accurately describe this system. Plots of the natural orbitals are shown in Figure 2.

The orbital in Figure 2A is the π-bonding combination of the Mn atom with the O_2 ligand. The weakly occupied antibonding counterpart is shown in Figure 2B. The σ bond between the Mn $3d_{z^2}$ orbital and the O_2 $1\pi_u{}^s$ orbital is shown in Figure 2C. This orbital contains an internal node due to the orthogonality of the Mn $3p_z$ function to the $4p_z$, which is used in this orbital. The nonbonding, singly occupied, counterpart (Figure 2D) is centered primarily on the Mn $3d_{z^2}$ function. The doughnut ring of $3d_{z^2}$ function of this orbital is distorted to bond with the O_2 ligand. The three "pure-metal" orbitals are shown in Figure 2E–G. The singly occupied Mn $3d_{x^2-y^2}$ and $3d_{yz}$ orbitals are shown in Figure 2E,F, respectively, and the weakly occupied Mn $3d_{xy}$ orbital is shown in Figure 2G. The lobes of the last orbital are distorted so that they are directed away from the O_2 atoms.

Discussion

The final results for both the Pauling geometry, **7**, and the Griffith geometry, **9**, place the three unpaired electrons in orbitals that are primarily Mn 3d in character. Thus, our results for both yield configurations that can be described in pseudocubic symmetry as "$t_2{}^2e^1$", in agreement with the ESR spectra.

The GMO–CI results appear to give the impression that the ground-state configuration of manganese–dioxygen porphyrins favor the Pauling geometry. However, the total energies listed in Table II show that neither geometry was favored in all calculations. The difference in the total energies of the GMO–CI calculations of **7** and **9** is 18 kcal mol^{-1}. This difference is small and could be quite different if we had used a different model or a slightly different geometry. Since wave functions for ground states are usually well-behaved, the poor representation of the Pauling geometry by a single configuration and the fact that the high-spin dissociative state is lower in energy than any of the quartet states would seem to preclude this structure from being the ground-state geometry. However, we cannot eliminate the possibility that at a slightly different Pauling geometry the calculations would behave.

Our conclusion, in agreement with both the ESR and IR but in disagreement with the previous ab initio results, is that the most likely ground-state structure is the side-on Griffith geometry. This work represents the first accurate theoretical calculations that show the plausibility of that geometry, and it illustrates the importance of including electron correlation in calculations on metal–dioxygen complexes.

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Registry No. Mn(O_2)P (end on), 73066-15-6; Mn(O_2)P (side on), 74077-48-8.

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Quantum-Chemical Investigations on the Interaction of Alkaline-Earth-Metal Ions with Macrocyclic Compounds

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The preferred conformations and the "macrocyclic effect" of the cyclic ligands 1,4,7,10-tetraazacyclododecane and 1,4,7,10-tetraoxacyclodecane and their metal complexes are investigated within the framework of the HF–LCAO–MO method. The results show that the general conformation before and after complexation remains the same (only torsion angles change), i.e. the alternate form for the N_4 and the maxidentate form for the O_4 cyclic ligands. For the factors influencing the "macrocyclic effect", our results indicate the effect of the "prestraining" of the cyclic ligands to dominate in the case of the O_4 ligand. An at least equally important factor for the N_4 ligands is the difference in energy gain by metal binding. The coincidence of metal ion size and ligand ring cavity size affects not only energy consumption upon conformational changes of the ring, being adjusted to the metal ion, but also the amount of energy gain in the binding step.

Introduction

The enhanced stability of the metal complexes of cyclic ligands such as polyamines or polyethers compared to that of their open-chain analogues has been named the "macrocyclic effect".[1] In previous papers,[2,3] we have investigated factors influencing this effect, finding that noncyclic ligands must spend much energy to arrange their donor atoms suitably around the metal ion and will experience steric hindrance during this process.[4,5]

Quantitative stereochemical considerations have led to a better understanding of such factors as ring size effects, steric interaction, and flexibility and their energetic consequences. It is generally accepted, that the stability and selectivity of cyclic ligand complexes depend on the ligand's ability to adjust itself to the electronic and geometrical requirements of the metal and on the relation between the size of the metal ion and the ring cavity of the ligand.[6-13]

Until now, no theoretical study on a series of macrocyclic complexes with mono- and divalent cations has been performed. We have investigated, therefore, the effect of both metal ion size

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Table I

(a) Total Energies (hartrees) for Various Ligand Conformations[a]

ligand	form	poly-N ligand	poly-O ligand
cyclic	chair	-452.026 59	-519.309 36
	planar	-452.099 54	-519.255 49
	tetrahedral	-451.955 06	-519.236 05
	maxidentate	-452.113 72	-519.363 77
	alternate	-452.120 12	-519.356 38
open chain (L_2)[b]		-453.095 60	-520.350 27
open chain (L_3)[b]		-454.069 44	-521.337 94

(b) Torsion Angels α (deg), Out-Of-Plane Distance X_a (Å) (for the Maxidentate Form), Metal-Donor Distance d (Å), and $N_1 \cdots N_3$ ($O_1 \cdots O_3$) Distance D (Å) for the Most Stable Conformations of 1,4,7,10-Tetraazacyclododecane (L_{1N}), 1,4,7,10-Tetraoxacyclododecane (L_{1O}), and Their Complexes

system	ionic radii, Å	L_{1a} (alternate)			L_{1b} (maxidentate)			
		α	d	D	α	d	D	X_a
L		70	1.89	3.78	65	2.05	4.10	
L + Li(I)	0.60	64	1.88	3.72	56	2.04	4.08	0.50
L + Na(I)	0.95	87	2.08	4.09	65	2.28	4.10	1.00
L + Be(II)	0.31	50	1.79	3.57	0[c]	1.78	3.56	0.20
L + Mg(II)	0.65	72	1.95	3.90	54	2.05	3.96	0.55
L + Ca(II)	0.99	99	2.41	4.34	68	2.36	4.18	1.05

[a] The relative order of stability remains identical for the cyclic compounds after complexation of any of the ions considered (energies for L_2 and L_3 are lower due to the additional H atoms in this ligands and cannot be compared directly, therefore). [b] For L_2 and L_3, only the conformations analogous to the most stable cyclic ligands were used. [c] For the torsion angle 0°, alternate and maxidentate forms are identical.

and charge on the conformation of cyclic ligands and analyzed the energetic contributions to the "macrocyclic effect" in these complexes.

In continuation of our previous study with Li(I) and Na(I),[5] the macrocyclic ligands 1,4,7,10-tetraazacyclododecane (L_{1N}) and 1,4,7,10-tetraoxacyclododecane (L_{1O}) have been considered and compared with their open-chain analogues 2,5,8,11-tetraazadodecane (L_{2N}), 2,5,8,11-tetraoxadodecane (L_{2O}), 2,5-diazahexane (L_{3N}), and 2,5-dioxahexane (L_{3O}). Be(II), Mg(II), and Ca(II) ions were chosen for the evaluation of metal size effects. In addition, Mg(II) and Ca(II) ions have nearly the same ionic radii as Li(I) and Na(I) ions (Li(I) = 0.60 Å, Be(II) = 0.31 Å, Mg(II) = 0.65 Å, and Ca(II) = 0.90 Å),[14] allowing thus the investigation of charge effects.

Method of Calculation

Ab initio MO–SCF calculations with a minimal GLO basis set[15] being used successfully in previous investigations[2,3] have been employed.

The nonsensitive geometrical parameters (bond lengths and bond angles) of the ligands obtained in the previous work[2] were kept constant throughout the calculations. To find the most stable conformation of the free ligands and the complexes, the planar, chair, maxidentate, alternate, and tetrahedral forms were considered. For the most stable forms a further optimization procedure was carried out, in which the torsion angles (α) around the C–C bond (α_{NCCN} and α_{OCCO}) and, by this, automatically also the ring size for the maxidentate and alternate forms were optimized with respect to the lowest total energy for free ligands and complexes. In the case of the complexes, the metal ions were positioned in the center of the ligand for the planar and maxidentate forms and the distance above the N or O plane (out-of-plane distance, X_a) was also optimized. The optimization process has been discussed in detail in ref 2.

All computations were performed on the CDC Cyber 74 computer of the University of Innsbruck.

Results and Discussion

I. Conformational Analysis. The total energies for the optimized complex conformations are given in Table Ia. The optimized parameters, torsion angles (α) and out-of-plane (X_a), metal–donor (d), and $N_1 \cdots N_3$ (and $O_1 \cdots O_3$) (D) distances, together with the most stable conformation of each metal–cyclic ligand–complex, are summarized in Table Ib.

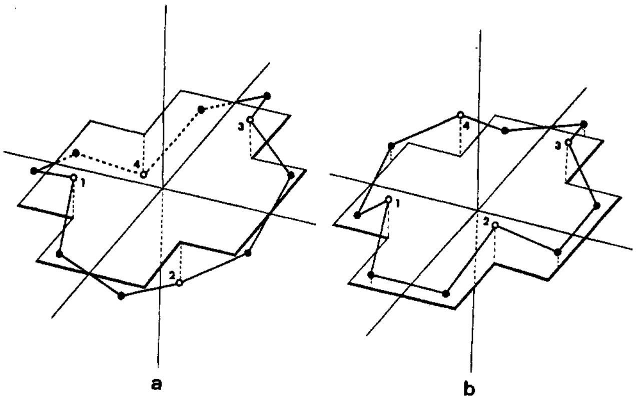

Figure 1. The most stable conformations of (a) 1,4,7,10-tetraazacyclododecane (alternate form) and (b) 1,4,7,10-tetraoxacyclododecane (maxidentate form).

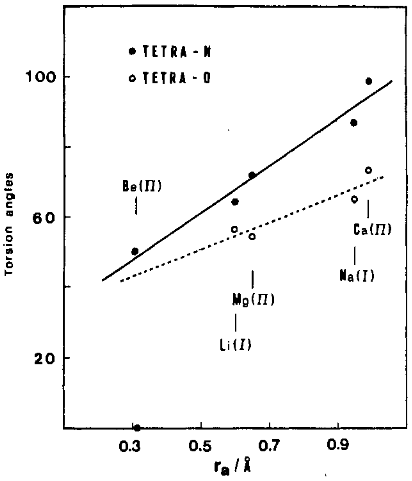

Figure 2. Torsion angles of the most stable ligand conformation in the complexes vs. ionic radii.

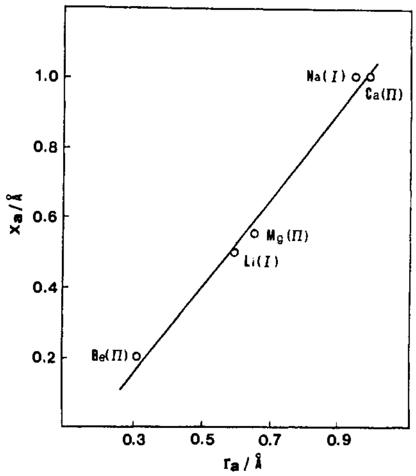

Figure 3. Out-of-plane distances for the most stable maxidentate complexes of 1,4,7,10-tetraoxacyclododecane as a function of ionic radii.

The minimum energy conformations for complexes and free ligands, namely the alternate form for L_{1N} (N_4; Figure 1a) and the maxidentate form for L_{1O} (O_4; Figure 1b), are the same in all cases. Only a change of the torsion angles (and hence of the $N_1 \cdots N_3$ or $O_1 \cdots O_3$ distances) occurs. It is noticed that a very small metal ion such as Be(II) can contract the O_4 ring, leading to a torsion angle of 0° (where the alternate and the maxidentate form become identical) and 50° for the N_4 ring. The ring deformation depends mostly on the ionic radii and somewhat less on the charge

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Table II. Energy Balance for the Complex Formation Processes of the Mono- and Divalent Cations with the Cyclic and Open-Chain Ligands (kcal mol^{-1})

process[b]	Li(I)[a]	Na(I)[a]	Be(II)	Mg(II)	Ca(II)
(I) Poly-N Ligands					
(a) Cyclic Ligand, L_{1N}					
1a	+0.9	+8.9	+6.1	+0.3	+21.3
2a	−123.6	−43.5	−413.3	−268.8	−125.1
3a	−122.7	−34.6	−407.2	−268.5	−103.8
(b) Noncyclic Ligand, L_{2N}					
1b	+17.7	+20.5	+26.4	+16.5	+27.3
2b	−107.6	−39.5	−386.2	−240.0	−116.4
3b	−89.9	−19.0	−359.8	−233.5	−89.1
(c) Noncyclic Ligand, L_{3N}					
1c	+1.8	+1.8	+1.8	+1.8	+1.8
2c	+29.1	+32.4	+39.7	+27.4	+27.3
3c	−90.3	−28.4	−361.3	−212.2	−87.5
4c	−59.4	+4.8	−319.8	−182.9	−58.4
(a) Cyclic Ligand, L_{1O}					
1a	+5.3	0.0	+37.1	+5.1	+0.2
2a	−57.6	−59.0	−229.4	−156.1	−151.5
3a	−52.3	−59.0	−192.3	−150.8	−151.3
(b) Noncyclic Ligand, L_{2O}					
1b	+44.8	+41.8	+114.4	+46.7	+42.0
2b	−61.3	−52.2	−223.6	−168.4	−139.3
3b	−16.5	−10.4	−109.2	−139.7	−97.3
(c) Noncyclic Ligand, L_{3O}					
1c	+5.1	+5.1	+5.1	+5.1	+5.1
2c	+39.0	+38.2	+147.1	+39.6	+58.3
3c	−67.4	−45.3	−217.5	−191.4	−124.4
4c	−23.3	+2.0	−65.3	−146.7	−61.0

[a] Value taken from ref 2. [b] Processes, a, b, and c correspond to eq a, b, and c.

Table III. Energy Gain of the Macrocyclic Effect ($\Delta E_{mac} = \Delta E_{3a} - \Delta E_{3b}$), Separated into the Energy Difference of the Conformational Change ($\Delta E_{conf}{}^{mac} = \Delta E_{1a} - \Delta E_{1b}$) and of the Binding Step ($\Delta E_{bind}{}^{mac} = \Delta E_{2a} - \Delta E_{2b}$) (kcal mol^{-1})

	tetraaza ligand			tetraoxa ligand		
ions	ΔE_{mac}	$\Delta E_{conf}{}^{mac}$	$\Delta E_{bind}{}^{mac}$	ΔE_{mac}	$\Delta_{Econf}{}^{mac}$	$\Delta E_{bind}{}^{mac}$
Li(I)	−32.8	−16.8	−16.0	−35.8	−39.5	+3.7
Na(I)	−15.6	−11.6	−4.0	−48.6	−41.8	−6.8
Be(II)	−47.4	−20.3	−27.1	−83.1	−77.3	−5.8
Mg(II)	−45.0	−16.2	−28.8	−11.1	−41.6	+30.5
Ca(II)	−14.7	−6.0	−8.7	−54.0	−41.8	−12.0

of the metal ion, especially in the case of the N_4 ring (Figure 2). For the O_4 ring (except in the case of the Be(II) complex), the metal ion stays above the plane of the O atoms rather than inducing a larger deformation of the ligand (cf. Figure 2).

In Figure 3, the out-of-plane distances for the most stable form of the O_4 complexes are plotted against the ionic radii of the metal ions, showing a linear relation (statistical significance: $R = 0.995$). Therefore, the binding distances apparently do not depend very much on the ion charge. In the case of the alternate tetraaza complexes, such a simple relation could not be found, as the metal ion rests in the center of the complex and all geometrical effects are related to more complex changes in the molecular backbone of the ligand.

Considering the complexation energies (Table II) and considering the influence of the atomic charge within metals of similar ionic radii, it can be concluded that the charge affects mainly the amount of the energy gain due to metal binding (for both cyclic and open-chain ligands; c.f. Table II) but also the ring cavity (torsion angles, Table Ib) and the specific energy gain of the macrocyclic effect (ΔE_{mac}, Table III), which will be discussed in the following section.

II. Energetic Analysis. The complex formation processes between metal ions and the cyclic (L_{1N}, L_{1O}) and noncyclic (L_{2N}, L_{2O}, L_{3N}, L_{3O}) ligands can be written as

$$\overbrace{L(\text{conf }1) \xrightarrow{(1a)} L(\text{conf }2) \xrightarrow{(2a)} ML^+}^{(3a) = (1a) + (2a)} \qquad (a)$$

$$\overbrace{L(\text{expand}) \xrightarrow{(1b)} L(\text{contract}) \xrightarrow{(2b)} ML^+}^{(3b) = (1b) + (2b)} \qquad (b)$$

$$\overbrace{2L(\text{trans}) \xrightarrow{(1c)} 2L(\text{cis}) \xrightarrow{(2c)} L_2(\text{dimer}) \xrightarrow[M^+]{(3c)} ML^+}^{(4c) = (1c) + (2c) + (3c)} \qquad (c)$$

M^+, L, and ML^+ (or $M(L_2)^+$) are the metal ion, ligand, and metal–ligand complex, respectively. Before complexation, the conformation of the cyclic ligands will be changed from the most stable conformation of the free ligand (conf 1) to that in the complex (conf 2) (eq a). For the open-chain ligands, the conformation of L_{2N} and L_{2O} have to be changed (eq b) from the most stable expanded chain form, L(expand), to the geometry suitable for complex formation, L(contract). In case of L_{3N} and L_{3O} ligands (eq c), the optimal trans form of the free ligands, L(trans), has to change to the cis conformation, L(cis), and to a pseudo dimer structure, L(dimer), suitable for complex formation. The bond lengths and angles for the configurations L(contract) and L_2(dimer) were the same as the corresponding optimized parameters for the cyclic compounds.

The results of the calculations for the above processes are summarized in Table II, demonstrating that the open-chain ligands consume much energy to arrange their donor atoms suitably around the metal ion (eq 1b, 1c, and 2c), thus compensating most of the energy gain in the binding step (eq 2b and 3c), especially in the case of the O_4 ligand. When the energy gain of the macrocyclic effect ($\Delta E_{mac} = \Delta E_{3a} - \Delta E_{3b}$, the subscripts *i*a, *i*b, and *i*c with $i = 1, 2, 3, 4$, correspond to eq a, b, and c) is separated into the energy gain related to the conformational changes ($\Delta E_{conf}{}^{mac} = \Delta E_{1a} - \Delta E_{1b}$) and the binding energies ($\Delta E_{bind}{}^{mac} = \Delta E_{2a} - \Delta E_{2b}$), as shown in Table III, it is clearly seen that only for the tetraoxa ligand is the prestrained conformation of the cyclic ligand the dominant factor determining the "macrocyclic effect" as assumed in ref 2–5. For the tetraaza ligands, the difference in the binding energies between cyclic and noncyclic ligands is even more important than that between strain energies, especially in the case of divalent cation complexes (cf. Table III). However, both binding energies (eq 1a) and strain energies (eq 2a) also clearly indicate metal specificities of both ligands within the series investigated.

On the relative scale, the order of the specific energy gain for the complexes (both cyclic and noncyclic) should be Li(I) < Na(I) and Be(II) < Mg(II) < Ca(II), but our results indicate a disorder of the $\Delta E_{bind}{}^{mac}$ of the Mg^{II}–N_4 complex and practically all complexes with the tetraoxa ligand. In ΔE_{mac}, we find exceptional behavior for Mg^{II}–N_4 and Na^{I}–O_4 and Ca^{II}–O_4 complexes. These are also the three cases with the best geometrical "fit" of ion size and ligand conformation (and, hence, the lowest conformation changes upon ion binding). It can be concluded, therefore, that a good "fit" of the metal ion size and the ring cavity of the ligand not only increases the "macrocyclic effect" due to less energy consumption for necessary conformational changes but also increases the amount of binding energy due to the maximal overlap of metal and ligand functions.

In Figure 4, $\Delta E_{3a}/q$ (q being the metal ion charge) is plotted vs. the ionic radii of the metal ions. A somehow linear relation is observed only for the tetraaza complexes (statistical significance: $R = 0.983$). Therefore, the binding of this cyclic ligand to the ions can be understood to a large extent on the basis of an electrostatic interaction, whereas this is surely not the main factor for the tetraoxa complexes.

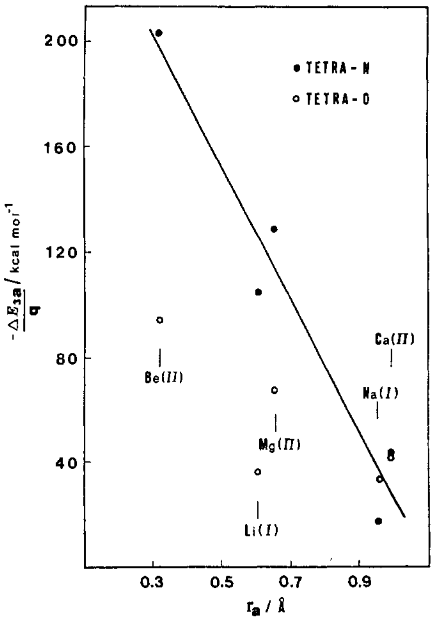

Figure 4. Charge-normalized stabilization energies of metal complexes with macrocyclic ligands vs. ionic radii.

Table IV. Calculated Stabilization Energies between the Metal Ions and the Cyclic Ligands (ΔE_{3a}) Compared to Calculated Hydration Energies per Water Molecule in the Octahedrally Coordinated First Hydration Shell ($\Delta E_{calcd}{}^{O_h}$) (kcal mol^{-1})

ions	$4\Delta E_{calcd}{}^{O_h\,a}$	$\Delta E_{3a}{}^{N_4}$	$\Delta E_{3a}{}^{O_4}$
Li(I)	-88.4	-122.7	-52.3
Na(I)	-61.6	-34.6	-59.0
Be(II)	-421.6	-407.2	-192.3
Mg(II)	-202.0	-268.5	-150.8
Ca(II)	-187.6	-103.8	-151.6

[a] Value taken from ref 17.

If binding energies for the cyclic (eq 2a) and noncyclic (eq 2b and 2c) ligands are compared, it can be seen that the electronic structure of a closed ring system is apparently very much in favor of electron density rearrangements upon metal binding, similar to the "electronic chelate effect" observed for two noncyclic ligands forming a ring system via hydrogen bonds.[16]

In Table IV, ΔE_{3a} is compared with calculated binding energies per water molecule in an octahedrally coordinated first hydration shell ($\Delta E_{calcd}{}^{O_h}$), computed with the same basis set as used in our work.[17] It can be assumed that the metal ion in the complex will be hydrated by only two water molecules,[18-24] because of steric reasons. In this case, four water molecules from the first hydration shell will be released upon complexation; i.e., the metal ion is supposed to form an energetically stable complex whenever $\Delta E_{3a} > 4\Delta E_{calcd}{}^{O_h}$. Our data predict, therefore, enthalpy-stabilized metal complexes ($\Delta E \simeq \Delta H < 0$) in aqueous solution only for Li(I) and Mg(II) with the tetraaza ligand but no such cases for the tetraoxa ligand.

Unfortunately, no experimental data for these specific complexes have been reported yet. It is obviously not sufficient to consider only hydration and the complexation energies of the metal ion, as entropy effects might have another considerable influence.[25] However, a similar prediction based on energies only was made by Fukui et al.,[23] using the CNDO/2 method (generally unsuitable for metal complexes[26-28] in calculations on complexes of alkali-metal ions with O_4 ligands.

Recent investigations by Clay[29] have shown that, for one and the same metal ion, differences in complex stability can be explained merely on the basis of the difference of hydration enthalpies in a series of macrocyclic ligands. This indicates that the principal results obtained in our investigation on the two model compounds (N_4 and O_4 cyclic ligands) should have a general validity even for higher analogues of these ligands, if metal ion and ligand character do not differ too much.

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Alkali-Metal and Ammonium Peroxyfluoroborates. First Synthesis of Peroxyfluoroborate Complexes

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It has been known for quite some time that orthoboric acid reacts in solution[1] with hydrogen peroxide giving peroxyboric acid, which most probably contains the $[B_2(O_2)_2(OH)_4]^{2-}$ anion. Alkali-metal salts of this anion are also known and constitute an important oxidizing component in many washing powders. The commercially most important compound in this context is $Na_2B_2(O_2)_2(OH)_4 \cdot 6H_2O$. No heteroligand peroxyborate is known to our knowledge. As a part of our program of synthesis, structural assessment, and studies of reactivities of peroxy compounds of metals,[2] we have extended our investigation to boron and expected that the results obtained would provide internally consistent data regarding the effect of heteroligands on the stability of peroxyborate systems. In this report we present an account of the synthesis and assessment of structures of the first examples of heteroligand peroxyborates of the types $A_2B(O_2)F_3 \cdot 4H_2O$ (A = Na or K) and $(NH_4)_2B_2(O_2)_3F_2$.

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