In summary, we have prepared and structurally characterized a five-membered AlN_4 ring compound. Evidently, compound **2** represents the first structurally characterized Group 13 element MN_4 system, although various binary M–N (M = Group 13 element) rings are known which show unique structural features.[12] The synthesis of **2** under mild conditions indicates that **1** is very reactive toward organic azides. Stimulated by this result, we are investigating the reaction of **1** with more bulky organic azides in an effort to prepare stable compounds containing Al=N double-bond systems.

Experimental Section

All manipulations were carried out under an argon atmosphere by using Schlenk line techniques.

2: Neat Me_3SiN_3 (0.23 g, 2 mmol) was added to a solution of **1** (0.44 g, 1 mmol) in toluene (20 mL) at $-78\,^{\circ}C$ leading to an immediate color change from red to orange-yellow. The mixture was allowed to warm to room temperature, and stirred for 1 h. The yellow solution was concentrated (ca. 5 mL) and stored at $-30\,^{\circ}C$ overnight to give yellow crystals of **2** (0.37 g, 58 %). M.p. 130 °C (decomp); ^1H NMR (C_6D_6): $\delta = 7.08$ (m, 6H; Ph), 5.04 (s, 1H; γ-CH), 3.48 (sept, 2H, $J = 6.8$ Hz; C*H*Me$_2$), 3.02 (sept, 2H, $J = 6.8$ Hz; C*H*Me$_2$), 1.52 (s, 6H; Me), 1.30 (d, 6H; CH*Me*$_2$), 1.20 (d, 6H; CH*Me*$_2$), 1.14 (d, 6H; CH*Me*$_2$), 1.02 (d, 6H; CH*Me*$_2$), 0.48 (s, 9H; $SiMe_3$), -0.14 (s, 9H; $SiMe_3$); ^{13}C NMR (C_6D_6): $\delta = 172.49$ (CN), 145.78, 142.68, 140.11, 125.67, 124.28 (Ph), 101.08 (γ-C), 28.91, 28.83, 25.22, 25.20 ($CHMe_2$), 24.07 (Me), 1.64, 0.62 ($SiMe_3$); ^{29}Si NMR (C_6D_6): $\delta = 4.89$, 3.08 ($SiMe_3$); EI-MS: *m/z* (%): 646 (20, [M^+]), 631 (100, [$M^+ - Me$]).

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[7] The data were collected on a Stoe-Siemens four-circle diffractometer using $Mo_{K\alpha}$ ($\lambda = 71.073$ pm) radiation. The structure was solved by direct methods (SHELXS-96)[13] and refined against F^2 using SHELXL-97.[14] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in the refinement in geometrically ideal positions. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-149345. 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). Crystallographic data for **2**: $C_{35}H_{59}AlN_6Si_2$, $M_r = 647.04$, monoclinic, $P2_1/n$, $T = 200(2)$ K, $a = 1245.71(11)$, $b = 2203.7(6)$, $c = 1413.6(2)$ pm, $\beta = 91.358(11)^{\circ}$, $V = 3.8793(12)$ nm^3, $Z = 4$, $\rho_{calcd} = 1.108$ g cm^{-3}; crystal size: $0.70 \times 0.60 \times 0.20$ mm, $7.02 \leq 2\theta \leq 50.1^{\circ}$; of the 10122 reflections collected, 6843 were independent and were used for the structure refinement of 413 parameters. The *R* values are $R1 = 0.0436$, $wR2 = 0.1110$ ($I > 2\sigma(I)$) and $R1 = 0.0511$, $wR2 = 0.1201$ (all data); min./max. residual electron density: $320/-256$ e nm^{-3}.

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Synthesis of Stable Organo(bis-silanetriols): X-Ray Powder Structure of 1,4-Bis(trihydroxysilyl)benzene[**]

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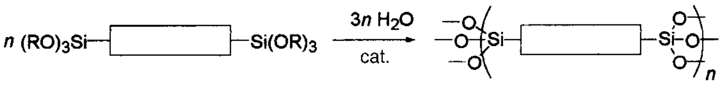
In the course of our work concerning nanostructured hybrid organic–inorganic materials,[1] we have been interested in finding an alternative route to the commonly used hydrolytic polycondensation (the sol–gel process).[2] This general method permits access to materials through a procedure that is very convenient from a practical point of view (Scheme 1). Moreover it allows easy processing of the compounds obtained during the sol step. However, the mechanism is highly complex since the polysubstitutions and polycondensations are concurrent with other reactions, and many points of this process are not well understood.[3] For these reasons we have examined the possibility of preparing and isolating stable silanetriols that contain at least two $Si(OH)_3$ groups in the



Scheme 1. The hydrolytic polycondensation process. The rectangle represents the bridging organo group.

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same molecule in order to find a new route for accessing nanostructured hybrid materials.

The chemistry of silanetriols is relatively new, compared to monosilanols and silanediols.[4] The use of this class of compounds as building blocks in material science and particularly for the synthesis of crystalline metallosiloxanes is a growing field of interest.[4] However the easy self-condensation of silanetriols[5] has considerably hindered their development. All the stable silanetriols reported in the literature possess one $Si(OH)_3$ group[6–18] and are stabilized by a balance between steric and electronic factors.

The relative stability of different types of silanetriols is due to their molecular association in the solid state through hydrogen bonding to form a variety of structures:

1) a double-sheet structure where the alkyl and the OH groups form alternating hydrophobic and hydrophilic double sheets respectively,[8, 9, 10]
2) tetrameric structures,[5]
3) hexameric and octameric cage structures for sterically hindered silanetriols,[11, 12]
4) tube structures with hydrophilic inside walls and hydrophobic outside walls.[13]

We have investigated the formation of silanetriols containing two $Si(OH)_3$ groups in the same molecule. We report here the synthesis and structure of two bis-silanetriols that contain either a phenyl group (**1T**) or a diphenyl group (**2T**) as a bridging moiety.

Two main routes to organosilanetriols are reported in the literature. The first one consists of a controlled hydrolysis of trimethoxysilane precursors in aqueous acetic acid at low temperature.[6] The second is the hydrolysis of trichlorosilanes in the presence of base (triethylamine or pyridine) at 0 °C; this is used in the case of bulky organic or aromatic groups.[8, 9, 11, 14, 16–18] It has been previously shown that organoalkoxysilanes are especially useful for the preparation of silanols since the cleavage products which are formed do not accelerate the condensation of the silanols. The two compounds **1T** and **2T** presented herein were prepared according to Scheme 2, which consisted of a controlled hydrolysis of **1** and **2**[19] under mild conditions. We modified the procedure reported[6] since it led to silsesquioxane material. This reaction is easily explained by the presence of six possible directions for substitution at silicon. The bis-silanetriols **1T** and **2T** were obtained, after 24 hours in a biphasic medium (diethyl ether/water), as white powders in high yields (93–95 %).

These solids were insoluble in the usual organic solvents and were soluble only in DMSO, because of the strong hydrogen bonding between DMSO and the OH groups. **1T** and **2T** were thermally stable up to 100 and 70 °C, respectively. The differential scanning calorimetry (DSC) curves exhibited very broad and highly asymmetric endothermic signals between 100 and 240 °C with a maximum at 196 °C for **1T**, and between 70 and 200 °C with a maximum at 152 °C for **2T**; these signals correspond to the polycondensation reactions. **1T** and **2T** were identified and characterized by elemental analysis, IR, ^1H, ^{13}C, and ^{29}Si NMR spectroscopy, and X-ray powder diffraction studies.

In both cases, the FTIR spectra (KCl pellets) exhibited a broad absorption band centered at 3200 cm^{-1}, attributed to hydrogen-bonded OH groups (no free O–H vibration modes were observed), and a broad band centered around 890 cm^{-1}, which was due to the Si–O(–H) bonds vibration modes. Moreover no absorption bands corresponding to Si–O–Si vibrations were detected around 1050 cm^{-1}. The NMR data were collected in deuterated DMSO. ^1H and ^{13}C NMR spectra of **1T** and **2T** displayed the expected resonances for the organic moiety in each case. The ^1H NMR spectra displayed a singlet at 6.36 or 6.42 ppm, respectively, which was assigned to the OH groups in the liquid medium. The ^{29}Si NMR spectra exhibited a sharp resonance at −54.3 ppm, in agreement with the chemical shifts already reported for silanetriols.[20]

From their X-ray powder diffraction patterns, the solids were indexed with the following cell parameters: $a = 10.056(2)$, $b = 6.879(2)$, $c = 6.937(2)$ Å, $\beta = 95.71(3)^\circ$ ($M(18) = 34$[21]) for **1T**, and $a = 14.030(7)$, $b = 6.953(4)$, $c = 6.86(1)$ Å, $\beta = 92.80(8)^\circ$ ($M(18) = 9$[21]) for **2T**. The parameters describing the plane of the oxygen and silicon atoms, that is, *b* and *c*, are similar for both cells. The *a* parameter, along the stacking axis, depends on the length of the organic group. Even though the pattern of **2T** exhibited much lower cristallinity than that of **1T**, the figure of merit obtained for **2T** with 18 peaks shows some reliability for this indexation. From these results, as well as those obtained from NMR and IR spectra, we could infer that the crystallographic arrangements for **1T** and **2T** would be highly similar.

The crystallographic structure determination of **1T** has been carried out with the Rietveld method[22] (Figure 1). This structure, determined without any predefined molecular model (ab initio), is highly reliable, despite the R_{wp} value of 14.4 (versus an R_{exp} of 13.8, Ref. [23] and Table 1), with regard to the arrangement and distances directly obtained; these are consistent with the chemistry and the literature.

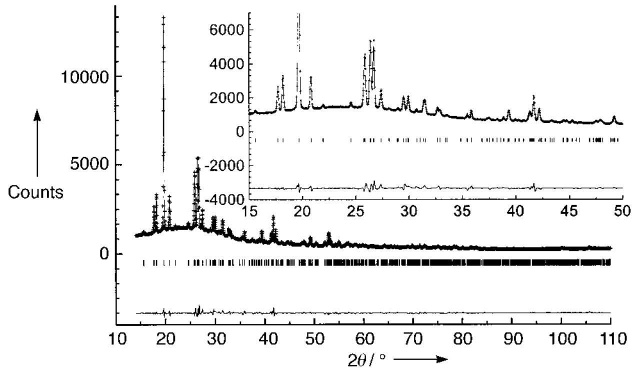
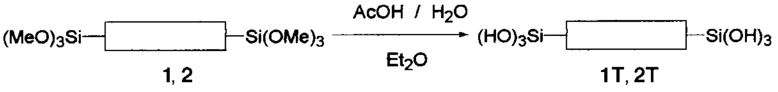


Figure 1. Experimental pattern (+), Rietveld-calculated pattern (solid line), difference (lower solid line), and Bragg positions (|) for the X-ray powder diffraction on **1T**.

As seen in Figure 2, **1T** is arranged in sheets and each molecule is eclipsed (Figure 3). The two triol



Scheme 2. Synthesis of **1T** and **2T**. In compounds **1** and **1T** the rectangle represents a bridging phenyl group, in compounds **2** and **2T** it represents a diphenyl group.

Table 1. Fractional atomic parameters and equivalent isotropic displacements for **1T**.[a]

Atom	*x*	*y*	*z*	B_{eq}[b] [Å^2]
Si	0.6963(3)	– 0.0231(5)	0.2790(5)	1.0
O1	0.6210(6)	0.1426(8)	0.3858(10)	1.0
O2	0.6341(6)	– 0.2492(10)	0.2900(10)	1.0
O3	0.6963(5)	0.0156(11)	0.0469(11)	1.0
C1	0.875(1)	– 0.012(2)	0.417(2)	2.0
C2	0.981(1)	– 0.056(2)	0.295(1)	2.0
C6	0.893(1)	0.046(2)	0.592(2)	2.0

[a] In each case the site was 4e. [b] $B_{eq} = 8\pi^2 \times U_{eq}$.

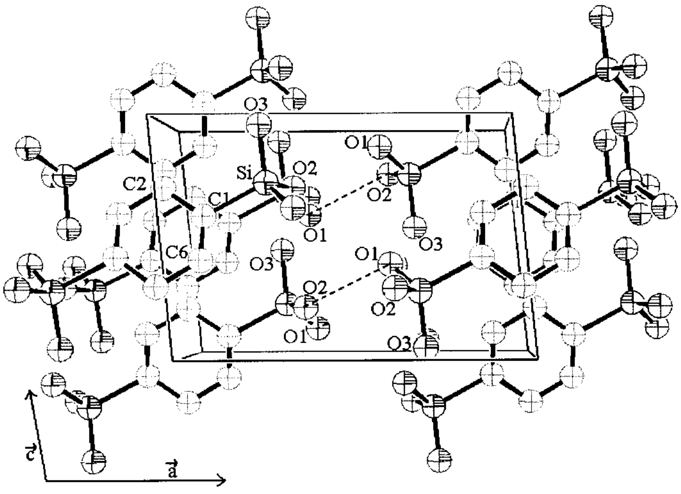


Figure 2. View along the *b* axis of two sheets of **1T**. Dashed lines represent hydrogen bonding at the interface between two sheets (hydrogen bonds in which one atom is not shown in the figure and hydrogen bonds within sheets have been omitted for clarity).

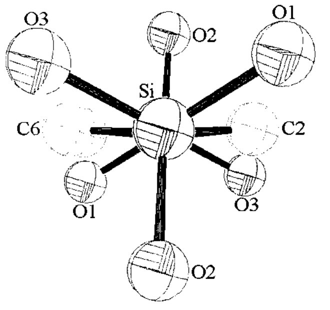


Figure 3. Topside view of a molecule of **1T** showing the eclipsed arrangement of the two triol end groups.

end groups form hydrophilic layers, whereas the body of the sheets form hydrophobic layers. It is interesting to examine more closely the hydrogen-bonding network which stabilizes the whole structure.

Within a sheet, we observed two types of hydrogen-bond distance. Starting from the O3 oxygen atom of one molecule, we found one oxygen atom O1 of a neighboring molecule at 2.68(1) Å and one oxygen atom O2 of another neighboring molecule at 2.59(1) Å (Table 2, Figures 2 and 4). It is noteworthy that this second hydrogen-bond distance is consistently shorter than the first one, but we observed also that the Si–O2 distance is 1.68(1) Å whereas the Si–O1 distance is 1.59(1) Å. The main point is that O3 has two hydrogen bonds within a sheet, and this implies, as observed, that the silicon–silicon axis of these flat molecules is inclined by 29° with respect to the *a* axis: thus, the Si–O3 bond points within its layer, whereas the Si–O1 and the Si–O2 bonds point toward the neighboring layer. The phenyl rings are mainly in the *ac* plane, even though they are tilted away from this plane alternately by +21.8° and –21.8° when moving along the *b* axis in Figure 4. Consequently, the phenyl rings make a 43.6° angle with respect to their four neighbors within a sheet, the closest of which is at 5.24(1) Å on the basis of silicon to silicon distances; the closest parallel phenyl rings within a sheet are 7.24(1) Å apart on the same basis.

Table 2. Selected bond lengths [Å] and angles [°] for **1T**.

Si-O1	1.59(1)	Intrasheet hydrogen bonds	
Si-O2	1.68(1)	O3 ··· O1[a]	2.68(1)
Si-O3	1.63(1)	O3 ··· O2[b]	2.59(1)
Si-C1	1.95(1)		
Phenyl (C–C) = 1.38(9)		Intersheet hydrogen bonds	
		O1 ··· O2[c]	2.82(1)
O1-Si-O2	116.4(4)	C1-Si-O1	101.6(5)
O1-Si-O3	112.9(4)	C1-Si-O2	110.0(5)
O2-Si-O3	103.4(4)	C1-Si-O3	112.8(5)

[a] Symmetry code: x, ½ – y, z – ½. [b] Symmetry code: x, – y – ½, z – ½. [c] Symmetry code: 1 – x, ½ + y, ½ – z.

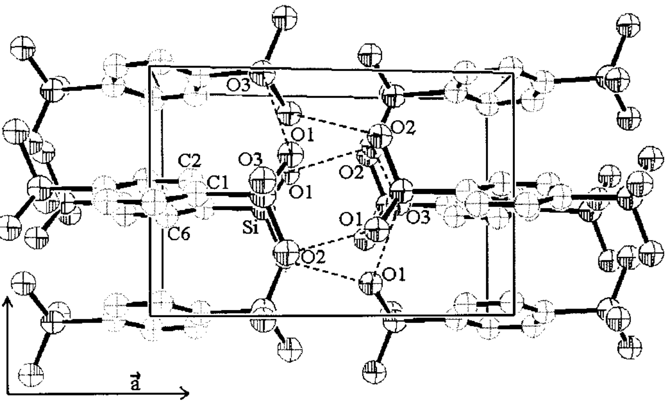


Figure 4. View along the *c* axis of two sheets of **1T**. Dashed lines represent selected hydrogen bonds at the interface.

Between two sheets, the structure is stabilized by hydrogen bonding (2.82(1) Å) between the O1 and O2 atoms (Figures 4 and 5). The oxygen atom O3 is not involved in any hydrogen bonding between two sheets.

So, in this compound each of the oxygen atoms supplies two hydrogen bonds. The hydrogen-bond distances are consistent with those found in the literature.[5] As previously mentioned, we can infer that **2T** presents the same type of structural arrangement as **1T**, with a thickness of 14.01 Å for a sheet, as observed in its X-ray powder diffraction pattern.

Layered structures have also been reported for bulky monosilanetriols, such as cyclohexylsilanetriol[10] or *tert*-butylsilanetriol.[8] A bilayer arrangement with distances directly connected with the lengths of the alkyl chains has also been proposed in the case of alkylsilanetriols containing long-chain alkyl groups.[24] In these structures, as well as those observed in some layered phosphonates,[25] the molecules are arranged in a head-to-tail manner, in a such way that we have alternately hydrophobic and hydrophilic interactions. In our

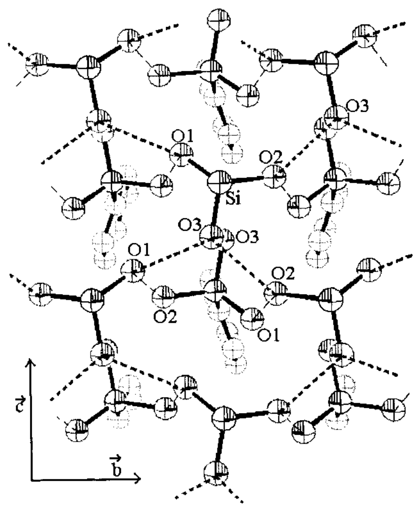


Figure 5. View along the *a* axis of one interface between two sheets of **1T**. Silicon atoms which are connected to carbon atoms belong to the inferior sheet whereas silicon atoms where the phenyl ring has been omitted belong to the superior sheet; bold dashed lines represent hydrogen bonding at the interface within the superior sheet; thin dashed lines represent hydrogen bonding at the interface between the two sheets (hydrogen bonds at the interface within the inferior sheet have been omitted for clarity).

cases, the two triol groups in *para* positions form the two hydrophilic ends of hydrophobic pillars.

We propose that the stabilization of ordered structures is the result of the formation of a strongly hydrogen-bonded network which induces the organisation of hydrophobic organic groups. There is a competition between the polycondensation reaction leading to polysiloxanes and the formation of hydrogen bonds. The formation of bis-silanetriols was possible thanks to the biphasic medium which allowed and favored the formation of the hydrophilic layer (strong hydrogen-bonded network) in the aqueous phase, while the polycondensation reaction with elimination of water was strongly slowed down. Moreover the hydrophobic interactions between organic groups certainly assisted the formation of ordered structures as shown in the case of alkyl long-chain systems.[24]

We have reported here the preparation of the first stable bis-silanetriols. The first structure of such a compound has been presented and provides evidence for the importance of the hydrogen bonding between neighboring silanol groups. The simultaneous presence of hydrophilic and hydrophobic interactions could be a driving force in the formation of ordered structures. The distance between the hydrophilic sheets was directly connected to the length of the organic group. When the organic pillar was shorter, the bis-silanetriol appeared more organized than with the longer one. The properties of this new class of solids are currently being studied. The first attempts show that the hybrid materials obtained by polycondensation exhibit different properties from those obtained by the usual route.[1]

Experimental Section

A mixture of 1,4-bis(trimethoxysilyl)benzene (1.6 g, 5 mmol) in 3 mL of diethyl ether and 2.2 mL of an aqueous solution of AcOH (0.5 vol %) was vigorously stirred at room temperature for 24 hours. During this period a white solid gradually precipitated out and was then separated by filtration. The white powder was washed with ethanol (3 × 20 mL), acetone (3 × 20 mL) and diethyl ether (3 × 20 mL). The resulting solid was dried under vacuum (2 mbar) at 20 °C during 24 hours to yield 93 % of **1T** (1.09 g, 4.65 mmol) as a white powder. Elemental analysis: calcd for $C_6H_{10}O_6Si_2$: C 30.16, H 4.30, Si 23.95; found: C 30.86, H 4.39, Si 24.20; ^{1}H NMR (DMSO-d6): $\delta = 6.36$ (s, 6H), 7.55 (s, 4H); ^{13}C NMR (DMSO-d6): $\delta = 133.7$, 138.7; ^{29}Si NMR (DMSO-d6): $\delta = -54.3$.

Compound **2T** was obtained from **2** by a similar method as a white powder with a 95 % yield. Elemental analysis: calcd for $C_{12}H_{14}O_6Si_2$: C 46.44, H 4.54, Si 18.09; found: C 45.44, H 4.70, Si 18.20; ^{1}H NMR (DMSO-d6): $\delta =$ 6.43 (s, 6H), 7.63 (d, 4H), 7.69 (d, 4H); ^{13}C NMR (DMSO-d6): $\delta = 126.3$, 135.5, 136.8, 141.2; ^{29}Si NMR (DMSO-d6): $\delta = -54.3$.

X-ray powder diffraction patterns were recorded on an INEL diffractometer equipped with a CPS 120 detector, with CuKα_1 radiation (40 kV × 30 mA) in transmission mode. The sample was sieved (particles size below 63 nm) and placed in a 0.3 mm diameter capillary. Peak positions were determined using the WinPLOTR package[26] and the pattern was indexed with DICVOL91.[27] Si, O, and C atom positions were determined by a direct method with the SIRPOW92 package.[28] Rietveld refinements were carried out with FULLPROF software[29], with fixed thermal parameters. $R_{exp} = 13.8$ reflects the quality of the pattern. The refinement with 603 Bragg peaks led finally to $R_{wp} = 14.4$, $R_B = 10.8$, and $\chi^2 = 1.09$. (See Supporting Information for more details.)

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[23] Crystallographic data for **1T**: $M = 210.3$ g mol^{-1}, monoclinic, space group $P2_1/c$ (No. 14); $a = 10.0495(4)$, $b = 6.8738(3)$, $c = 6.9367(3)$ Å, $\beta = 95.746(3)°$, $V = 476.77(3)$ Å^3, $Z = 4$, $D_c = 1.464$ g cm^{-3}; $T = 293$ K,

λ(Cu-Kα_1) = 1.5406 Å, μ = 32.27 cm^{-1}. The pattern was collected with transmission geometry, from 14 to 110° (2θ). 603 reflections (206 independent) were used with 25 structural parameters and 8 profile parameters. $R_{exp} = [(N\text{-}P)/\Sigma wi(yi_{obs})^2]^{1/2} = 13.8$, $R_p = \Sigma | yi_{obs} - yi_{calcd} | / \Sigma yi_{obs} = 17.3$, $R_{wp} = [\Sigma wi | yi_{obs} - yi_{calcd} |^2 / \Sigma wi(yi_{obs})^2]^{1/2} = 14.4$, $R_B = \Sigma | Ik_{obs} - Ik_{calc} | / \Sigma Ik_{obs} = 10.8$, GOF = $(R_{wp}/R_{exp})^2 = 1.09$. Details about the structure solution and refinement are given in the Supporting Information. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-147044. 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).

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The Essential Role of a Zn^{II} Ion in the Disproportionation of Semiquinone Radical Anion by an Imidazolate-Bridged Cu^{II}–Zn^{II} Model of Superoxide Dismutase**

Hideki Ohtsu and Shunichi Fukuzumi*

Copper–zinc superoxide dismutase (Cu,Zn-SOD) contains an imidazolate-bridged Cu^{II}–Zn^{II} heterodinuclear metal center in its active site.[1–6] This enzyme catalyzes a very rapid two-step dismutation of toxic superoxide ($O_2^{\bullet -}$) into dioxygen and hydrogen peroxide by alternating reduction and oxidation of the copper ion of the active site.[5–7] Superoxide first reduces the Cu^{II} center of Cu,Zn-SOD to produce O_2, and then another molecule of superoxide oxidizes the Cu^{I} center to produce H_2O_2.[6, 7]

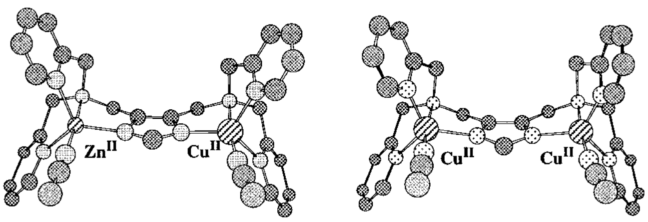
Since the oxidation potential of $O_2^{\bullet -}$ ($E^0_{ox} = -0.16$ V versus the normal hydrogen electrode (NHE) at pH 7.0)[8] is more negative than the reduction potential of Cu,Zn-SOD ($E^0_{red} = 0.36$ V versus NHE at pH 7.4),[9] the oxidation of $O_2^{\bullet -}$ may occur rapidly by electron transfer from $O_2^{\bullet -}$ to the Cu^{II} center of Cu,Zn-SOD, whereas outer-sphere electron transfer from the Cu^{I} center of Cu,Zn-SOD to $O_2^{\bullet -}$ is highly endergonic. Therefore, coordination of $O_2^{\bullet -}$ to the Zn^{II} center of Cu,Zn-SOD was suggested to be essential to accelerate electron transfer from the Cu^{I} center of Cu,Zn-SOD to $O_2^{\bullet -}$ which is bound to the Zn^{II} center.[10] A central issue in bioinorganic chemistry is to clarify how the Zn^{II} ion can facilitate both the oxidation and reduction of $O_2^{\bullet -}$ in Cu,Zn-SOD.[1–7] However, the instability of the reaction intermediates and the lack of appropriate model complexes which contain the substrate binding sites has so far precluded studying the essential role of the Zn^{II} ion in Cu,Zn-SOD.[1–7, 9–11]

We succeeded in preparing the imidazolate-bridged Cu^{II}–Zn^{II} heterodinuclear and Cu^{II}–Cu^{II} homodinuclear complexes **1** and **2** by using the novel dinucleating ligand Hbdpi

$[CuZn(bdpi)(CH_3CN)_2](ClO_4)_3 \cdot 2\,CH_3CN$ **1**

$[Cu_2(bdpi)(CH_3CN)_2](ClO_4)_3 \cdot CH_3CN \cdot 3\,H_2O$ **2**

(Hbdpi = 4,5-bis(di(2-pyridylmethyl)aminomethyl)imidazole; Figure 1).[10] In these SOD model complexes, each metal center has a pentacoordinate environment that includes a solvent molecule which can be readily replaced by a substrate. Here we report on the dramatic difference in the stoichiometric disproportionation of semiquinone radical anion ($Q^{\bullet -}$) with the imidazolate-bridged Cu^{II}–Zn^{II} heterodinuclear (**1**) and Cu^{II}–Cu^{II} homodinuclear (**2**) complexes in propionitrile (EtCN). The presence of Zn^{II} ion is shown to be essential for disproportionation of $Q^{\bullet -}$ to occur. The use of $Q^{\bullet -}$ instead of $O_2^{\bullet -}$ provides valuable mechanistic insights into the essential role of the Zn^{II} ion in Cu,Zn-SOD, since the reaction intermediates are stable enough to be well characterized.



$[CuZn(bdpi)(CH_3CN)_2]^{3+}$ $[Cu_2(bdpi)(CH_3CN)_2]^{3+}$

Figure 1. Structures of **1** and **2**.

The addition of less than one equivalent of $Q^{\bullet -}$ to a deaerated solution of **1** in EtCN results in the appearance of a new absorption band at 585 nm, the absorbance of which increases linearly with increasing concentration of $Q^{\bullet -}$ (Figure 2a). The addition of more than two equivalents of $Q^{\bullet -}$ results in no further increase in the absorption band at 585 nm, but decay of the absorption band due to $Q^{\bullet -}$ ($\lambda_{max} = 422$ nm) is observed (Figure 2a). The decay rate obeys first-order kinetics (Figure 2a, inset), and the rate constant k_{obs} at 193 K is 0.4 s^{-1}. Further addition of $Q^{\bullet -}$ after the initial disappearance of $Q^{\bullet -}$ resulted in reappearance of the absorption band due to $Q^{\bullet -}$, which was stable under the present experimental conditions.

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