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3,3′-{(1*E*,2*E*)-Hydrazine-1,2-diylidenedi[(*E*)methylylidene]}dibenzene-1,2-diol (BCAz-H_4): an easy to prepare but very useful building block for the self-assembly of triple-stranded helicates; the X-ray crystal structure of $Na_4[(BCAz)_3Ti_2]\cdot 7$ dmf$\cdot H_2O$

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Abstract

The azine bridged dicatechol ligand **BCAz**-H_4 forms triple-stranded dinuclear helicates with titanium(IV) ions in the presence of alkali metal carbonate. The X-ray structure of $Na_4[(\mathbf{BCAz})_3Ti_2]\cdot 7$ dmf$\cdot H_2O$ shows that countercations can be encapsulated in the interior of the helicate binding not only to internal oxygen atoms of the catecholates but also to nitrogen atoms of the spacer.

Keywords: Crystal structure; Dicatechol; Helicate

1. Introduction

In 1987 Lehn introduced the term helicate for linear oligonuclear coordination compounds in which two or more linear organic ligands wrap around two or more metal centers [1]. Simple mixing of the ligands with appropriate metal ions leads in a self-assembly process to double- or triple-stranded helicates (and in some special cases even to quadruple- [2] or hexa-stranded complexes [3]). Starting in 1987 the chemistry of helicates became a more and more intensely studied and rapidly developing topic of metallosupramolecular chemistry and many different aspects, like stereochemistry, regiochemistry, or control mechanisms of the self-assembly of the oligonuclear complexes were studied [4].

In most investigations nitrogen donor ligands were used to form double- as well as triple-stranded helicates [5]. This is to some extend surprising, because a first triple-stranded helicate formed from an oxygen donor ligand was already described in 1985 by Raymond [6] and the siderophore Rhodoturulic acid is a natural product which forms a dinuclear triple-stranded helicate with iron(III) ions in nature [7].

The outcome of a self-assembly experiment—to obtain helicates—highly depends not only on the nature of the metal and of the ligand but also on the kind of spacer, which is introduced to connect the metal binding sites [8]. In addition secondary effects like stabilizing π–π interactions [1] or templating [9] may play an important role. A simple (and inexpensive) way to obtain ligands for helicate formation was described by Hannon, who prepared imines of appropriate pyridinocarbaldehydes and diamines [10]. Ziessel used related imines to obtain double-stranded helicates which show mesomorphic behaviour [11].

In this paper we use Hannons method [8] for the preparation of a dicatechol ligand [12] and obtain in a one step procedure the ligand **BCAz**-H_4 (biscatechol azine = 3,3′-{(1*E*,2*E*)-hydrazine-1,2-diylidenedi[(*E*)methylylidene]}dibenzene-1,2-diol) which forms dinuclear triple-stranded helicates with titanium(IV)

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ions in the presence of alkali metal carbonate as base. In the solid state the tetraanionic triple-stranded helicate encapsulates countercations which bind to internal catechol oxygen atoms, azine nitrogens and solvent molecules.

2. Experimental

2.1. Materials

Solvents were purified by standard methods. 2,3-dihydroxybenzaldehyde was purchased from Aldrich, $(acac)_2TiO$ from Merck-Schuchardt.

2.2. Spectroscopic methods

^1H NMR and ^{13}C NMR spectra were recorded on a Bruker DRX 500 spectrometer using DEPT techniques for the assignment of the multiplicity of carbon atoms. FT-IR spectra were recorded by diffuse reflection (KBr) on a Bruker IFS spectrometer. Mass spectra (EI, 70 eV; pos. FAB with 3-NBA as matrix) were taken on a Finnigan MAT 90 mass spectrometer. UV–Vis spectra were obtained with a Perkin Elmer Lambda2 Spectrometer. Elemental analyses were obtained with a Heraeus CHN-O-Rapid analyzer. Melting points: Büchi B-540 (uncorrected).

The data set for the X-ray structure analysis was collected with a Nonius Kappa CCD diffractometer. Programs used: data collection COLLECT (Nonius B.V., 1998), data reduction Denzo-SMN, absorption correction SORTAV, structure solution SHELXS-97, structure refinement SHELXL-97 (G.M. Sheldrick, Universität Göttingen, 1997) [13].

2.3. Preparation of 3,3′-{(1E,2E)-hydrazine-1,2-diylidenedi[(E)methylylidene]}dibenzene-1,2-diol (BCAz-H_4)

2,3-Dihydroxybenzaldehyde (1.38 g, 10.0 mmol), *p*-toluenesulfonic acid (10 mg) and hydrazine hydrate (300 mg, 6.00 mmol) were dissolved in toluene (34 ml). After heating overnight with continuous destillative removal of water and cooling to r.t., the precipitated product is filtered off to obtain 1.29 g (95%) of an orange solid; mp 257–259 °C (dec.). *Anal*. Calc. for $C_{14}H_{12}N_2O_4$ (272.26): C, 61.76; H, 4.44; N, 10.29; Found: C, 61.46; H, 4.30; N, 10.28. ^1H NMR ($CDCl_3$): $\delta = 10.85$ (s, br, 2H), 9.39 (s, br, 2H), 8.95 (s, 2H), 7.11 (dd, $J = 7.9$, 1.3 Hz, 2H), 6.94 (dd, $J = 7.8$, 1.3 Hz, 2H), 6.77 (t, $J = 7.8$ Hz, 2H). ^{13}C NMR ($CDCl_3$): $\delta = 163.9$ (CH), 147.9 (C), 146.1 (C), 121.8 (CH), 119.9 (CH), 119.3 (CH), 118.9 (C). UV–Vis (MeOH): $\lambda_{max} = 324$ nm. IR (KBr): 3416, 2950, 1942, 1914, 1853, 1626, 1466, 1270 cm^{-1}. MS (EI, 70 eV) $m/z = 272$ (100%) [M^+], 255 (9%), 137 (44%), 122 (1%), 109 (6%), 108 (16%). HRMS m/z: [M^+] Calc. for $C_{14}H_{12}N_2O_4$, 272.0797; Found, 272.0791.

2.4. Preparation of triple-stranded helicates $M_4[(BCAz)_3Ti_2]$ (M = Li, Na, K)

2.4.1. General procedure

The ligand **BCAz**-H_4 (100 mg, 0.37 mmol), $TiO(acac)_2$ (64 mg, 0.25 mmol), and 0.25 mmol of the alkali metal carbonate are dissolved in 100 ml of methanol and the solution is stirred overnight. After evaporation of the solvent, the orange–red residue is purified by filtration over Sephadex LH20.

2.4.2. Characterization of $Li_4[(BCAz)_3Ti_2]$

Yield: 153 mg (quant.); red solid. *Anal*. Calc. for $C_{42}H_{24}Li_4N_6O_{12}Ti_2 \cdot 5H_2O \cdot 3MeOH$ (1114.38): C, 48.50; H, 4.16; N, 7.54; Found: C, 48.76; H, 4.45; N, 7.26. ^1H NMR (MeOH-d_4): $\delta = 8.59$ (s, 2H), 6.97 (d, $J = 7.8$ Hz, 2H), 6.52 (t, $J = 7.8$ Hz, 2H), 6.45 (d, $J = 7.6$ Hz, 2H). ^{13}C NMR (MeOH-d_4): $\delta = 160.8$ (C), 158.9 (C), 155.4 (CH), 117.6 (CH), 116.6 (C), 116.1 (CH), 113.0 (CH). UV–Vis (MeOH): $\lambda_{max} = 199$, 311 nm. IR (KBr): 3346, 3058, 1622, 1555 cm^{-1}. MS (+FAB, 3-NBA) $m/z = 929$ [HM^+].

2.4.3. Spectroscopic characterization of $Na_4[(BCAz)_3Ti_2]$

Yield: 122 mg (93%); orange–red solid. *Anal*. Calc. for $C_{42}H_{24}N_6Na_4O_{12}Ti_2 \cdot 5H_2O$ (1082.46): C, 46.60; H, 3.17; N, 7.76; Found: C, 47.25; H, 4.03; N, 7.88. ^1H NMR (MeOH-d_4): $\delta = 8.55$ (s, 2H), 7.05 (d, $J = 8.0$ Hz, 2H), 6.54 (t, $J = 7.8$ Hz, 2H), 6.46 (d, $J = 7.6$ Hz, 2H). ^{13}C NMR (MeOH-d_4): $\delta = 160.7$ (C), 158.6 (C), 152.5 (CH), 117.6 (CH), 116.8 (C), 115.4 (CH), 113.0 (CH). UV–Vis (MeOH): $\lambda_{max} = 199$, 224, 305 nm. IR (KBr): 3617, 3293, 3057, 1618, 1593, 1557 cm^{-1}. MS (+FAB, 3-NBA) $m/z = 993$ [HM^+], 1016 [NaM^+].

2.4.4. Spectroscopic characterization of $K_4[(BCAz)_3Ti_2]$

Yield: 132 mg (97%); brown solid. *Anal*. Calc. for $C_{42}H_{24}K_4N_6O_{12}Ti_2 \cdot 3H_2O$ (1110.86): C, 45.41; H, 2.72; N, 7.56; Found: C, 45.50; H, 2.95; N, 7.25. ^1H NMR (MeOH-d_4): $\delta = 8.53$ (s, 2H), 7.00 (dd, $J = 8.0$, 1.3 Hz, 2H), 6.51 (t, $J = 7.8$ Hz, 2H), 6.44 (dd, $J = 7.6$, 1.5 Hz, 2H). ^{13}C NMR (MeOH-d_4): $\delta = 160.6$ (C), 159.0 (C), 153.4 (CH), 117.6 (CH), 116.9 (C), 115.6 (CH), 112.8 (CH). UV–Vis (MeOH): $\lambda_{max} = 201$, 308 nm. IR (KBr): 3415, 1617, 1589, 1553 cm^{-1}. MS (+FAB, 3-NBA) $m/z = 1057$ [HM^+].

2.5. Data collection and processing

X-ray structural analysis of $Na_4[(\mathbf{BCAz})_3Ti_2] \cdot 7$ dmf$\cdot H_2O$: formula $C_{42}H_{24}N_6Na_4O_{12}Ti_2 \cdot 7C_3H_7NO \cdot H_2O$,

$M = 1522.12$, red crystal $0.20 \times 0.10 \times 0.05$ mm^5, $a = 13.214(1)$, $b = 15.398(1)$, $c = 20.077(1)$ Å, $\alpha = 68.90(1)°$, $\beta = 88.82(1)°$, $\gamma = 71.39(1)°$, $V = 3591.3(4)$ Å^3, $\rho_{calc} = 1.408$ g cm^{-3}, $\mu = 3.26$ cm^{-1}, absorption correction via SORTAV ($0.938 < T < 0.984$), $Z = 2$, triclinic, space group $P\bar{1}$, $\lambda = 0.71073$ Å, $T = 198$ K, 20 973 reflections collected ($\pm h$, $\pm k$, $\pm l$), $((\sin\theta)/\lambda)_{max} = 0.59$ Å^{-1}, 12730 independent ($R_{int} = 0.059$) and 7447 observed reflections ($I \geqslant 2\ \sigma(I)$), 958 refined parameters, $R = 0.061$, $wR_2 = 0.130$, max. residual electron density 0.85 (−0.49) e Å^{-3}. Hydrogens at the water molecule were obtained from the difference Fourier map. The unbound dmf molecule shows some disorder.

3. Results and discussion

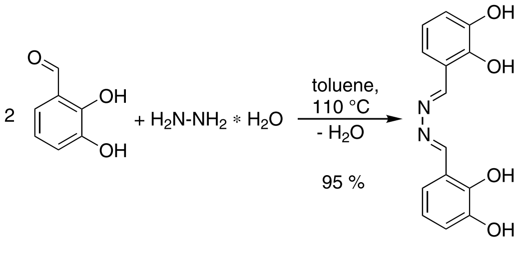
3.1. Preparation of the ligand BCAz-H$_4$

The ligand **BCAz**-H$_4$ is prepared in close to quantitative yield by simply heating 2,3-dihydroxybenzaldehyde and hydrazine hydrate in a 2:1 ratio in toluene overnight. Water is removed by azeotropic distillation [14]. After some while, the ligand starts to precipitate and after cooling the ligand **BCAz**-H$_4$ can be isolated in 95% by filtration. Spectroscopic and analytical data are in accordance with the expected ones.Scheme 1.

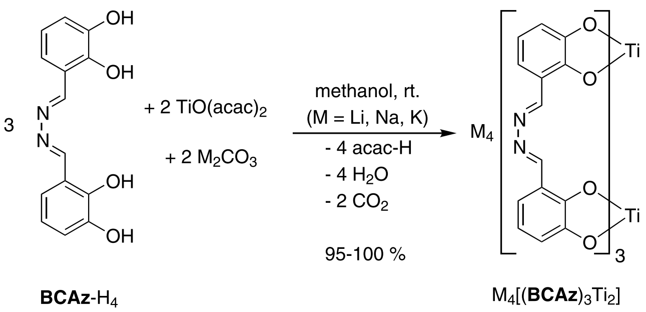
3.2. Self-assembly of dinuclear triple-stranded helicates $M_4[(BCAz)_3Ti_2]$ (M = Li, Na, K) and their spectroscopic characterization

The dinuclear complexes $M_4[(\mathbf{BCAz})_3Ti_2]$ (M = Li, Na, K) are prepared by dissolution of 3 equiv. of **BCAz**-H$_4$, 2 equiv. of TiO(acac)$_2$, and 2 equiv. M_2CO_3 in methanol and stirring over night. After removal of the solvent in vacuum the obtained orange–red material can be purified by filtration over Sephadex LH20 [15].Scheme 2.

The complexes $M_4[(\mathbf{BCAz})_3Ti_2]$ are characterized by microanalysis and different spectroscopic methods. Positive FAB-MS (3-NBA as matrix) shows characteristic peaks for the dinuclear triple-stranded helicates at $m/z = 929$ ($\{HLi_4[(\mathbf{BCAz})_3Ti_2]\}^+$), 993 and 1016 ($\{HNa_4[(\mathbf{BCAz})_3Ti_2]\}^+$ and $\{Na_5[(\mathbf{BCAz})_3Ti_2]\}^+$), or



Scheme 1.



Scheme 2.

1057 ($\{HK_4[(\mathbf{BCAz})_3Ti_2]\}^+$), respectively. Due to the high symmetry of the ligand and the averaged C_{3h} symmetry of the dinuclear complexes in solution, the NMR spectra are very simple. The ^{1}H NMR in methanol-d_4 shows four signals for each of the complexes at $\delta = 8.53$–8.59, 6.97–7.05, 6.51–6.54, and 6.44–6.46. Thus, no significant differences are observed for the different alkali metal salts in the ^{1}H NMR. ^{13}C NMR reveals seven signals of carbon atoms. Only the signal of the −*C*H=N carbon atom shows a significant shift differences ($\Delta_{max} = 2.0$ ppm) depending on the cation (Li: 155.4 ppm, Na: 152.5 ppm, K: 153.4 ppm). This indicates, that some—although weak—interaction occurs between the tetraanions and the countercations in solution [16]. Hereby, the observation of a shifting of the imine carbon atom indicates that the different alkali metal cations bind to the N-donor atoms in the spacer and lead to different NMR shifts at this position.

3.3. X-ray structural analysis

X-ray quality crystals of $Na_4[(\mathbf{BCAz})_3Ti_2]\cdot 7\ dmf\cdot H_2O$ are obtained by slow diffusion of ether into a solution of $Na_4[(\mathbf{BCAz})_3Ti_2]$ in wet DMF. A small amount of water is necessary to enable an optimized packing in the crystal. The complex crystallizes in the triclinic space group $P\bar{1}$.

Fig. 1 shows the structure of the tetraanion $[(\mathbf{BCAz})_3Ti_2]^{4-}$ in the solid state. The two titanium atoms are bridged by three ligands **BCAz** and possess a pseudooctahedral coordination geometry with the same configuration at both metal complex units (→helicate) [17]. The two titanium triscatecholate units are bridged by three −CH=N−N=CH− moieties which show different conformations. Bond lengths in the spacer are in the region of 1.276–1.290 Å for the CH=N and of 1.396–1.422 Å for the N−N bond. The shortest contacts are observed for one of the spacers which adopts an s-*cis* orientation at the N−N σ-bond. The nitrogen atoms of this spacer are orientated to the outside of the helicate cavity and the diazadiene moiety possesses a dihedral angle C=N−N=C of 63.7°. The two other azine units are s-*trans* orientated with dihedral angles of 178.8° and

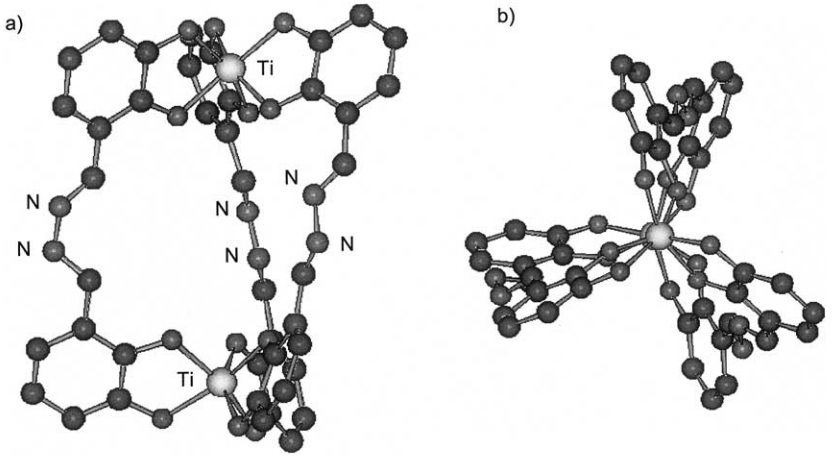


Fig. 1. Representation of the tetraanion $[(\mathbf{BCAz})_3Ti_2]^{4-}$ in the solid state. (a) Side view of the triple-stranded helicate, showing the different conformations of the three spacers. (b) View along the Ti–Ti axis, showing the helical twist of the complex.

153.5°. Thus, the latter two spacers have one nitrogen atom orientated to the inside and one to the outside of the cavity. The internal N-atoms are used to fix two sodium countercations in the interior of the helicate (Fig. 2) [16]. Each of the two sodium cations is hexacoordinated with a more or less distorted octahedral geometry. The two atoms are bound to two internal catechol oxygen atoms of one of the complex units and to a nitrogen atom of the s-*trans* configurated spacers [18]. In addition one dmf molecule is binding from the outside of the cavity to each of the sodium ions and one water and one dmf molecule are bridging the two cations. Two additional Na^+ are bound to external oxygen atoms of the helicates and are bridged by dmf molecules to lead to a polymeric chain $\{[Na_2(dmf)_3][(Na_2(dmf)_3(H_2O) \subset (\mathbf{BCAz})_3Ti_2]\}_n$ in the solid state. A further (disordered) dmf molecule is present in the crystal structure without close binding contacts to neighbouring atoms.

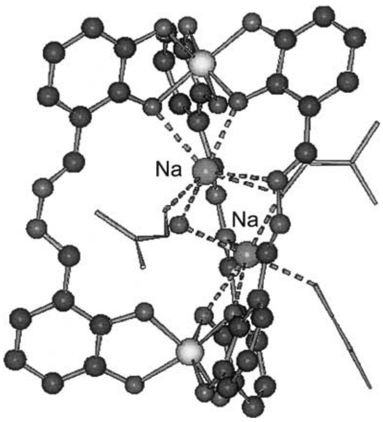


Fig. 2. The same representation of the sodium complex as in Fig. 1a, including the encapsulated sodium cations and representing the dmf molecules, which bind to the internal sodium ions.

4. Conclusion

In this paper we presented a novel type of azine-bridged dicatechol ligand for metallosupramolecular chemistry. The easy to obtain ligand smoothly forms dinuclear triple-stranded helicates with titanium(IV) ions in the presence of alkali metal carbonate. The X-ray structure of $Na_4[(\mathbf{BCAz})_3Ti_2]\cdot 7\,dmf\cdot H_2O$ shows that countercations are encapsulated in the interior of the dinuclear titanium complex which not only bind to catecholate oxygen atoms or solvent molecules but also interact with the azine spacers (^{13}C NMR gives a hint, that such an interaction might also take place in solution). Studies to introduce redox active metal centers [19] and to use the conjugated azine unit as an electronically non-innocent spacer are underway in our laboratories.

5. Supplementary material

Crystallographic data (excluding structure factors) for the structure reported in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC-190512. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

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