It thus appears that some intrinsic stability is associated with the *facial* geometry in all octahedral systems thus far investigated. One might speculate that the NO group might have a large trans effect and the mutually trans NO groups in the meridional isomer would be unstable. However, a trans arrangement is found in a square-pyramidal Cu(II) complex.[12] Clearly, an understanding of the preference for the facial isomer in octahedral systems must await further investigations.

Acknowledgment. The authors thank the Research Corp. for support and Mr. Paul Worley for his participation in the early stages of this investigation.

Registry No. I, 63864-72-2; II, 13681-88-4; III, 15169-25-2; Na[Co^{III}(acac)$_2$(NO$_2$)$_2$], 14024-47-6; ^{13}C, 14762-74-4.

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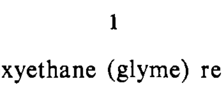
B-Dimethylaminomethyl-Substituted 1,2,5,6-Bis(boratazonia)cyclohexane

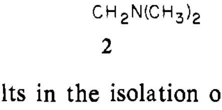
Norman E. Miller

Received December 20, 1976 AIC608993

Modification of synthesis conditions[1,2] of the valence saturated, BCN sequenced heterocycle **1** by addition of 1,2-dimethoxyethane (glyme) results in the isolation of a new *B*-dimethylaminomethyl derivative, **2**, a low melting solid, stable in air, and readily water soluble to give a strongly basic solution. The synthesis and characterization are described.

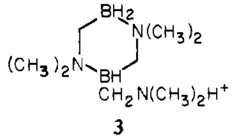


1



2

Formally named as a cyclohexane anologue, 1-dimethylaminomethyl-1,2,5,6-bis(boratazonia)cyclohexane, **2**, reacts as a typical tertiary amine to form proton salts, **3**, and a simple borane adduct, **4**. It reacts with methylene chloride nominally to exchange trimethylamine for methylene dichloride to give a new *B*-dichloromethyl derivative



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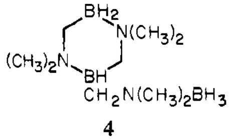

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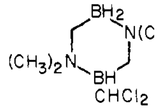

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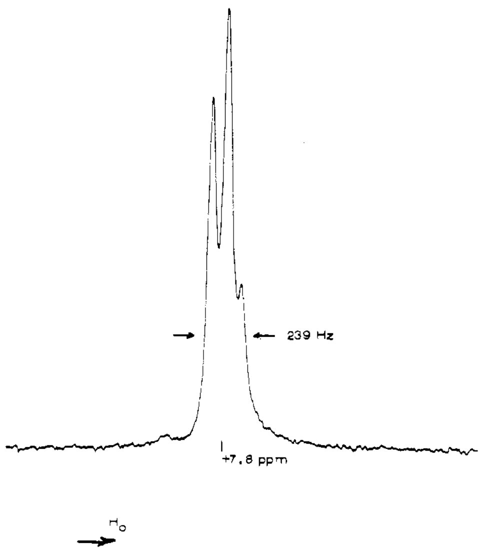

Figure 1. A 28.874-MHz ^{11}B NMR of $H(CH_3)_2NCH_2\overline{BHCH_2N(CH_3)_2}BH_2CH_2N(CH_3)_2{}^+PF_6{}^-$ in acetonitrile.

Results

Characterization of Structures. Elemental analyses and infrared spectral data support structures **2** through **5**, but key structural data are the mass spectra of **2** and **5** and the ^{11}B NMR spectrum of **3**. Structural representations show only ring sequences; a rapidly converting chair form structure for **1** in solution is likely since the chair form obtains for the solid state.[3]

Mass spectral data, Table I, for the dimethylamino derivative, **2**, shows a significant parent ion at *m/e* 199. Because boron hydrides often have mass patterns with the P − 1 as the highest significant peak,[4] it is reasonable, in view of the structure proposed, to assume that the 199 peak arises by proton abstraction from the plasma to give the P − 1 peak of the ammonium salt **3**. Lower mass fragments correspond very closely to the splitting pattern observed for the parent heterocycle, **1**. The highest mass peak at 141 for this residue pattern arises from loss of the very stable methylenedimethylammonium ion, $(CH_3)_2N{=}CH_2{}^+$, from the parent. Relative ratio of the 141 to 140 peaks is close to the 2:1 statistical distribution expected ratio for B_2 species. The similar ratio of the 139 to 138 peaks is difficult to explain short of facile loss of H_2 from the P − 1 or highest fragment of **1**. Indeed, Hseu and Larsen[3] report that $B_2C_6H_{17}N_2$ fits well the high-resolution mass numbers for the 138, 139 peaks. The fragmentation pattern observed at lower excitation voltage by these workers compares generally with that reported here at a higher ionization voltage; the greater abundancies of the higher mass species are reasonably expected for an acid–base

Table I. Mass Spectral Fragmentation of **2** and **1**[a]

	2			1[e]	
m/e	Intens	Theory[c]	Assign	Intens	Lit. intens[f]
200	0.7 (5.4)[b]	(4.0)[b]			
199	5.8 (46)[b]	(46)[b]	$B_2C_9H_{27}N_3$		
198	12.7 (100)[b]	(100)[b]	$B_2C_9H_{26}N_3$		
197	5.5 (43)[b]	(40)[b]			
196	0.9 (7)[b]	(4.6)[b]			
142	4			1 (6)[b,d]	6
141	52 (100)[b]			P − 1 18 (100)[b]	72
140	29 (56)[b]			10 (56)[b]	39
139	43 (83)[b]			P − 3 15 (83)[b]	37
138	20.5 (39)[b]			7 (39)[b]	16
127	6			4	9
125	4			3	5
					36 (m/e 115)
114	8			4	11
113	8			8	16
112	8			2	4
					19 (m/e 106)
99	11.5			2	9
96	8			4	7
95	5			3	4
85	4.5			38	99
84	66			38	61
83	8			13	22
82	11			7	5
71	6.6			7	11
70	100		$(CH_3)_2NCH_2BH^+$	100	100
69	30		$(CH_3)_2NCH_2BH^+$	28	40
68	21			16	11
67	7			5	3
58	65		$(CH_3)_2NCH_2^+$	81	100
57	5.4			4	3
56	82			42	50
55	24			12	14
54	16			18	12
53	6			7	4
44	11			9	1

[a] Samples run by Morgan and Schaeffer, Montreal, Quebec, Canada; indirect inlet, 250 °C with 70-V ionization. [b] Relative intensities normalized to highest peak of cluster. [c] Normalized intensities calculated for statistical isotope distribution and 0.31 $B_2C_9H_{27}N_3$ and 0.69 $B_2C_9H_{26}N_3$. m/e 200 peak represents the combined probability of ^{13}C, ^{15}N, ^2H isotopes. [d] m/e 142 accountable by ^{13}C, ^{15}N, ^2H combined abundancies of 7.7% in the P − 1 fragment. [e] Sample prepared by D. L. Reznicek of this department. [f] A 25-V electron beam mass spectrum, of compound 1.

Table II. Parent Ion Mass Spectrum Distribution in **5**[a]

m/e	Intens[b]	Assign[c]	Theory[d]
229			0.4[e]
228	9	2B(11)2Cl(37)	6
227	15	B(10)B(11)2Cl(37)	13
226	39	2B(10)2Cl(37); 2B(11)Cl(35)Cl(37)	39
225	64	B(10)B(11)Cl(35)Cl(37)	67
224	79	2B(10)Cl(35)Cl(37); 2B(11)2Cl(35)	78
223	100	B(10)B(11)2Cl(35)	100
222	42	2B(10)2Cl(35)	38
221	9		4

[a] Commercial analysis; Morgan and Schaeffer, Montreal, Quebec. Sample run at 70 V and 60 °C direct inlet. [b] Relative intensity compared to largest peak in cluster. [c] Isotope distributions listed for P, or parent, only. [d] Calculated assuming statistical distribution and presence of 0.6 $B_2Cl_2C_7H_{19}N_2$ and 0.4 $B_2Cl_2C_7H_{20}N_2$. [e] m/e 229 peak calculated for total abundancy of ^2H, ^{13}C, ^{15}N isotopes.

Table III. Mass Spectral Fragmentation **5**[a]

m/e	Intens	m/e	Intens
223[b]	3	90	12
168	8	84	43
166	13	83	13
165	6	70	60
120	4	69	16
119	6	68	8.5
118	88	61	22
106	32	60	9
104	25	59	9
99	6	58	100

[a] Commercial analysis. See Table II. [b] Highest peak in parent cluster.

dimer such as **1** subject to less dissociation at lower plasma energies.

The ^{11}B NMR at 28.8 MHz for **3** is shown in Figure 1. At least two environments for boron are implicated, but the peak overlap prevents unambiguous assignment to the triplet and doublet expected for rapidly converting chair form conformations.[1,3] Double irradiation experiment showed collapse to a 50 Hz wide slightly unsymmetrical singlet at 7.8 ppm[5] upfield from boron trifluoride–etherate.

Mass spectral data for **5** are summarized in Tables II and III. It is seen that the highest mass cluster is simulated by statistical distribution of boron and chlorine isotopes in a 0.6/0.4 mixture of P − 1 and P ions, respectively. Lower mass fragments suggest that **5** loses $(CH_3)_2NCH_2BH$ (m/e 70) fragment ion characteristic of **1**. Since there is no significant 141 peak of **1** present, the fragmentation of **1** is considered irreversible. The large intensity of the 70 peak would make even a small amount of recombination detectable. A moiety with considerable inherent stability is inferred for the m/e 70 fragment, and possibly a cyclic structure is important.

Reaction with Methylene Chloride. The exchange of the $-CH_2N(CH_3)_2$ and $-CHCl_2$ moieties observed by simple

Table IV. ^{1}H NMR

Compd^a	Resonance shift,^{b} ppm	Area	Assignment
3-PF_6^-/CD_3CN	2.77	8	$(CH_3)_2NH^-$
	2.62	9	ring$(CH_3)_2NBH_2$
	2.59	4.7	ring$(CH_3)_2NBH$
	2.43		
	2.33, 2.00, 1.80	6.7	CH_2
2/C_6D_{12}	2.77	3	ring$(CH_3)_2NBH$
	2.62	3	
	2.50	6	ring$(CH_3)_2NBH_2$
	2.13	6	$(CH_3)_2N$-substituent
	1.9, 1.8, 1.4, 1.2, 0.9	8	CH_2
4/CH_2Cl_2	2.67	3.3	ring$(CH_3)_2NB$
	2.57	7.5	ring$(CH_3)_2NB + N(CH_3)_2BH_3$
	2.43	6	ring$(CH_3)_2NB$
	2.36		
	2 br, 1.7	5	CH_2
5/CH_2Cl_2	2.85, 2.72, 2.67, 2.63, 2.57 mult		$CHCl_2$?
	2.5–2.0 br		
	0.30		

^{a} Solvent shown. ^{b} Downfield from tetramethylsilane.

dissolution of **2** in methylene chloride may be a general reaction for aminomethyl substitution on boron. An attempt to extend the reaction to the analogous strong base $(CH_3)_3NBH_2CH_2\ddot{N}(CH_3)_2$[1,6] did indeed produce a new chlorine-containing product, but it was not as stable as **5**, and proper isolation techniques remain to be worked out. The mechanism and reaction parameters of this interchange remain a matter of continuing research. Present evidence, mainly with ^{1}H NMR monitoring supports a rapid reaction (3 h) leading to loss of the $-CH_2N(CH_3)_2$ moiety and apparent production of a new solid "salt" with $-CH_2Cl$ substitution on nitrogen—similar to that reported[7] for trimethylamine and methylene chloride. Pyrolytic reaction at 120–150 °C (high vacuum) leads to conversion to **5** and production of an equimolar amount of trimethylamine.

Experimental Section

Dihydridobis(trimethylamine)boron chloride was prepared by reaction of trimethylamine-borane, iodine, and trimethylamine, followed by isolation and purification via the hexafluorophosphate salt and ion exchange to the chloride salt by standard procedures.[8,9] Commercial grade (Alfa) *n*-butyllithium in hydrocarbon (pentane or hexane) was handled via syringes. Solvents were rendered anhydrous by distillation from lithium aluminum hydride (for glyme) or contact with calcium hydride (for hydrocarbons). A standard high-vacuum apparatus was used in various manipulations. Proton NMR data were collected on Varian A60A and Hitachi/Perkin-Elmer R24B high-resolution spectrometers. Melting points were run on a Hoover-Thomas melting point apparatus and are uncorrected for emergent stem.

Synthesis of 2. A stirrable suspension of 1.513 g (9.14 mmol) of borane chloride salt in pentane was treated dropwise with 14.1 mmol (5.2 mL, 2.72 M) of *n*-butyllithium with stirring for several hours using a 50-mL flask with side-arm attachment for septum. Solvent and volatile products were distilled through a U-trap cooled to −35 °C which stopped 0.42 mmol (5%) of $(CH_3)_3NBH_2CH_2\ddot{N}(CH_3)_2$, isolated as the $H^+PF_6^-$ salt, and an unmeasured but small amount of **1**. To the dry residue in the reaction were added 2 mL of pentane and 1 mL of glyme. The mixture was stirred about 1 h, volatiles were removed through a −35 °C trap, and the residue was heated slowly to 150 °C. White solid collecting on connecting tubes and in the cold trap was dissolved in acidified water and converted to the hexafluorophosphate, yield 262 mg (6%). Recrystallization from hot ethanol gave 185 mg of purified material, mp 176–180 °C. Anal. Calcd for $C_9H_{28}N_3B_2PF_6$: C, 31.3; H, 8.2; N, 12.2; B, 6.3. Found: C, 31.6, 31.8; H, 8.4, 8.4; N, 12.95, 12.0; B, 6.1, 6.4.

The free base, $(CH_3)_2\ddot{N}CH_2\overline{BHCH_2N(CH_3)_2BH_2CH_2N}(CH_3)_2$, was obtained by stirring 89 mg (0.26 mmol) of $H^+PF_6^-$ salt in 1 mL of 1 M sodium hydroxide and 25 mL of pentane for 2 h. The pentane phase was separated and evaporated to leave 55 mg of white solid. Dissolution in C_6D_{12} for ^{1}H NMR, followed by volatilization of solvent, produced a white solid free base with somewhat higher melting point and recovered solvent found to contain small amounts of water, measured as 1 mmol by gas evolution with calcium hydride. This behavior is explicable by formation of hydrate of the free base. Assumption of a monohydrate gives a 97% yield for the base. The infrared spectrum (Table III) showed BH stretch at 2400 cm^{-1} and sharp absorptions at 2790 and 2840 cm^{-1} characteristic of the $(CH_3)_2\ddot{N}CH_2$– moiety.[10] A sample dried in hexane solution over calcium hydride and then sublimed melted at 39–40 °C, sealed capillary.

A neutralization equivalent of 197 mg/mmol (198.95 theory) was determined by titration under nitrogen using a pH meter and microburet.

Borane Adduct 4. Free base recovered from ^{1}H NMR was dissolved in 2 mL of pentane and treated with 50% excess diborane. Separation of unused diborane showed that 0.11 mmol of diborane was consumed, supporting a 1.1:1 base:BH_3 ratio. Sublimation of product under high vacuum at 90 °C gave 34 mg of a white solid adduct, mp 120–125 °C. Anal. Calcd for $C_9H_{30}N_3B_3$: C, 50.8; H, 14.2; N, 19.7. Found: C, 50.5; H, 14.2; N, 19.35.

Dichloromethyl Derivative, 5. A solution in methylene chloride of free base was evaporated and the residue sublimed. The sublimate at 150 °C, full vacuum, was collected and resublimed to give white solid. Anal. Calcd for $C_7H_{14}N_2B_2Cl_2$: C, 37.4; H, 9.0; N, 12.5; B, 9.6; Cl, 31.5. Found: C, 37.9; H, 8.6; N, 12.6; B, 9.95; Cl, 26.1.

In an NMR experiment, 43 mg of **2** in 0.5 mL of methylene chloride was monitored at machine temperature (~38 °C). The large singlet at 2.10 ppm for the $-CH_2N(CH_3)_2$ moiety diminished and disappeared over 3 h, the pattern of multiplets at 2.5 ppm changed markedly, and three equivalent singlets developed to maximum area at 2.87, 3.21, and 3.41 ppm, but no peak at 0.30 ppm appeared. Evaporation of solvent left a white solid, but volatiles showed not a trace of trimethylamine by NMR analysis. Sublimation/pyrolysis of the residue gave 34 mg (0.15 mmol) of **5** and 0.17 mmol of trimethylamine collected in a −196 °C U-trap. ^{1}H NMR (Table IV) of the product matched that of previously prepared samples of 5: complex multiplet with peaks at 2.57, 2.63, 2.67, 2.72, and 2.85, broad absorption at 2.0–2.5 ppm, and a small singlet at 0.30 ppm.

Table V. Infrared Frequencies^a

Compd	Absorptions
2	2840 w, 2790 m, 2360 m, 1410 w, 1330 w, 1305 m, 1280 w, 1270 w, 1180 s, 1160 m, 1140–1135 w, d, 1120–1100 m, d, 1055 vw, sh, 1040 m, 1020 w, 990 m, 945 w, 900 m, 880 m, 800 w, br, 755 m
3-PF_6^-	3250 s, 2350 s, b, 1410 m, 1325 w, 1305 w, 1180 s, 1170 m, sh, 1130 m, 1110 m, 1090 m, 1055 w, 1035 w, 1015 m, 995 w, 975 s, 930 w, d, 850 vs, 750 m
4	3040 w, 2340 s, 2320 s, 2270 m, 1400 w, 1390 w, 1320 m, d, 1290 w, 1235 w, 1225 vw, 1175 s, 1140 m, 1130 m, 1120 sh, 1105 m, 1100 sh, 1085 m, 1030 m, 1020 m, 1005, 970 m, 965 sh, 930 w, 905 w, 885 m, 860 m, 845 m, 820 m, 780 w, 745 m
5	2440 w, 2340 w, 2260 vw, sh, 1320 m, 1170 s, 1130 w, 1105–1095 w, d, 1070 s, 1000 m, 960 s, 895 m, 870 w, 830 w, 780 w, 745 m, 720 s

^{a} As mineral oil mulls, absorptions in cm^{-1}, run on Perkin-Elmer 237 B grating spectrophotometer. Absorptions in common with mineral oil not reported. Abbreviations: s, strong; m, medium; w, weak; vw, very weak; br, broad; d, doublet; sh, shoulder.

Acknowledgment. Support of this work by a grant (GP 14902) from the National Science Foundation is gratefully acknowledged. The author is also appreciative of assistance from Dr. Walter Knoth of Central Research and Development, E. I. du Pont de Nemours & Co., Inc., in obtaining the ^{11}B NMR.

Registry No. 1, 50830-61-0; **1** (coordinated form), 14102-49-9; **2**, 63448-93-1; **2** (coordinated form), 63412-98-6; **3**-PF_6, 63448-95-3;

3-PF_6 (coordinated form), 63412-99-7; **4**, 63448-96-4; **4** (coordinated form), 63413-00-3; **5**, 63448-98-6; **5** (coordinated form), 63412-97-5; dihydrobis(trimethylamine)boron chloride, 18517-67-4; methylene chloride, 75-09-2.

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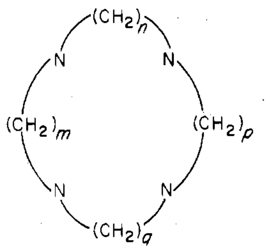
Correspondence

Coplanar Coordination of the Smallest Tetraaza Macrocycle: Low-Spin 1,4,7,10-Tetraazacyclododecanenickel(II)

AIC70230B

Sir:

Selectivity of macrocyclic ligands toward metal ions depends on (i) the effective fitting of the cation into the macrocyclic hole and (ii) the ligand's ability to adjust itself to the electronic and geometrical requirements of the metal. In the case of tetraaza macrocycles, the synthetic availability[1] of 12- to 16-membered ligands has made it possible to consider the superimposing effects of i and ii on the stereochemistry, thermodynamic stability, ligand field parameters, etc., of 3d metal macrocyclic complexes.



$m = n = p = q = 2$	[12]aneN_4
$m = n = p = 2; q = 3$	[13]aneN_4
$m = p = 2; n = q = 3$	[14]aneN_4
$m = 2; n = p = q = 3$	[15]aneN_4
$m = n = p = q = 3$	[16]aneN_4

For the Co(III),[2] Ni(II),[2] and Fe(II)[3] with most of the above ligands, a tetragonal stereochemistry, with the four nitrogen atoms occupying the equatorial sites, is the most common. Calculations have been made[2] in order to evaluate the conformational energy which a macrocycle expends in arranging its donor atoms at the corners of a square; [14]aneN_4 was found to have the least strain, the ideal M–N distance being 2.07 Å. In the case of nickel(II) complexes, the strongest metal–nitrogen interaction, measured as Dq_{xy}, has been found with [14]aneN_4,[2] in which the x-ray determined Ni–N distance is 2.06 Å[4] and is closest to the theoretical one. Furthermore, it has been recently shown that for copper(II) (Cu–N distance guessed from analogous tetragonal copper polyamine complexes: 2.01–2.09 Å)[5] the strongest in-plane interaction, as measured from the energy of the d–d band,[6] is evident with [14]aneN_4, and this correlates well with the large negative enthalpy of complex formation in water (the most exothermic among complexes with both cyclic and open tetramines).[7]

As the macrocyclic ligand hole becomes smaller, coplanar chelation becomes more and more difficult. The smallest macrocycle [12]aneN_4 (or 1,4,7,10-tetraazacyclododecane) has not been found, thus far, to coordinate Co(III) in a planar fashion, but it folds around the metal ion producing a cis complex.[8] In aqueous solution *cis*-(diaquo)Co([12]aneN_4)$^{3+}$ does not isomerize to the *trans*-diaquo species,[9] as, for instance, Co([14]aneN_4)$^{3+}$ does.[10]

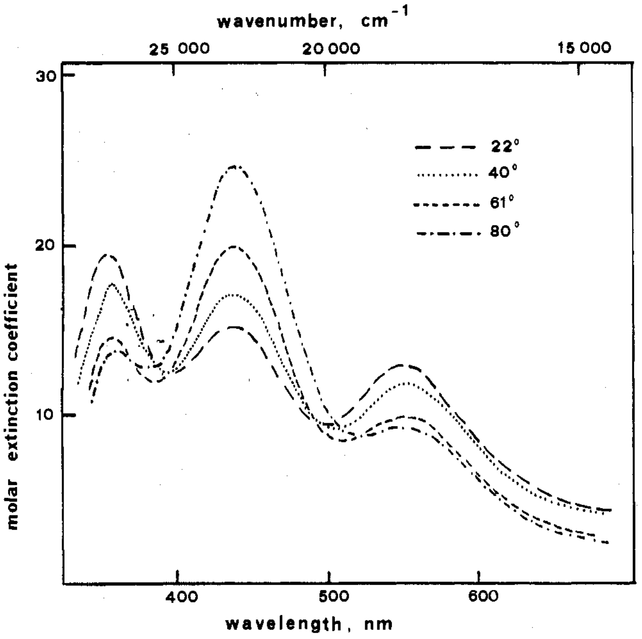


Figure 1. The visible absorption spectra of Ni([12]aneN_4)$^{2+}$ in aqueous 6 M $NaClO_4$, recorded at different temperatures.

An aqueous solution of Ni([12]aneN_4)$^{2+}$ is blue and its electronic spectrum is typical of a high-spin octahedral complex, which is presumably *cis*-diaquo. However, on addition of large amounts of inert electrolyte (e.g., $NaClO_4$) the solution turns brownish. Furthermore, if the solution is heated to boiling, its color becomes bright yellow. An increase in either salt concentration or temperature increases the intensity of a new absorption band at 23 000 cm^{-1}. The intensities of the other bands simultaneously decrease. The electronic spectra of Ni([12]aneN_4)$^{2+}$ in 6 M $NaClO_4$, recorded at different temperatures, are reported in Figure 1.

The absorption band at 21 000–23 000 cm^{-1} is typical of a yellow diamagnetic nickel(II) complex, these properties resulting from a *coplanar* arrangement of the four nitrogen atoms.[11] On the other hand, it is well known that the blue-to-yellow interconversion (1) is strongly favored by ionic

$$\underset{\text{blue, high spin}}{[NiL(H_2O)_2]^{2+}} \rightleftarrows \underset{\text{yellow, low spin}}{[NiL]^{2+}} + 2H_2O \qquad (1)$$

strength and temperature.[12]

We have demonstrated that *the smallest macrocyclic ligand [12]aneN$_4$ is able to reach a* (more or less distorted)