transition state on the reaction coordinates.

In conclusion, the present work strongly suggests that the thermally activated nonradiative decay process is the same for Rh$_2$(TMB)$_4^{2+}$ in all environments tested. As the BB correlation holds in single-crystal, dilute-crystal, and dilute-plastic environments, the deactivation process does not depend on the close proximity of two or more Rh$_2$(TMB)$_4^{2+}$ ions. However, the present work does not imply a mechanism for the deactivation. We have previously postulated that the thermal activation from the $^3A_2$ state is possibly to a nonemissive ligand field state.[1] While the current results are not inconsistent with this interpretation, they are by no means conclusive proof. Other reasonable mechanisms can be envisioned, such as a thermally activated distortion within the $^3A_2$ state, which leads to direct crossing to high vibrational levels of the ground state. Further work is in progress on the intimate details of the photophysics of dinuclear d^8–d^8 metal complexes.

Acknowledgment. I thank Drs. Harry B. Gray, David S. Kliger, Robert A. Goldbeck, and Steven F. Rice for helpful discussions during the course of this work. The National Science Foundation (Grants CHE81-20419, PMC83-17044) is acknowledged for partial support of this work.

Registry No. Rh$_2$(TMB)$_4^{2+}$, 73367-41-6.

Contribution from the Department of Chemistry,
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Anomalous Metal Ion Size Selectivity of Tetraaza Macrocycles

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Received September 24, 1984

The apparent paradox that larger metal ions coordinate more strongly to the small macrocycle 12-aneN$_4$ than to the large 14-aneN$_4$ is examined. (12-aneN$_4$ = 1,4,7,10-tetraazacyclododecane; 14-aneN$_4$ = 1,4,8,11-tetraazacyclotetradecane.) Molecular mechanics calculations (MM) show that, in its trans-I conformer, 12-aneN$_4$ has a larger cavity, with best-fit M–N lengths of 2.11 Å, compared with 2.05 Å for 14-aneN$_4$. In addition, the macrocyclic ring of 12-aneN$_4$ is more flexible than that of 14-aneN$_4$, allowing better response to a change of metal ion size. Thus, as explained by using the MM calculations, most metal ions complex most strongly to 12-aneN$_4$, with only small metal ions such as Cu(II) preferring the large 14-aneN$_4$. In order to supplement and check existing formation constants on the tetraaza macrocycles, log K_1 values for the following metal ions were determined: with 12-aneN$_4$, Cu(II) 23.29; with 13-aneN$_4$, Cu(II) 24.36; with 14-aneN$_4$, Cu(II) 26.5 (all at 25 °C and in 0.5 M NaNO$_3$, determined spectroscopically by using the variation in the UV-visible spectrum as a function of pH); with 13-aneN$_4$, Pb(II) 13.48, Cd(II) 12.71; with 14-aneN$_4$, Pb(II) 10.83, Cd(II) 11.23 (all determined by glass-electrode potentiometry in 0.1 M NaNO$_3$ at 25 °C).

Molecular mechanics (MM) calculations have been carried out[1,2] to calculate the hole sizes in tetraaza macrocycles. These calculations have been confined to the case where the metal ion is constrained to lie within the plane of the four nitrogen donors and give best-fit metal to nitrogen bond lengths for these macrocycles as follows:[1] 12-aneN$_4$, 1.82 Å; 13-aneN$_4$, 1.92 Å; 14-aneN$_4$, 2.07 Å; 15-aneN$_4$, 2.22 Å; 16-aneN$_4$, 2.38 Å. By analogy with the behavior with the crown ethers,[3] if the metal ions were constrained to lie in the plane of the nitrogen donors, we might expect the highest stability in the complexes of metal ions with the member of the above series that most closely fitted the bond length requirements of the metal ion.

Examination of the literature[4] shows that this is not the case. First, a metal ion such as Zn^{2+}, which has a best-fit M–N length in the range 2.1–2.2 Å, shows its greatest stability[4] with the very smallest macrocycle, 12-aneN$_4$, rather than 14-aneN$_4$ or 15-aneN$_4$, which should fit it more closely if the requirement of planar coordination is adhered to. Interestingly, the relative preference for 12-aneN$_4$ over the larger members of the series increases as the metal ion becomes larger. This is seen in Figure 3, where Hg^{2+} has log K_1 for 12-aneN$_4$ some 2 orders of magnitude larger than for cyclam. We have extended the data on log K_1, the formation constant, for the tetraaza macrocycles by using glass-electrode potentiometry, in this work. With the very large Pb^{2+} ion, as seen in Figure 3, the preference for 12-aneN$_4$ becomes even more marked.

When we examined the reported[5] log K_1 values for Cu(II) with the tetraaza macrocycles from 12-aneN$_4$ through 14-aneN$_4$, a rather puzzling feature was the fact that the stability peaked at 13-aneN$_4$. The reported[6] values of ΔH and the energy of the d–d transitions peak at the 14-aneN$_4$ complex, which, with a best-fit M–N length[1,2] of about 2.05 Å, should fit perfectly around Cu(II) with a strain-free Cu–N length[7] of 2.03 Å. It is thus a rather surprising result that the stability should peak at a macrocycle that is too small for Cu(II), particularly as ΔH and the d–d energies do not peak here. The previous[5] study of the 12-aneN$_4$ through 14-aneN$_4$ complexes of Cu(II) was carried out polarographically. An alternate, and potentially more reliable method, is to study these systems by following the electronic spectra as a function of pH. This would require an "out-of-cell" study of the kind carried out by Zompa[8] on Ni(II) with the cyclic amine 9-aneN$_3$, where the solutions would be allowed to equilibrate in sealed flasks, each corresponding to a single titration point, before the spectra were recorded.

In this paper, then, we report the glass-electrode potentiometric determination of the formation constants of complexes of Pb(II) and Cd(II) with 13-aneN$_4$ and 14-aneN$_4$ and the spectroscopic determination of the Cu(II) complex formation constants with these two ligands, plus 12-aneN$_4$. A very clear pattern emerges from all these constants plus the existing literature values, namely, that the larger the metal ion, the greater its preference for 12-aneN$_4$ becomes. We have carried out MM calculations on tetraaza macrocycles,[2,9,10] which have indicated that metal ion size preference exhibited by these ligands varies with conformation. We examine here the question of how the adoption of different conformers can enable the small ligand 12-aneN$_4$ to complex more effectively with large metal ions.

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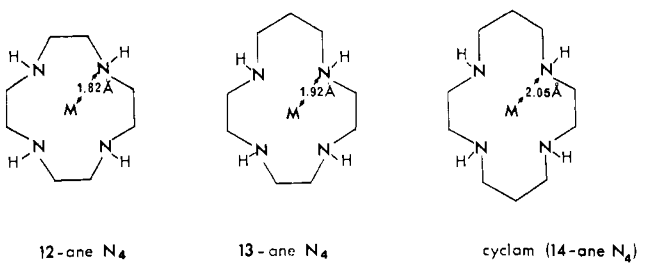

Figure 1. Complexes of ligands discussed in this paper. The distances from the metal to the nitrogen donors in each complex are the ideal "best-fit" metal nitrogen bond length for fitting into the macrocycle in its trans-III conformer.[2]

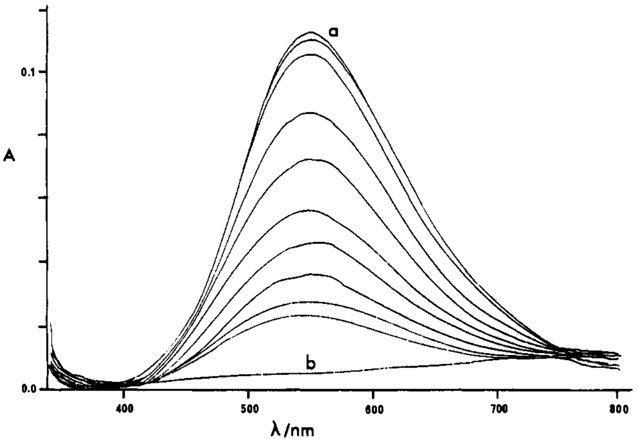

Figure 2. Spectra of a series of solutions containing 1.101 × 10^{-3} M 13-aneN_4 and 5 × 10^{-4} M Cu^{2+}, with varying amounts of acid and with the total ionic strength of the HNO_3/$NaNO_3$ mixture being kept constant at 0.5 M. The spectrum marked a is that of the complex in 0.5 M $NaNO_3$ with no acid present, while that marked b is of a 5 × 10^{-4} M solution of Cu^{2+} with no 13-aneN_4 present, in 0.5 M $NaNO_3$. The intermediate spectra are with acid added to give the following calculated pH values, in order of decreasing intensity from solution a: 1.536, 0.983, 0.690, 0.595, 0.517, 0.451, 0.394, 0.343, 0.298.

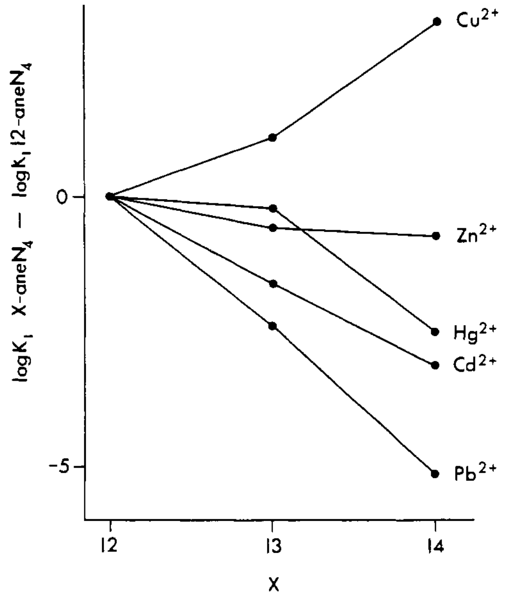

Figure 3. Stability of complexes of the X-aneN_4 macrocycles (13- and 14-aneN_4) relative to the stability of the 12-aneN_4 complex as a function of X, the number of atoms in the macrocyclic ring of X-aneN_4.

Table I. Thermodynamic Values for Complexation of Metal Ions by Tetraaza Macrocycles[a]

metal ion	function	12-aneN_4	13-aneN_4	14-aneN_4
Cu^{2+}	log K_1	23.29 (6)[b]	24.36 (5)[b]	26.5 (1)[b]
	log K_1 (lit.)	(24.8)[c]	(29.1)[c]	(27.2)[c]
	ΔH[c]	−22.7	−25.6	−32.4
	ΔS[c]	30	26	13
Pb^{2+}	log K_1	15.9[d]	13.48 (5)[e]	10.83 (7)[e]
Cd^{2+}	log K_1	14.3[d]	12.71 (5)[e]	11.23 (3)[e]
H^+	pK_{a1} (lit.)		11.02[f] (11.0)[g]	11.3[f] (11.6)[h]
	pK_{a2} (lit.)		9.96 (10.0)	10.23 (10.6)
	pK_{a3} (lit.)		1.96 (1.6)	1.43 (1.61)
	pK_{a4} (lit.)			2.27 (2.42)

[a] This work and literature values for comparison were all performed at 25 °C. For abbreviations of ligands, see Figure 1. [b] At ionic strength 0.5, maintained with 0.5 M H^+/Na^+ NO_3^-. pK_a values for calculating log K_1 are from ref 15 and 16. [c] Values at ionic strength 0.1, from ref 5. The ΔH values are from ref 6 and were used to calculate the ΔS values shown, assuming that ΔH would not be affected by differences in ionic strength. [d] Reference 4, ionic strength 0.1. [e] This work, 0.1 M $NaNO_3$. Figures in parentheses are estimated standard deviations. [f] This work, ionic strength 0.1. Estimated standard deviations on pK_a values are 0.01 log unit. [g] Values from ref 15, ionic strength 0.1. [h] Values from ref 16. The agreement is reasonable with our own values considering the difference in ionic strength (0.1 and 0.5). Particularly noteworthy is the fact that we also find a value of pK_{a3} for cyclam which is less than pK_{a4}, as found in ref 16.

Experimental Section

Materials. 14-aneN_4 was obtained as the free ligand from Strem Chemicals, while 12-aneN_4 was obtained as the tetrahydrochloride from the Parish Chemical Co. 13-aneN_4 was synthesized by a literature method[11] and obtained as a hydrobromide. It was found that the freshly recrystallized material analyzed as having 3.75 HBr per amine molecule but that, after extensive drying under vacuum, the analysis indicated that there were 3.33 HBr per amine molecule. Stock solutions of the amines were prepared and then standardized by titration with acid. For the 12-aneN_4 and 13-aneN_4 stock solutions, the halide ions were removed by addition of the calculated quantity of $AgNO_3$ followed by filtration and restandardization. The metal ion solutions were prepared from the AR nitrate salts and standardized by standard procedures.

Instrumentation. The electronic spectra were recorded on a Varian 2300 spectrophotometer with cells thermostated to 25 °C.

Potentiometry. The potentiometric titrations were carried out as described previously.[12] It was found that equilibration of the solutions of Cd(II) and Pb(II) ions with 13-aneN_4 and 14-aneN_4 was rapid and that no special measures were necessary in obtaining the log K_1 values for these systems. For Cu(II), the solutions made up ranged in acid strength from 0.5 M HNO_3 to pH values of about 4, over which range it was found that, for all the macrocycles, the equilibrium varied from virtually complete breakup to complete formation of the complex. For the spectrum of the copper(II) ion with no complex formation, solutions with no macrocycle present were used. The spectra of the set of solutions for Cu(II) with 13-aneN_4 as a function of acid concentration are seen in Figure 2. Equilibration of the Cu(II) macrocycle solutions took 1 week. The pK_a and log K_1 values determined are seen in Table I.

Molecular Mechanics Calculations. These were carried out as described previously.[9] The important feature of these MM calculations is to discover what happens to the strain energy of the complex as the size of the metal ion is varied. To be completely rigorous, one should do the calculations with constants appropriate for each metal ion. However, a simpler, and more informative, approach is to keep all the constants, such as N–M–N and M–N–C bending constants and the M–N stretching force constant, fixed at those for one metal ion, in this case the Ni(II) ion, because it is an "average" ion, with M–L bonds that are neither very strong nor very weak and neither very ionic nor very covalent. All that is varied is the r^0 value, i.e. the strain-free M–N length that the metal ion would have in the absence of any steric effects. One is in this way effectively varying the size of the metal ion, and a curve of strain energy, U, vs. M–N bond length can be obtained. The minima in these curves indicate what the best-fit metal ion size is for the particular ligand. Of interest here is the fact that this is different[9] for the different conformations of the complex, and we report here the results on the conformers that were previously identified[9] as being the most stable for 12-aneN_4 and 14-aneN_4, which we believe explains the paradoxical behavior whereby the largest metal ions prefer the smallest macrocycle most strongly.

Results and Discussion

The formation constants for the complex with 12-aneN_4, 13-aneN_4, and 14-aneN_4 are seen in Table I. It is seen that the

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(11) Fabbrizzi, L. *J. Chem. Soc., Dalton Trans.* **1979**, 1857.

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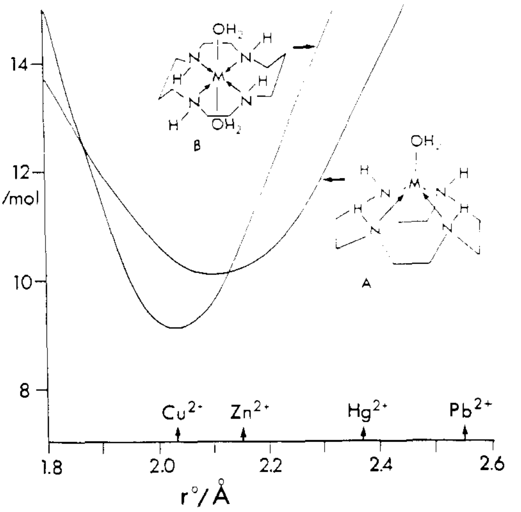

Figure 4. Relationship between strain energy, U, and ideal M–N bond length, $r°$, for the trans-I form of 12-aneN_4 complex (A) and the trans-III form of 14-aneN_4 complex (B). Diagrams A and B show these conformers for the 12-aneN_4 and 14-aneN_4 complexes, respectively. The arrows indicate the strain-free bond lengths for Cu(II), Zn(II), and Hg(II), showing that Cu(II) will have a complex with 14-aneN_4 that is more stable than that with 12-aneN_4, that Zn(II) will show a weak preference for 12-aneN_4, and that Hg(II) will have a strong preference for 12-aneN_4. As discussed in the text, the curve for 14-aneN_4 is the calculated one, while that for 12-aneN_4 has been shifted upward slightly.

constants determined for Cu(II) by us are in considerable disagreement with those reported previously.[5] The accuracy with which our constants were determined is considered to be better than 0.1 log unit, and we believe that our constants are to be preferred. We have combined our constants with the previously reported[6] values of ΔH to calculate the values of ΔS shown in Table I. It is seen that the ΔS values for the 12-aneN_4 and 13-aneN_4 complexes are much more favorable than for cyclam. This is reasonably accounted for by the idea that the two smaller macrocycles will form complexes with Cu(II) that are five-coordinate, as indicated by crystal structures,[9,13] whereas the cyclam complex probably retains two axial water molecules. The more favorable entropy for the 12- and 13-aneN_4 complexes is thus accounted for by loss of more water molecules than is the case for cyclam on complex formation.

Figure 3 shows the variation in log K_1 for the macrocycles 12- through 14-aneN_4 relative to the stability of the 12-aneN_4 complex. It is seen that only for Cu(II) is there an increase in stability from 12-aneN_4 to cyclam. For all the other metal ions, which are larger than Cu(II), there is a small to sharp decrease in stability, depending on the size of the metal ion. Thus, for the moderately large Zn(II), the downward drift in stability is small, but for the very large Pb(II) ion, it is very marked.

This, then, is the anomalous set of results that are to be analyzed by MM calculation. From the fact that the thermodynamic and crystallographic evidence suggests that the coordination number of the Cu(II) varies along the series of macrocycles and that there exists the possibility that the macrocycles may adopt[9] any one of several conformers, including folded and planar forms, this could be pursued in great detail, adding only to the confusion surrounding the problem. However, a very simple approach can serve to clear up the apparent paradox.

Our previous work[9] showed that for 12-aneN_4 complexes the lowest strain energy form was the trans-I isomer,[20] shown in Figure 4, while for cyclam complexes, the lowest strain energy form was for most metal ions the trans-III form, which is that observed in the vast majority of cyclam complexes. The minimum in the curve of strain energy, U, vs. metal to nitrogen bond length occurs at 2.11 Å in the 12-aneN_4 complex in its trans-I form, while for cyclam, the minimum occurs at 2.05 Å M–N length in its most stable conformer, the trans-III form. In addition, as seen in Figure 4, the shapes of the two curves differ, in that the curve of U vs. R for 12-aneN_4 complexes is very much flatter than for those of cyclam. This indicates that the trans-I conformer of the 12-aneN_4 ligand is very much more tolerant to change in metal ion size than is the case for the trans-III form of cyclam. This can be understood in terms of the fact that the six-membered chelate rings present in the cyclam complex are rather like cyclohexane rings in having an optimal arrangement of the hydrogen atoms with respect to torsional effects; i.e., the hydrogens on adjacent atoms of the ring are in the staggered rather than the eclipsed position. This positioning of the hydrogens leads to considerable resistance to expansion or contraction of the macrocyclic ring, whereas in 12-aneN_4 the hydrogens cannot achieve any such optimal arrangement and there is relatively facile expansion and contraction of the macrocyclic ring.

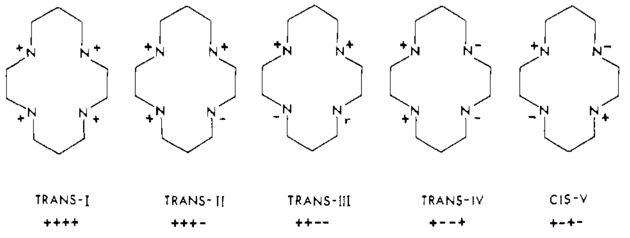

Figure 5. Convention used for describing the nitrogen configurations of the coordinated tetraaza macrocycles, used in this paper, which is that according to Bosnich et al.[18] The cis and trans prefixes indicate whether the two remaining ligand sites in octahedral coordination would be cis or trans to each other. The signs + and – indicate whether the hydrogens on the nitrogens would lie above or below the plane of the page with the macrocycle flattened so as to lie in the plane.

The curves of U vs. R for the complexes of 12-aneN_4 and cyclam in Figure 4 have been adjusted vertically relative to each other so as to accord with the observable chemistry. Thus, we account for the preference of Cu(II) for cyclam by virtue of the fact that the strain energy for cyclam is lower than for 12-aneN_4 for metal ions of M–N length below about 2.12 Å. Zn(II) occurs just slightly above this transition point and so shows a weak preference for 12-aneN_4, while for larger metal ions, this preference for 12-aneN_4 becomes rapidly stronger as the M–N length increases. Examination of the U vs. $r°$ curves for 13-aneN_4 complexes shows[9] behavior of an intermediate nature, so that, for simplicity, these are not included in Figure 4. As already mentioned, the two curves in Figure 4 have been adjusted relative to each other in a vertical sense so as to accord with the observed chemistry. It would be more correct to calculate them relative to the energies of the free ligands and use this increase in strain energy on complex formation to adjust them relative to each other, as has been done for other ligand systems.[14] If this is done, it is found that the curve for the 12-aneN_4 complexes is lower than that for the 14-aneN_4 complexes at all $r°$ values. The most important factor here is obviously the change in coordination number, which appears from the thermodynamics to occur in passing from the cyclam to the 12- and 13-aneN_4 complexes of Cu(II). The latter two ligands close off one of the axial sites on the metal ion, as seen in Figure 4, so that the Cu(II) complexes are five-coordinate, whereas the cyclam complex most likely still retains both axially coordinated water molecules, which probably leads to a stabilization of the Cu(II) complex of the latter ligand as compared with the 12- and 13-aneN_4 complexes. Another contributing factor here is the fact that our calculations have been carried out by using a constant value of the metal–nitrogen force constants, appropriate to high-spin Ni(II). This simplifying feature neglects the fact that M–N force constants for metal ions with short M–N bonds should

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generally be stronger than for large metal ions which have long M–N bonds. Large metal ions, such as Pb(II) with a M–N length in the vicinity of 2.5–2.7 Å (depending on coordination number), should thus have weak M–N force constants and be tolerant of considerable distortion of the M–N bonds. Thus, the fact that coordination to the trans-I conformer of 12-aneN_4 requires the metal to lie some 0.5 Å above the plane of the four nitrogen donor atoms[9] should present no problem. However, for smaller metal ions such as Cu(II), where such distortion of the M–N bonds will be met by strong resistance from the much larger force constants, the requirement of lying well above the plane of the nitrogen donors will cause considerable steric strain. This would lead to a destabilization of the 12- and 13-aneN_4 complexes relative to the cyclam complex, where the metal ion lies in the plane of the ligand. Yet another complicating feature which we might consider is that[9] for large metal ions (r° above 2.2 Å) the folded cis-V and trans-I forms of cyclam complex become more stable than the trans-III form, which we have considered here. This, however, serves only to narrow the gap in stability between the 12-aneN_4 and cyclam complexes for large metal ions, and there is no need to consider this in any detail either.

Figure 4 thus serves as an excellent, if rather simplified, analysis of the hole-size preference of the tetraaza macrocycles, indicating why it is that larger metal ions tend to prefer the smaller 12-aneN_4 macrocycle over cyclam. An important proviso here is that the metal ion should be able to tolerate having its M–N bonds distorted so that it lies some 0.5 Å above the plane of the nitrogen donors, which is likely to be met for all large metal ions.

A reviewer has pointed out that it is not clear that one can speak of hole size when the metal ion lies well out of the plane of the donor atoms, as for 12-aneN_4 complexes. What we have shown here and elsewhere[9] is that the tetraaza macrocycles are much more flexible than might have been appreciated. This becomes apparent when we compare the variation in log K_1 produced by varying the number of six- vs. five-membered rings in the open-chain tetraaza ligand along the series trien, 2,3,2-tet, 3,2,3-tet, and 3,3,3-tet (1,4,7,10-tetraazadecane, 1,4,8,11-tetraazaundecane, 1,5,8,12-tetraazadodecane, 1,5,9,13-tetraazatridecane). It is found[17] that the variation in log K_1 along this series parallels, but is often larger than, that along the analogous series of macrocycles from 12- to 15-aneN_4. This indicates that the variation in log K_1 along the latter series is related to the presence of five- vs. six-membered rings and is not connected with the presence of a macrocyclic structure. It is thus probably doubly true that we should not speak of hole size in relation to the tetraaza macrocycles. Indeed, our further investigations appear to indicate that the decrease in log K_1 that occurs for large metal ions as six-membered rings are substituted for five-membered rings is a general phenomenon. One of many examples of this effect is found in comparing complexes of EDTA (ethylenediaminetetraacetate) with those of TMDTA (trimethylenediaminetetraacetate). For small metal ions such as Cu(II) or Al(III) there is a small increase in log K_1 in passing from the EDTA complex with its five-membered ring to the TMDTA complex with its six-membered chelate ring.[19] For large metal ions such as Pb(II) or Sr(II) there is a large decrease in stability in making this change, of up to 5 log units.[19] We are at present extending our molecular mechanics calculations to examine this more general phenomenon, in the hope of explaining it and developing it as a tool for controlling selectivity for metal ions on the basis of their size.

Acknowledgment. We thank the Council Research Grants Committee of the University of the Witwatersrand and the Council for Scientific and Industrial Research for generous financial support.

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(20) For key to nomenclature on conformers, see Figure 5.

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Synthesis and Electrochemistry of Iron(II) Clathrochelates

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A series of clathrochelates of iron(II) has been prepared from various dioximes (cyclohexanedione dioxime, dimethylglyoxime, and diphenylglyoxime) and boron capping agents (boron halides, borate esters, and boronic acids). New synthetic routes have been developed to introduce various boron substituents (e.g. chloro, bromo, methyl, and hydrido) into these complexes. Cyclic voltammetric studies reveal a pseudoreversible redox couple (Fe(II)/Fe(III)), the potential of which varies over 280 mV as the substituent on the boron cap is changed. The correlation of this potential shift with the Hammett σ_p parameters of the boron substituents has led to a division of the complexes into two groups (group I = Br, Cl, F, OH, OCH_3; group II = CH_3, H, C_6H_5, n-C_4H_9). Both groups show essentially linear redox potential behavior within their group with respect to the Hammett σ_p parameters. Attempts to correlate the ^{11}B NMR shifts with the redox potential of the Fe(II)/Fe(III) couple have failed to produce interpretable results. Controlled-potential electrolysis studies have not produced stable Fe(III) species. Decomposition occurs during the course of electrolysis, generating electroactive products as evidenced by very large n values (>10). The B–H-capped clathrochelate exhibits remarkable stability in acidic media. Material isolated from refluxing glacial acetic acid (67 h) still possesses a B–H bond as evidenced by infrared studies (ν_{B-H} = 2485 cm^{-1}). ^{11}B NMR studies of this complex reveal a crude doublet centered at −13.76 ppm vs. $B(OCH_3)_3$; J_{B-H} = 120 Hz.

Introduction

Clathrochelates, multicyclic ligand systems that completely encapsulate a metal ion, were first proposed by Busch.[1] Recently numerous examples of clathrochelates containing transition-metal ions have been reported.[2-10] Studies of the redox properties of these "cage" complexes have begun to yield much information concerning electron-transfer mechanisms, the stability of novel oxidation states, and the effect of peripheral groups on the redox properties of the central metal ion.[5,8-17]

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