. N. Raymond, J. Am. Chem. Soc. 1993, 115, 1842-1851.
- [17] The term *meso*-helicate, which is often used in the literature, is not applicable here owing to the two different stereocenters {TiS₆} and {TiO₆} present.
- [18] X-ray diffraction study: Crystals of $Na(PNP)_3[Ti_2(1)_3] \cdot CH_3OH \cdot$ H₂O·Et₂O were obtained by diffusion of diethyl ether into a methanol solution of Na(PNP)₃[Ti₂(1)₃], C₁₆₇H₁₅₄N₉NaO₁₅P₆- S_6Ti_2 , $M_r = 3023.96$, red crystal, $0.10 \times 0.07 \times 0.04 \text{ mm}^3$, P1, a =13.594(3), b = 17.190(4), c = 18.900(4) Å, a = 66.722(4), $\beta =$ 79.188(4), $\gamma = 82.523(4)^{\circ}$, $V = 3977.6(15) \text{ Å}^3$, $ho_{
 m calcd} =$ 1.262 g cm⁻³, $\mu = 0.306$ mm⁻¹, semi-empirical absorption correction (0.9701 $\leq T \leq$ 0.9879), ω - and ϕ -scans, 24856 measured intensities $(2.4^{\circ} \le 2\theta \le 45.2^{\circ})$, 20191 independent $(R_{int} = 0.0583)$ and 13406 observed $(I \ge 2\sigma(I))$ intensities, $\lambda = 0.71073$ Å, T =123(2) K, Z=1, R=0.0771, $wR^2 = 0.1645$ (refinement against $\langle F^2 \rangle$ with H atoms on calculated positions). The diethyl ether molecule in the unit cell is disordered, positional parameters for the hydrogen atoms of the water and methanol OH protons were not determined. CCDC 234748 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).
- [19] a) B. A. Borgias, S. R. Cooper, Y. B. Koh, K. N. Raymond, *Inorg. Chem.* **1984**, *23*, 1009–1016; b) F. E. Hahn, S. Rupprecht, K. H. Moock, *J. Chem. Soc. Chem. Commun.* **1991**, 224–225.
- [20] M. Könemann, W. Stüer, K. Kirschbaum, D. M. Giolando, *Polyhedron* **1994**, *13*, 1415–1425.
- [21] R. Krämer, J.-M. Lehn, A. De Cian, J. Fischer, Angew. Chem. 1993, 105, 764–767; Angew. Chem. Int. Ed. Engl. 1993, 32, 703– 706.
- [22] R. Krämer, J. M. Lehn, A. Marquis-Rigault, Proc. Natl. Acad. Sci. USA 1993, 90, 5394–5398.
- [23] F. E. Hahn, C. Schulze Isfort, R. Fröhlich, unpublished results.