

realized with a number of clusters.⁴⁹ The closest resemblance to **1** is found with three Mo₃S₄ complexes.^{49b-d} Recent advances in Sn-N chemistry by Veith and co-workers⁵⁰⁻⁵² have provided topological equivalents of **1** and **2**, which are depicted in Figure 9. Here pyramidal Sn(II) and RN²⁻ simulate tetrahedral Fe(II,III) and S²⁻ atoms, respectively. The structure of Sn₃-(NCMe₃)₄H₂ has been crystallographically established.⁵⁰ The two hydrogen atoms are presumably associated with the nitrogen atoms in the open face of the cage, but their positions have not been located. The structure of Sn₂(Me₂Si)₃(NMe)₅⁵¹ is consistent with its ¹H NMR spectrum and the usual stereochemical preferences of the framework atoms. It has not been demonstrated by X-ray diffraction. The upper SiMe₂ group simulates Fe(SR)₂. The NMe bridge between the lower two SiMe₂ groups has been omitted to emphasize the topological similarity to **2**, especially **2a**. The set of compounds also includes cubane-like Sn₄-(NNMe₂)₄⁵² (not shown), similar to Fe₄S₄ clusters.²² Topological approaches to the cyclic [Fe₃S₃]³⁺ site in *Av* Fd I are provided by Me₆Sn₃X₃,^{53,54} a point originally recognized by Ghosh et al.^{3a}

Although the linear cluster **3** is not a representative of the 3-Fe site in the "native" form of any protein so far examined, it has been found under certain conditions in one protein. In an unfolded form of aconitase, obtained by incubation at pH >9.5, the linear structure has been identified by several methods,⁵⁵ including Mössbauer spectroscopy. Efforts to produce the nonlinear [Fe₃S₄]⁺ unit by isomerization of **3** or other means continue in this laboratory. At present, the only property shared by the clusters [Fe₃S₄(SR)₄]³⁻ and protein 3-Fe sites is the formation of the [Fe₄S₄]²⁺ core when treated with Fe(II).^{11,18,19,23b}

Acknowledgment. This research was supported at Harvard University by NIH Grant GM 28856, at M.I.T. by the National Science Foundation, and at the Lawrence Berkeley Laboratory by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. We thank J. M. Berg for the preparation of Figure 9 and for useful discussions, Professor H. Beinert for disclosure of results prior to publication, and Professor E. Münck for insightful commentary. We also thank Dr. S. Foner for help with the magnetization measurements.

Registry No. (Et₄N)₃[Fe₃S₄(SEt)₄], 85647-20-7; (Et₄N)₃[Fe₃S₄(SPh)₄], 82661-12-9.

Supplementary Material Available: Contributing states and relative weights in the total spin state |S = 5/2, S_z = 5/2>, including a brief derivation of the results (3 pages). Ordering information is given on any current masthead page.

(49) (a) (C₄H₅)₃Mn₃(NO)₄: Elder, R. C.; Cotton, F. A.; Schunn, R. A. *J. Am. Chem. Soc.* **1967**, *89*, 3645. (b) [(C₂H₅)₃Mo₃S₄]⁺: Vergamini, P. J.; Vahrenkamp, H.; Dahl, L. F. *Ibid.* **1971**, *93*, 6327. (c) [Mo₃S₄(CN)₉]²⁻: Müller, A.; Reinsch, U. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 72. (d) [Mo₃S₄(SCH₂CH₂S)₃]²⁻: Halbert, T. R.; McGauley, K.; Pan, W.-H.; Czernuszewicz, R. S.; Stiefel, E. I. *J. Am. Chem. Soc.* **1984**, *106*, 1849. (e) [W₃O₄F₉]²⁻: Mattes, R.; Mennemann, K. *Z. Anorg. Allg. Chem.* **1977**, *437*, 175. (f) [Mo₃O₄(C₂O₄)₃(H₂O)₃]²⁺: Bino, A.; Cotton, F. A.; Dori, Z. *J. Am. Chem. Soc.* **1978**, *100*, 5252. (g) [(Mo₃O₄)₂(EDTA)₃]⁴⁻: Bino, A.; Cotton, F. A.; Dori, Z. *Ibid.* **1979**, *101*, 3842. (h) [Mo₃O₄(OAc)₃(H₂O)₃]²⁺: Bino, A.; Cotton, F. A.; Dori, Z. *Inorg. Chim. Acta* **1979**, *33*, L133. (i) [Mo₃-(OMe)₄(NO)₃(CO)₆]⁻: Kirtley, S. W.; Chanton, J. P.; Love, R. A.; Tipton, D. L.; Sorrell, T. N.; Bau, R. *J. Am. Chem. Soc.* **1980**, *102*, 3451. (j) [Mo₃O₄(MeN(CH₂CO₂)₂)₃]²⁻: Gheller, S. F.; Hambley, T. W.; Brownlee, R. T. C.; O'Connor, M. J.; Snow, M. R.; Wedd, A. G. *Ibid.* **1983**, *105*, 1527.

(50) Veith, M. *Z. Naturforsch., B: Org. Chem., Org. Chem.* **1980**, *35B*, 20.

(51) Veith, M.; Grosser, M.; Rechtenwald, O. *J. Organomet. Chem.* **1981**, *216*, 27.

(52) Veith, M.; Schlemmer, G. *Chem. Ber.* **1982**, *115*, 2141.

(53) X = S: (a) Menzebach, B.; Bleckmann, P. *J. Organomet. Chem.* **1975**, *91*, 291. (b) Jacobsen, H.-J.; Krebs, B. *Ibid.* **1977**, *136*, 333.

(54) (a) X = Se: Dräger, M.; Blecher, A.; Jacobsen, H.-J.; Krebs, B. *J. Organomet. Chem.* **1978**, *161*, 319. (b) X = Te: Blecher, A.; Dräger, M. *Angew. Chem.* **1979**, *18*, 677.

(55) Kennedy, M. C.; Kent, T. A.; Emptage, M. H.; Merkle, H.; Beinert, H.; Münck, E. *J. Biol. Chem.*, in press.

Molecular Mechanics and Crystallographic Study of Hole Sizes in Nitrogen-Donor Tetraaza Macrocycles

Vivienne J. Thöm, Christine C. Fox, Jan C. A. Boeyens,* and Robert D. Hancock*

Contribution from the Department of Chemistry, University of the Witwatersrand, Johannesburg, South Africa 2001. Received February 6, 1984

Abstract: The preparation and crystal structure of [Cu(13-aneN₃O)Br]Br (compound I) (13-aneN₃O = 1-oxa-4,7,11-triazacyclotridecane) and of [Ni(14-aneN₄)(NO₃)₂] (II) are reported, with R factors of 0.099 and 0.063 (14-aneN₄ = 1,4,8,11-tetraazacyclotetradecane). In I the complex cation consists of an approximately square-pyramidal arrangement, with the axial position occupied by a bromide ion and the Cu atom 0.47 Å above the plane formed by the donor atoms of 13-aneN₃O. In II the nitrate ions occupy the axial positions with long Ni-O lengths of 2.169 Å, while the mean Ni-N lengths are short, at 2.055 Å. Molecular mechanics (MM) calculations are used to determine best-fit sizes for metal ions fitting into tetraaza macrocycles in the trans-I and trans-III conformers. The MM calculations show that the trans-I conformer of 12-aneN₄ (1,4,7,10-tetraazacyclododecane) will be more stable in planar coordination than the trans-III form and that metal ions with M-N lengths of 2.11 Å will fit best into the trans-I form. The MM shows that for 13-aneN₄ (1,4,7,11-tetraazacyclotridecane) the best-fit M-N length for the trans-I form will be 2.03 Å, accounting for the adoption of this conformation by [Cu(13-aneN₃O)Br]⁺, with Cu-N = 2.02 Å. The trans-III form has a best-fit size of 1.92 Å and is preferred by smaller metal ions. The best-fit M-N length for 14-aneN₄ in the trans-III conformation is 2.05 Å, while the trans-I will be more stable above 2.29 Å. Octahedral coordination would involve severe steric strain for trans-I conformers, and if octahedral coordination must be maintained, then the folded cis-V conformer is preferred at M-N lengths above 2.09 Å. The origin of the short Ni-N bond lengths in II is examined. The MM suggests that this is not due to compression by the macrocycle, but it is a consequence of the presence of the two axial oxygen atoms. The long Ni-O bonds are the result of steric repulsion by the hydrogen atoms on the macrocycle.

Many of the properties of the complexes of macrocycles appear to be controlled by the size of the cavity in the center of the

macrocycle. Busch et al.¹ have calculated the best-fit metal-nitrogen (M-N) bond lengths for metal ions fitting into the cavities

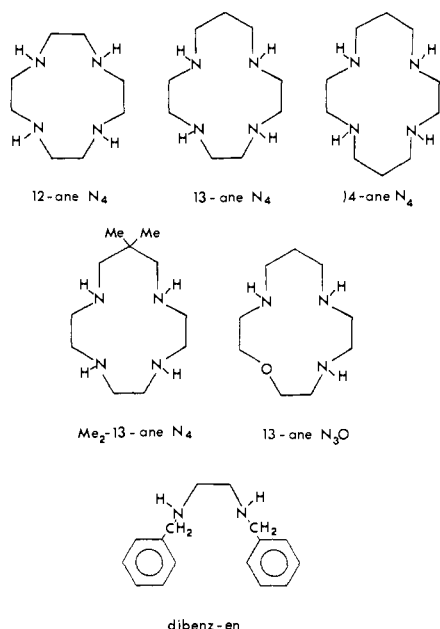


Figure 1. Ligands discussed in this paper.

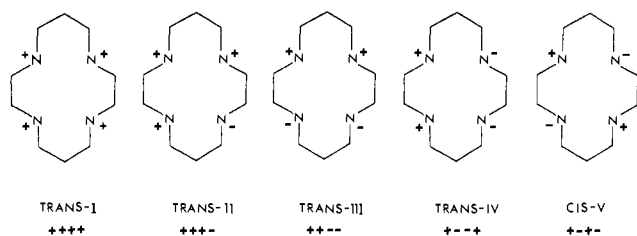


Figure 2. Nomenclature for the configuration of coordinated tetraaza macrocycles. The + indicates that the hydrogen of the NH group is above the plane of the flattened macrocycle, while the - indicates that it is below. The macrocycle shown is 14-aneN₄. For 12-aneN₄ the trans-III and -IV configurations are equivalent, while for 13-aneN₄ two forms of the trans-II are possible.

of the saturated tetraaza macrocycles 12-aneN₄ through 16-aneN₄ (see Figure 1 for structures of ligands), but these calculations were only for a single conformer of each macrocycle. We have supported² the values obtained by Busch et al.¹ using similar calculations. All of the macrocyclic complexes used by us² for the molecular mechanics (MM) calculations have the nitrogens in configuration III in Figure 2. This is the configuration actually found for virtually all octahedral complexes of saturated tetraaza macrocycles where the macrocycle has planar coordination. A proviso here would appear to be that the metal ion is not too large for the macrocyclic cavity by more than about 0.05 Å. Thus, square-planar Ni(II) has a strain-free M-N length of 1.89 Å⁴ (i.e., the M-N length that would be observed in the absence of any steric distortion), and therefore fits easily into Me₂-13-aneN₄ (Figure 1), which, like 13-aneN₄, should have a cavity into which metal ions with M-N bond lengths of 1.92 Å fit best.¹ In accord with this good fit we find that [Ni(Me₂-13-aneN₄)₂]²⁺ has⁵ nitrogen configuration III.

If, however, the metal ion is too large for the macrocyclic cavity, the available crystal structures indicate at least three types of result:

(1) If the metal ion is not obliged to be octahedral, but can assume square-pyramidal (e.g., Cu(II)) or square-planar (e.g. Ni(II)) coordination geometry, then it is possible for it to adopt

(1) Martin, L. Y.; De Hayes, L. J.; Zompa, L. J.; Busch, D. H. *J. Am. Chem. Soc.* **1974**, *96*, 4047-4048.

(2) Hancock, R. D.; McDougall, G. J. *J. Am. Chem. Soc.* **1980**, *102*, 6553-6555.

(3) Curtis, N. F. In "Coordination Chemistry of Macrocyclic Compounds"; Melson, G. A., Ed.; Plenum Press: New York, 1979; p 223.

(4) Fabbrizzi, L. *J. Chem. Soc., Dalton Trans.* **1979**, 1861-1875.

(5) Waters, J. M.; Whittle, K. R. *J. Inorg. Nucl. Chem.* **1972**, *34*, 155.

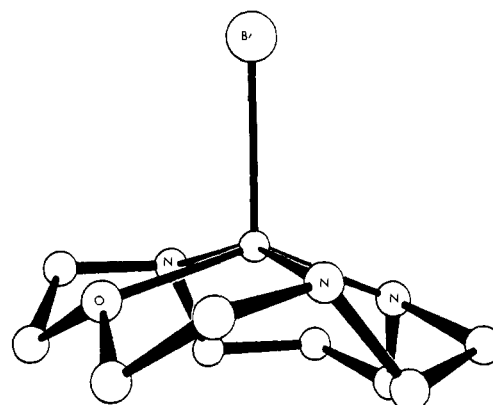


Figure 3. ORTEP³⁹ drawing of the [Cu(13-aneN₃O)Br]⁺ cation, showing how the copper atom is raised above the plane of the donor atoms. The ligand has the trans-I configuration (see Figure 2), and one sees how in this configuration the alkane bridges between the donor atoms lie effectively below the coordination plane.

the type I type of configuration in Figure 2. In the case of Cu(II), which has⁶ a mean Cu-N bond of 2.03 Å to the four in-plane nitrogens in tetragonally distorted structures, the type I configuration is found for several complexes of 12-aneN₄⁷ and alkyl-substituted 12-aneN₄ derivatives,^{8,9} where the copper has square-pyramidal coordination. A Li⁺ complex with benzo-13-crown-4 has been reported.¹⁰ It was shown that¹⁰ the Li⁺ was too big for the macrocyclic cavity, and the macrocycle has effectively configuration I, with all the oxygen lone pairs on the same side of the macrocycle. An additional example in this class is reported here, [Cu(13-aneN₃O)Br]Br, isolated as part of a program^{11,12} on mixed donor macrocycles. The complex of low-spin Ni(II) (M-N ideal = 1.89 Å) with 12-aneN₄ (best-fit M-N = 1.83 Å) has been suggested also to be five-coordinate.¹³

(2) If the metal ion has a strong preference for remaining octahedral (Co(III), Rh(III), Cr(III), and, to a lesser extent, high-spin Ni(II)), then the type I configuration does not offer any relief from steric compression. This is because in the type I configuration, the alkyl bridges (-CH₂CH₂-, -CH₂CH₂CH₂-) linking the nitrogens together all lie on one side of the macrocycle, effectively below the plane of the four nitrogens, and block off coordination on that side. If the metal ion is too large the most likely result will be a folded complex, which in examples observed to date all have the type V configuration.

(3) A last possibility is that the metal ion will adopt neither course 1 nor 2, but it will actually be compressed¹ by the macrocycle. This apparently has happened to the high-spin nickel in [Ni(14-aneN₄)Cl₂], the first complex of a saturated N-donor macrocycle¹⁴ to be studied crystallographically. The complex has the type III configuration, with the two chlorides coordinated axially. The Ni-N bond lengths are very short for high-spin Ni(II), being 2.058 (8) Å, instead of the strain-free value of 2.10 Å. Accompanying this shortening of the Ni-N bond lengths is a distortion of the axial Ni-Cl bonds out to the very long bond length of 2.492 (3) Å. It was suggested that the long Ni-Cl bonds were due to steric interaction between the chlorine atom, and the

(6) Thom, V. J.; Boeyens, J. C. A.; McDougall, G. J.; Hancock, R. D. *J. Am. Chem. Soc.* **1984**, *106*, 3198.

(7) Clay, R.; Murray-Rust, P.; Murray-Rust, J., *Acta Crystallogr., Sect. B* **1979**, *B35*, 1894-1895.

(8) Sakurai, T.; Kobayashi, K.; Hasegawa, A.; Tsuboyama, B.; Tsuboyama, K. *Acta Crystallogr., Sect. B* **1982**, *B38*, 107.

(9) Desimone, R. E.; Blinn, E. L.; Mucker, K. F. *Inorg. Nucl. Chem. Lett.* **1980**, *16*, 23.

(10) Shoham, G.; Lipscomb, W. N.; Olsher, U. *J. Am. Chem. Soc.* **1983**, *105*, 1247-1252.

(11) Hancock, R. D.; Thom, V. J. *J. Am. Chem. Soc.* **1982**, *104*, 291-292.

(12) Thom, V. J.; Hancock, R. D. *Inorg. Chim. Acta* **1983**, *77*, L231-233.

(13) Plassman, W. H.; Swisher, R. G.; Blinn, E. L. *Inorg. Chem.* **1980**, *19*, 1101-1103.

(14) Bosnich, B.; Mason, R.; Pauling, P. J.; Robertson, G. B.; Tobe, M. L. *J. Chem. Soc., Chem. Commun.* **1965**, 97-98.

Table I. Crystal Data and Details of Crystallographic Analyses

	C ₉ H ₂₃ N ₃ O ₂ CuBr ₂	C ₁₀ H ₂₄ N ₆ O ₆ Ni
mol formula	C ₉ H ₂₃ N ₃ O ₂ CuBr ₂	C ₁₀ H ₂₄ N ₆ O ₆ Ni
<i>M</i>	428.7	383.1
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> , Å	7.753 (7)	7.664 (6)
<i>b</i> , Å	14.78 (2)	12.87 (2)
<i>c</i> , Å	13.83 (2)	8.93 (1)
β, deg	104.4 (2)	114.2 (2)
<i>V</i> , Å ³	1534.6	803.6
<i>Z</i>	4	2
<i>D</i> _c , g cm ⁻³	1.855	1.582
λ(Mo Kα), Å	0.71069	0.71069
μ, cm ⁻¹	64.8	11.8
<i>F</i> (000)	852	404
diffractometer	Philips PW 1100	Philips PW 1100
range, deg	3° ≤ θ ≤ 24°	3° ≤ θ ≤ 24°
scan	ω-2θ	ω-2θ
scan width, deg	1.2	1.1
scan speed, deg/s	0.037	0.037
obsd data	1328	1030
obsd criterion	<i>F</i> > 4σ(<i>F</i>)	<i>F</i> > σ(<i>F</i>)
<i>R</i>	0.099	0.063
unresolved <i>s</i> , e Å ⁻³	< 0.6	< 0.5

hydrogens of the macrocycle.¹⁴ This raises the possibility that the short Ni-N bonds are not due to compression of the metal ion but rather to shortening of the Ni-N bonds which accompanies the steric lengthening of the Ni-Cl bonds. The structure of [Ni(14-aneN₄)(NO₃)₂], reported here, is related to that of [Ni(14-aneN₄)Cl₂]. The nitrate complex is more convenient to analyze with use of force-field calculations, since the appropriate parameters for Ni-Cl interactions are not available.

The assumption of type I configuration when the metal ion is too large was assessed by MM calculations on type I complexes of 12-aneN₄, 13-aneN₄, and 14-aneN₄, the tetraaza macrocycles likely to experience problems with metal ions that are too large. These calculations were carried out for square-planar geometry, but the results should be applicable to square-pyramidal forms where the metal ion is not in the plane of the four nitrogen donors, and the axial ligand is well away from the macrocycle. Previous² calculations on type III conformers with water molecules occupying the axial positions were repeated with water removed to give square-planar forms, so as to be comparable with the calculations on the type I forms. The question of macrocycles folding was examined for 14-aneN₄ complexes by MM calculations on both the folded and planar type III [M(14-aneN₄)(H₂O)₂]ⁿ⁺ complexes. The two reported structures of macrocycles coordinated to metal ions which are too large for the macrocyclic cavity and the results of the MM calculations are presented to clarify questions such as whether the Ni(II) is really compressed in the [Ni(14-aneN₄)(NO₃)₂] complex.

Experimental Section

Materials. 13-aneN₃O was prepared as described previously.¹² An aqueous solution of 13-aneN₃O·3HBr was neutralized and added to one of Cu(NO₃)₂·3H₂O. After evaporation of the water, the solid obtained was recrystallized from ethanol to give blue crystals of a quality suitable for an X-ray structural study. 14-aneN₄ was obtained from Strem chemicals. A 1:1 stoichiometric mixture of the ligand with Ni(NO₃)₂·6H₂O in ethanol gave pale purple crystals of [Ni(14-aneN₄)(NO₃)₂] of a quality suitable for X-ray diffraction.

Structure Determination. For both compounds, diffraction quality crystals were selected by standard oscillation and Weissenberg techniques, using Cu Kα radiation. The space group and approximate cell constants were determined at the same time. Intensity data and accurate cell dimensions were obtained on a Phillips PW 1100 diffractometer with use of Mo Kα radiation. The crystal data and details of the crystallographic analyses are shown in Table I. The final fractional coordinates are given in Table II for [Cu(13-aneN₃O)Br]Br and in Table III for [Ni(14-aneN₄)(NO₃)₂], while respective bond lengths and angles of interest are in Figures 4 and 5. Tables of calculated and observed structure factors are available as supplementary material.

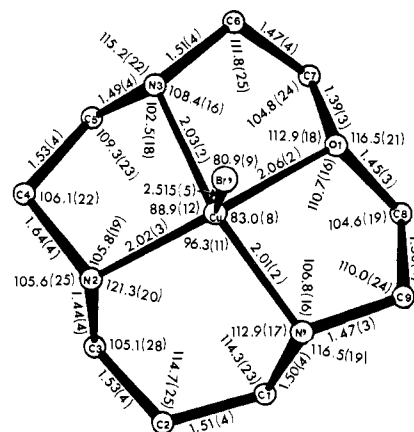
Molecular Mechanics Calculations. These were carried out with use of a program originally devised by Boyd¹⁵ and modified by Snow.¹⁶ All

Table II. Fractional Coordinates (×10³), with Estimated Standard Deviations, of All Non-Hydrogen Atoms for [Cu(13-aneN₃O)Br]Br

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Cu	325.0 (5)	96.5 (3)	279.7 (3)
Br(1)	612.1 (4)	178.2 (2)	353.4 (3)
N(1)	150 (3)	191 (1)	299 (2)
N(2)	262 (3)	102 (2)	129 (2)
N(3)	433 (3)	-27 (1)	272 (2)
O(1)	261 (2)	37 (1)	401 (2)
C(1)	-16 (4)	193 (2)	216 (2)
C(2)	17 (5)	201 (2)	113 (2)
C(3)	80 (4)	114 (2)	73 (2)
C(4)	326 (4)	6 (2)	92 (3)
C(5)	323 (4)	-63 (2)	175 (3)
C(6)	420 (4)	-81 (2)	363 (3)
C(7)	260 (4)	-57 (2)	396 (3)
C(8)	105 (3)	79 (2)	422 (2)
C(9)	125 (4)	177 (2)	400 (2)
Br(2)	190.3 (4)	79.3 (2)	800.1 (3)
O(2)	476 (4)	316 (2)	504 (2)

Table III. Fractional Coordinates (×10⁴), with Estimated Standard Deviations, of All Non-Hydrogen Atoms for [Ni(14-aneN₄)(NO₃)₂] and (×10³) for the Hydrogen atoms

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Ni	5000	5000	5000
N1	2301 (8)	5267 (5)	3236 (6)
N2	4625 (8)	3518 (5)	4048 (7)
C1	1836 (11)	4385 (7)	2080 (9)
C2	2601 (11)	3403 (7)	3022 (10)
C3	5481 (11)	2664 (6)	5261 (11)
C4	7558 (12)	2821 (7)	6330 (11)
C5	1943 (11)	6302 (7)	2440 (9)
N3	7291 (8)	5193 (5)	2833 (7)
O1	6044 (7)	5572 (4)	3234 (6)
O2	8166 (11)	4411 (6)	3483 (9)
O3	7697 (12)	5622 (7)	1823 (11)
H(N1)	129 (9)	524 (6)	333 (10)
H(N2)	539 (9)	357 (6)	359 (10)
H1(C1)	268 (9)	455 (5)	156 (10)
H2(C1)	52 (9)	425 (5)	155 (10)
H1(C2)	228 (9)	274 (6)	248 (10)
H2(C2)	188 (9)	325 (6)	355 (10)
H1(C3)	466 (9)	262 (6)	570 (10)
H2(C3)	538 (8)	194 (6)	485 (10)
H1(C4)	825 (9)	293 (6)	591 (10)
H2(C4)	820 (9)	214 (6)	678 (10)
H1(C5)	52 (9)	642 (5)	184 (10)
H2(C5)	292 (9)	631 (5)	205 (10)

**Figure 4.** ORTEP³⁹ drawing of the [Cu(13-aneN₃O)Br]⁺ cation, showing the atom numbering scheme and bond parameters (Å and deg) of interest.

calculations were carried out with the parameters used previously.¹⁷ A technique which we have developed^{2,18} is to scan the structure as a

(15) Boyd, R. H. *J. Chem. Phys.* **1968**, *49*, 2574.(16) Snow, M. R. *J. Am. Chem. Soc.* **1970**, *92*, 3610.

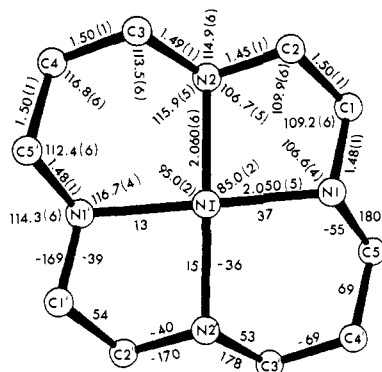


Figure 5. Diagram to define the atomic numbering scheme for the [Ni(14-aneN₄)(NO₃)₂] structure and the molecular geometry of the macrocycle. Bond lengths (Å) and angles (deg) are shown in the upper half and torsion angles (deg) in the lower half.

function of metal ion size. Thus, all the parameters involving the metal ion are kept constant at those for Ni(II) (high spin), which has metal-to-nitrogen bonds which are neither very strong nor very weak. The ideal M–N bond length, i.e., the M–N bond length which would be observed in the absence of any steric distortion, is varied in increments of about 0.05 Å from 1.80 to 2.4 Å. The resulting curves of strain energy, U , vs. bond length, r , indicate the best-fit M–N length for fitting into the ligand system. If the calculations are carried out for more than one conformer, the crossover point indicates where one conformer becomes more stable than the other as a function of metal ion size. The narrowness of the curves is also an indication of the tolerance of the ligand to change in metal ion size, with very flat curves indicating a high tolerance.

All the calculations for complexes where the macrocycle is coordinated in a planar fashion were carried out with a square-planar metal ion. This is in contrast to previous calculations,^{2,17} which were for the trans-octahedral forms, with two water molecules occupying the axial coordination sites.

Where possible, trial coordinates were taken from actual crystal structures. This should minimize the chances of the program finding a false energy minimum. Thus, the trial coordinates for the 12-aneN₄ were taken from those reported for [Cu(12-aneN₄)NO₃]⁺, discarding the nitrate so as to give a square-planar complex. The type I form of 13-aneN₄ was generated from the structure of [Cu(13-aneN₃O)Br]⁺ reported here, discarding the bromide ion and adding a hydrogen to the oxygen to turn it into a nitrogen. The type I form of 14-aneN₄ was generated from the structure of the Ni(II) complex of tetramethylcyclam,¹⁹ discarding the *N*-methyl groups.

The type III conformers were generated from the energy-minimized forms obtained previously,² removing the axially coordinated water so as to give square-planar forms. In all cases this produced a drop in U . For both 13-aneN₄ and 12-aneN₄ two slightly different conformers resulted, depending on whether the metal ion remained in the plane of the nitrogen donors or not, and which displayed rather different metal ion size preferences. The folded form of [M(14-aneN₄)(H₂O)₂]²⁺ was generated from the coordinates of [Co(14-aneN₄)(en)]³⁺,²⁰ discarding the en (ethylenediamine) and replacing it with water molecules. Calculations on the *trans*-[M(14-aneN₄)(H₂O)₂]²⁺ complexes are those reported previously.²

Results and Discussion

A. The Structure of [Cu(13-aneN₃O)Br]Br. The complex is seen in Figure 3 in side view, showing that the Cu atom is raised above the macrocyclic plane through the three nitrogen and one oxygen donor atoms by 0.467 Å. There is a slight distortion away from the square-pyramidal toward trigonal-bipyramidal coordination, in that the N–Cu–N angle is 159.1 (8)°, while the O–Cu–N angle is only 144.1 (9)° for trans donor atoms. The ligand has the trans-I configuration, with the rings having the λλδγ conformation, where λ and δ refer to chiralities and γ indicates a chair form of the six-membered ring. The numbering scheme is seen in Figure 4.

A computer-based literature search²¹ indicated from an analysis of 16 complexes of Cu(II) containing one- or two-coordinated bromides associated with amine ligands that Cu–Br lengths in such complexes lie in the range 2.36–2.45 Å, with a mean value of 2.42 Å, for in-plane bromides. Bond lengths for axially coordinated bromides on Cu(II) are rather scarce.²¹ The only truly comparable structure is that for²² [Cu(dibenz-en)₂Br]Br, where the axial Cu–Br length is 2.547 (1) Å, compared with 2.515 (5) Å in our own. The N–Cu–N angles involving trans nitrogens are²² 164.8 and 143.5°, indicating a similar degree of distortion toward trigonal-bipyramidal in [Cu(dibenz-en)Br]Br as in [Cu(13-aneN₃O)Br]Br. The Cu–N bond lengths in the former complex are considerably longer at 2.08 Å than in the latter at 2.02 Å, which almost certainly reflects the steric effects of the *N*-benzyl groups, such Cu–N bond lengths being normal for *N*-alkylated amines.⁶ Other structures with which comparison might be made are more strongly distorted toward trigonal-bipyramidal geometry, with "axial" Cu–Br lengths of 2.598²³ and 2.702 Å.²⁴ In the regular trigonal-bipyramidal CuBr₅³⁻ ion the longer equatorial Cu–Br bonds give²⁵ bond lengths of 2.519 Å.

The important point is that according to crystallographic evidence the coordination geometry around the Cu(II) in [Cu(13-aneN₃O)Br]Br is like that found²² in comparable structures where no macrocyclic constraints are present. In other similar structures the distortion toward trigonal-bipyramidal geometry^{23,24} indicates that, whether for steric or electronic reasons, the Cu(II) ion with an axial bromide will not lie in the plane of the four other donor atoms, even in the absence of macrocyclic constraints.

B. The Structure of [Ni(14-aneN₄)(NO₃)₂]. The complex is seen in Figures 5 and 6. The macrocycle, cyclam, has the normal trans-III conformation, and the complex resembles very closely the structure of its dichloro analogue.¹⁴ The Ni–N bond lengths are 2.050 (5) and 2.060 (6) Å, which, as in the dichloro analogue, are short for high-spin Ni(II), where strain-free Ni–N is¹⁷ 2.10 Å. Similarly, the axial Ni–O bond lengths are rather long at 2.169 (4) Å. The molecule geometry, atomic numbering, and hydrogen bonding between the ions are summarized in Figures 5 and 6. There is remarkable correspondence with the parameters obtained²⁶ by crystallographic molecular trial and error for the perchlorate complex of the isomeric *cis* compound isocyclam. It is of interest to note that the two isomeric perchlorates form isomorphous crystals with disordered structures. Superposition of two cyclam rings, by analogy with the disordered arrangement (26) of isocyclam, is shown in Figure 7. The two disordered arrangements are so alike that the observed isomorphism becomes readily understood.

C. Molecular Mechanics of 13-aneN₄ Complexes. In Figure 8b is seen a plot of calculated U for various conformers of the 13-aneN₄ complex as a function of r , the M–N bond length. The solid lines are final U as a function of the final energy-minimized M–N bond length, while the broken lines are final U as a function of ideal (initial) strain-free M–N length. What is of immediate interest is that there are three conformers separated by only a small energy difference which give a wide range of best-fit metal ion sizes from the minima in the U vs. r curves. Thus, we have the trans-I isomer with a minimum at 2.03 Å. Two forms of trans-III isomer are of low U , depending on whether the metal ion must remain in the plane of the four donor atoms or not. These two forms are seen in Figure 9. In the planar form, with the metal lying in the coordination plane, the minimum in U occurs at 1.92 Å, as was found² previously for the octahedral diaquo complex. In the out-of-plane ++-- (trans-III) form the metal ion is raised above the ring (Figure 9), and here the energy minimum occurs at 1.98 Å.

(21) The Cambridge Structural Database, Cambridge University, 1982 update.

(22) Ladd, M. F. C.; Perrins, D. H. G. *Z. Kristallogr.* **1981**, *154*, 155–162.

(23) Elder, M.; McKenzie, E. D. *Inorg. Chim. Acta* **1978**, *31*, 211–215.

(24) Singh, P.; Copelano, V. C.; Hatfield, W. E.; Hodgson, D. J. *J. Phys. Chem.* **1972**, *76*, 2887–2891.

(25) Goldfield, S. A.; Raymond, K. N. *Inorg. Chem.* **1971**, *10*, 2604–2607.

(26) Boeyens, J. C. A. *Acta Crystallogr., Sect. C* **1983**, *C39*, 846.

(17) McDougall, G. J.; Hancock, R. D.; Boeyens, J. C. A. *J. Chem. Soc., Dalton Trans.* **1978**, 1438.

(18) McDougall, G. J.; Hancock, R. D. *J. Chem. Soc., Dalton Trans.* **1980**, 654.

(19) Daniello, M. J.; Mocella, M. T.; Wagner, F.; Barefield, E. K.; Paul, I. C. *J. Am. Chem. Soc.* **1975**, *97*, 192.

(20) Lai, T. F.; Poon, C. K. *Inorg. Chem.* **1976**, *15*, 1562–1566.

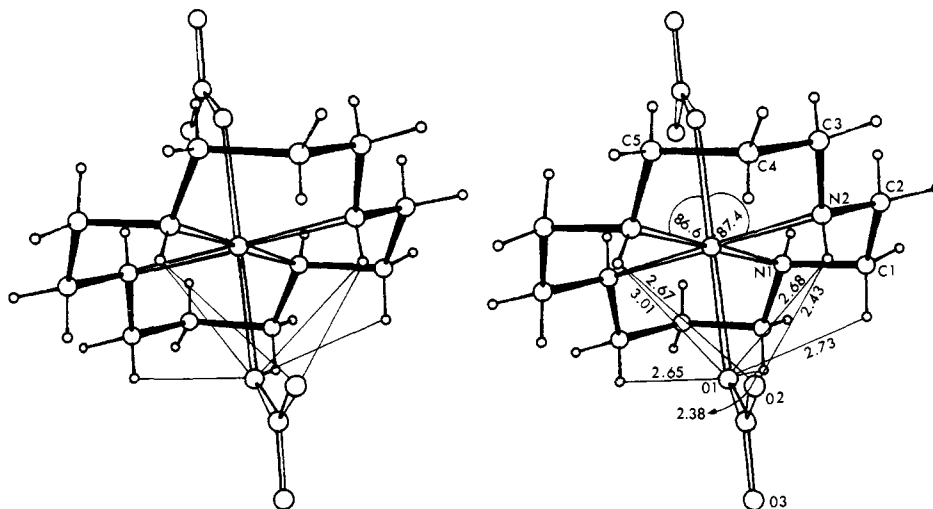


Figure 6. Stereoscopic drawing of the $[\text{Ni}(14\text{-aneN}_4)(\text{NO}_3)_2]$ molecule to illustrate the relative orientation of the nitrate groups and interionic hydrogen bonds. Note the short O--H contacts of 2.65 Å between the oxygen donor atom and the methylene hydrogens responsible for lengthening of the Ni—O bond.

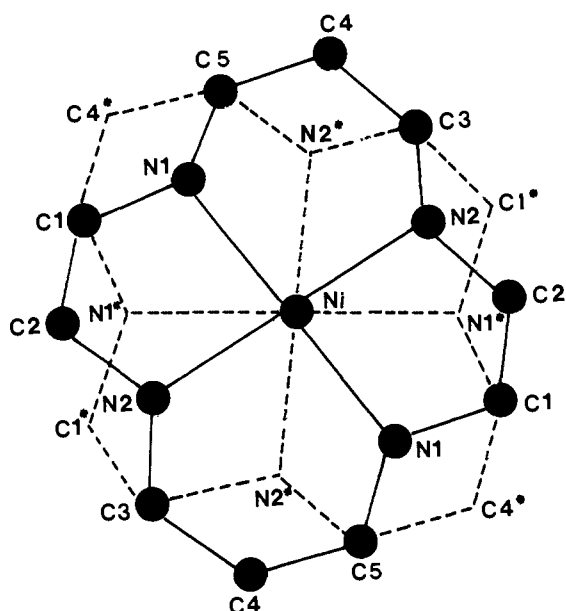


Figure 7. Two cyclam units as found in the structure of the nitrate complex, here shown in an overlap mode that mimics the disordered arrangement of isocyclam units as they appear in the structure of the perchlorate complex.²⁶

The trans-I and trans-III out-of-plane forms cause the metal ion to lie considerably outside the coordination plane. Thus, at its best-fit size of 2.03 Å, the metal ion in the trans-I form is predicted by the MM calculations to lie 0.40 Å out of the plane, while for the trans-III out-of-plane structure at its best-fit size the metal ion is predicted to lie some 0.43 Å above the coordination plane. This requirement of lying out of the plane precludes these conformers for octahedral coordination, since the axial ligand on the side of the macrocycle away from the metal ion would be pulled up against the macrocyclic ring, with highly unfavorable non-bonded repulsive contacts.

An important point should be made here in relation to the relative energies of the conformers in Figure 8. In the MM calculations, N—M—N angles larger than 130° are ignored. This is necessary, since the N—M—N bending force constants apply to cis nitrogens with N—M—N angles of 90°, and without this condition the program would also try to make the trans N—M—N angles of 180° into 90° angles. It is quite possible to include extra terms for making the trans N—M—N angles tend to 180°, with separate force constants for these angles. We have chosen not to, however, in this instance, since, as will become apparent below,

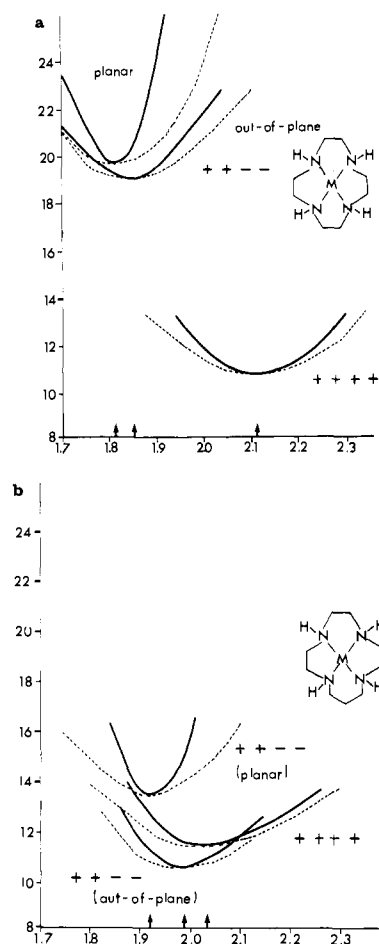


Figure 8. The final energy minimized value of U , the strain energy, of the complex, as a function of r , the M—N bond length, for complexes of 12-aneN₄ (Figure 8 a) and 13-aneN₄ (Figure 8 b). The curves are for initial strain-free r (···) or final energy-minimized r (—). The arrows indicate the positions of the minima for each curve, which are then the best-fit M—N lengths for coordination to that particular conformer of the macrocycle.

the tendency to remain planar will vary highly from metal ion to metal ion. It should be borne in mind, though, that *where the requirement for planarity is strong, the planar trans-III form, in which the metal ion lies almost exactly in the plane of the donor atoms, will be stabilized relative to the trans-I and trans-III out-of-plane forms.* Thus we find for $[\text{Ni}(\text{Me}_2\text{-13-aneN}_4)]^{2+}$ the

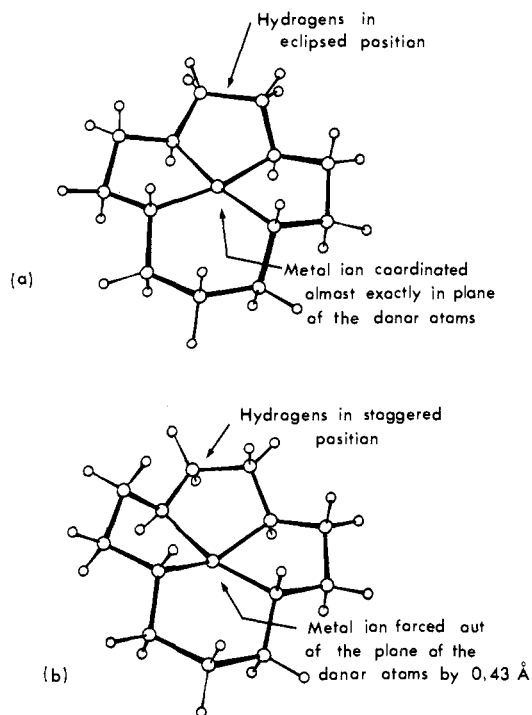


Figure 9. ORTEP³⁹ drawings of the forms of the trans-III (+ + - -) complex of 13-aneN₄: the planar (a) and out-of-plane (b) forms.

planar form of the trans-III structure,⁵ which suggests that square-planar Ni(II) has a strong tendency to lie in the coordination plane.

On the other hand, our examination of the structures of complexes of copper(II) with axially coordinated bromide²²⁻²⁴ reveals that, even in the absence of macrocyclic constraints, the Cu is raised above the coordination plane. Thus, the copper(II) ion could have the lower energy trans-I or trans-III (out-of-plane) structures. In the structure of [Cu(13-aneN₃O)Br]⁺ described here we find a geometry which matches very closely that predicted for trans-I 13-aneN₄. The mean Cu-L in-plane bond lengths in [Cu(13-aneN₃O)Br]⁺ are 2.04 Å, almost a perfect fit for the trans-I form, with a best-fit M-N length of 2.03 Å. Our calculations predict that in the trans-I form at this bond length the metal ion should be raised above the coordination plane by 0.43 Å, as compared with an observed amount of 0.467 Å.

Our calculations indicate that the trans-III out-of-plane form is more stable than the trans-I form at shorter bond lengths, and at the M-L bond length observed in the 13-aneN₃O complex (2.04 Å) it should still be more stable than the trans-I conformer by some 0.4 kcal mol⁻¹. That the trans-I form is the one actually observed in [Cu(13-aneN₃O)Br]⁺ could be due to a variety of causes, such as crystal packing forces or possibly less favorable van der Waals contacts between the macrocyclic ring and the bromide ion. The most likely cause, however, is that the calculations in Figure 8 were carried out with M-N force constants appropriate to high-spin Ni(II), and the Cu-N force constants are likely to be much larger than this, since coordination to the + + - - (out-of-plane) form would require much more bond stretching than the trans-I form, the latter conformer being favored by an increase in M-N stretching constant.

Figure 9 highlights a problem which arises when an ethylene bridge must span nitrogens with the same sign (+ + or - -) in the + + - - isomers. For planar coordination the ethylene bridge is forced to have the eclipsed hydrogen configuration (Figure 9a), which on its own results in 2.8 kcal mol⁻¹ of strain energy. This problem becomes even more severe in the 12-aneN₄ ring, discussed below, where both + + and - - pairs of nitrogens are bridged by ethylene groups. Inspection of Figure 9a shows how the trimethylene bridge, which leads to the formation of a six-membered chelate ring, is able to bridge the + + nitrogens and retain the symmetry which allows planar coordination to the metal ion.

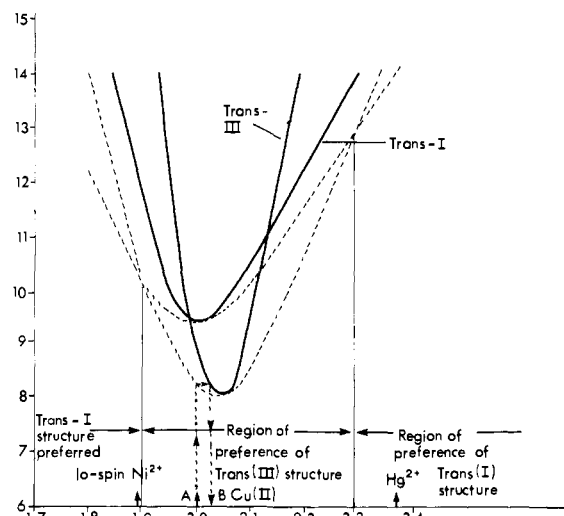


Figure 10. U vs. r curve for 14-aneN₄ complexes, showing regions of preference for the trans-I and trans-III configurations. A useful application of such diagrams is shown for Cu(II). At point A the strain-free Cu-N length of 2.00 Å allows us to read off from the curve for the final energy-minimized M-N lengths (—) an energy-minimized Cu-N length of 2.03 Å, at point B which can be compared with an observed²⁹ Cu-N length of 2.04 Å.

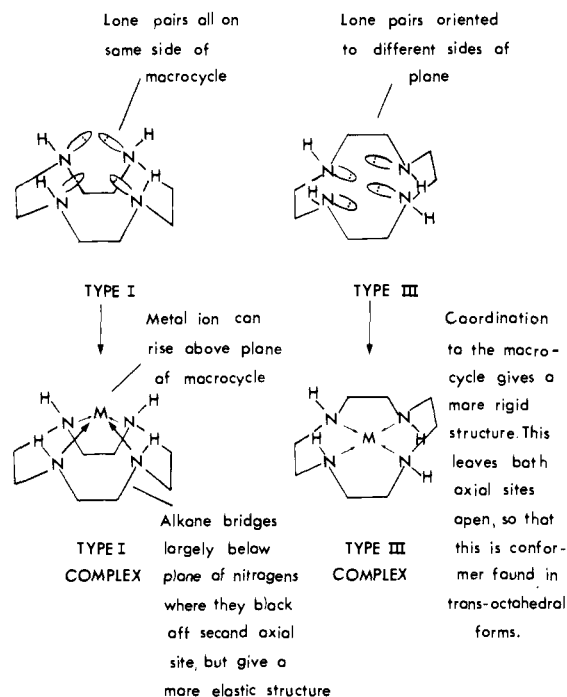


Figure 11. Diagrammatic representation of the trans-I and trans-III forms of tetraaza macrocycles, summarizing the differences in coordinating properties of the two conformers.

A final important point raised by Figure 8 is that the trans-I forms have very flattened U vs. r curves compared with the trans-III forms. This means that they will display very much greater tolerance of variation in metal ion size than will the trans-III forms. This is clearly seen in Figure 11. As the metal ion becomes larger, the nitrogens simply rotate so that the metal ion is raised further and further above the plane of the donor atoms. This is not possible for trans-III forms, since the + + nitrogens are oriented out of the plane of the macrocycle in the opposite direction to the - - nitrogens, and so cannot produce the concerted movement found in the trans-I forms, where all the lone pairs are oriented to the same side of the macrocycle.

D. Molecular Mechanics of 12-aneN₄ Complexes. The U vs. r curves for 12-aneN₄ conformers are seen in Figure 8a. Here the trans-I conformer is so very much more stable than the two

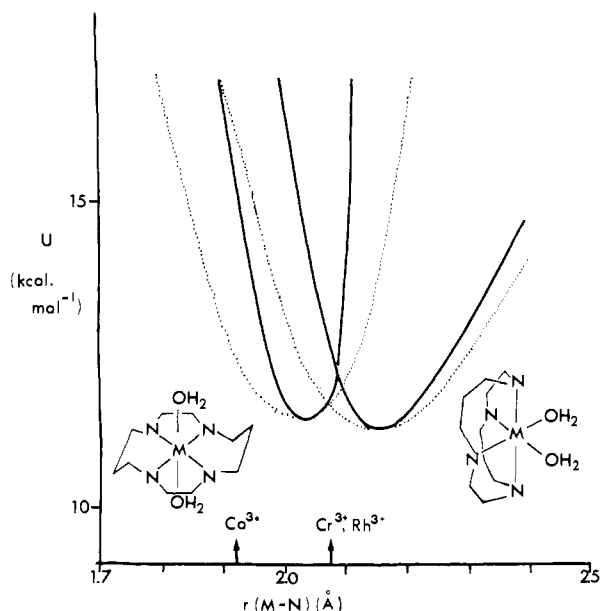


Figure 12. U vs. r curve for the trans-III and cis-V forms of $[M(14\text{-aneN}_4)(\text{OH}_2)_3]^{n+}$ complexes. This shows that the best-fit size for the trans-III form is 2.05 Å, while the best-fit M-N length for the cis-V form is 2.15 Å, with the crossover point occurring at 2.09 Å. The arrows indicate the strain-free M-N lengths for the metal ions indicated, which predict, as is actually found, that the cis and trans forms should be of equal stability for Cr(III) and Rh(III), but that for Co(III) the trans form will be strongly favored.

trans-III conformers that it would seem to be the only conceivable conformer of forms with all of the donor atoms lying in a single plane. The trans-I conformer of 12-ane N_4 shows a very broad flat U vs. r curve, meaning that it will probably be able to accommodate the full range of metal ion sizes, provided they do not require octahedral coordination, since one axial coordination site is blocked off. Thus this is the conformation found in five-coordinate Cu(II) complexes of 12-ane N_4 and its derivatives.⁷⁻⁹ In the Ni(II) complex of tetra(N-methyl)12-ane N_4 a trans-I conformer is found²⁷ very similar to that in $[\text{Cu}(12\text{-aneN}_4)\text{NO}_3]^+$, except that the ethylene bridges are $\lambda\lambda\lambda\delta$ instead of of $\lambda\lambda\lambda\lambda$. The Cu in 12-ane N_4 is extruded from the plane of the four nitrogens by 0.5 Å,⁷ whereas the Ni is extruded by²⁷ only 0.29 Å in its Me_4 -12-ane N_4 complex. This can be compared with a predicted value of 0.55 Å, showing the greater preference for planarity in the Ni(II). Models suggest that van der Waals repulsions between the four methyl groups in the Me_4 -12-ane N_4 complex contribute to the nonplanarity of coordination to Ni(II). The two forms of the trans-III conformer of 12-ane N_4 differ in the same way as the two forms of the trans-III conformer of 13-ane N_4 . Thus, the higher energy form has the planar conformation with the ethylene bridges across the ++ and -- nitrogens in the eclipsed position and the metal ion in the plane of the donor atoms. The slightly lower energy form has one of these ethylene bridges with hydrogens eclipsed, while the other has the hydrogens staggered. As with 13-ane N_4 , this leads to extrusion of the metal ion from the coordination plane by some 0.22 Å at the best-fit M-N length of 1.85 Å. As stated above, both these isomers are of such large U values that it seems extremely unlikely that any complexes having these conformations will be prepared. Thus, the yellow Ni(II) complex of 12-ane N_4 ⁴ will almost certainly have the trans-I structure. Interestingly, as shown in Figure 8, the metal ion with its preferred M-N length of 1.89 Å⁴ in its low-spin form will not be experiencing compression from 12-ane N_4 . Rather, the problems of accommodating the metal ion will be that the cavity of the trans-I form of 12-ane N_4 will be too big for low-spin Ni(II), with a cavity such that metal ions with M-N lengths of 2.11 Å will fit best. The second problem for Ni(II) will be achieving in-plane

coordination. A crystallographic study of yellow $[\text{Ni}(12\text{-aneN}_4)]^{2+}$ would be extremely interesting. One would predict that it would be square-planar with the trans-I structure.

The trans-I conformer of 12-ane N_4 is in many ways simply a larger version of 9-ane N_3 , which has the ++ hydrogen orientation, and a best-fit metal ion size of 2.08 Å.⁶ It is thus not surprising that the larger homologue 12-ane N_4 has a larger preferred hole size of 2.11 Å. One would venture that with sufficiently large metal ions, just as two 9-ane N_3 ligands can coordinate to a metal ion to give an octahedral coordination geometry, so two 12-ane N_4 ligands might give an eight-coordinate complex. This type of structure has already been found²⁸ in the bis(12-crown-4) complex of Mn(II).

E. Molecular Mechanics of Planar Complexes of 14-ane- N_4 .

In Figure 10 are seen the U vs. r curves for the trans-I and trans-III complexes of 14-ane N_4 . It is seen that as for the 13- and 12-ane N_4 complexes the curve for the trans-I conformer is fairly shallow, and has a minimum at $r = 2.01$ Å. The curve for the trans-III form (dotted line) for initial strain-free r crosses that for the trans-I form at a strain-free r of 1.9 Å, and again at 2.29 Å. Between these two strain-free bond lengths the trans-III form should be the more stable, and in agreement with this we find that the 14-ane N_4 complex of square-planar Cu(II) (ideal M-N = 2.00 Å) has the trans-III structure.²⁹ Hg(II), which has mean Hg-N bond lengths of 2.37 Å in its five-coordinate structure with cyclam,³⁰ has, would be expected from Figure 10, the trans-I structure. The trans-I conformer of 14-ane N_4 differs from those of 12- and 13-ane N_4 in that, except at very long bond lengths, the metal ion lies very nearly in the plane of the four nitrogen donors. At the observed mean Hg-N length of 2.37 Å, the Hg atom is raised some 0.80 Å out of the plane of the nitrogens,³⁰ but at an M-N of 2.0 Å the metal should only be some 0.06 Å out of the plane. Figure 10 makes the prediction that for metal ions with ideal M-N lengths of 1.90 Å, the trans-I and trans-III isomers should be of equal stability, provided they are square-planar and not octahedral. It must be remembered that the trans-I form involves severe steric strain for octahedral coordination. Low-spin Ni(II) is square-planar with an ideal M-N of 1.89 Å,⁴ and it will be of considerable interest to see whether both forms can be detected in solution, or isolated in the solid state.

A useful application of diagrams such as Figures 8 and 10 can be illustrated with Figure 10. At point A we have the strain-free bond length of square-planar Cu(II). We can then read off at point B the final energy-minimized Cu-N bond length predicted for $[\text{Cu}(14\text{-aneN}_4)]^{2+}$, of 2.03 Å, which can be compared with the observed bond length of 2.04 Å.²⁹

F. The Origin of the Distortion in $[\text{Ni}(14\text{-aneN}_4)\text{X}_2]$ Complexes ($\text{X} = \text{NO}_3^-, \text{Cl}^-$). As mentioned above, the ideal Ni-N bond length is¹⁷ 2.10 Å, so that the Ni-N bond length of 2.055 (6) Å in $[\text{Ni}(14\text{-aneN}_4)(\text{NO}_3)_2]$ would appear to be a clear-cut case of compression.¹ Two considerations are of importance here.

(1) The ideal M-N bond length of 2.1 Å appears to apply only when all six donor atoms around Ni(II) are saturated nitrogens. Thus, for the series of complexes $[\text{Ni}(\text{en})(\text{H}_2\text{O})_4]^{2+}$, $[\text{Ni}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$, and $[\text{Ni}(\text{en})_3]^{2+}$, the Ni-N bond lengths are 2.065 (6),¹⁸ 2.09,³¹ and 2.12 Å.³² We thus have a shortening of the Ni-N bond as nitrogens are replaced by oxygens. Since the ideal Ni-N bond length is usually some 0.02 Å shorter than observed, this indicates that for four amine nitrogen and two oxygen donors around Ni(II), the ideal Ni-N bond length is 2.07 Å. This is almost a perfect fit for 14-ane N_4 , which requires an M-N bond length of 2.05 Å. The origin of the shorter Ni-N bond lengths in association with oxygen-donor atoms is most simply viewed as a steric effect. In the present series of calculations van der Waals

(27) Coates, J. H.; Hadi, D. M. M. A.; Hambley, T. W.; Lincoln, S. F.; Rodgers, J. R. *Cryst. Struct. Commun.* **1982**, *11*, 815-821.

(28) Hughes, B. B.; Haltiwanger, R. C.; Pierpont, C. G.; Hampton, M.; Blackmer, G. L. *Inorg. Chem.* **1980**, *19*, 1801-1803.

(29) Tasker, P. A.; Sklar, L. *Cryst. Mol. Struct.* **1975**, *5*, 329-344.

(30) Alcock, N. W.; Curson, E. H.; Herron, N.; Moore, P. *J. Chem. Soc., Dalton Trans.* **1979**, 1987-1993.

(31) Minacheva, L. Kh.; Antsyshkina, A. S.; Porai-Koshits, M. A. *J. Struct. Chem.* **1974**, *15*, 408-411.

(32) Cramer, R. E.; Honeke, J. T. *Inorg. Chem.* **1978**, *17*, 365-374.

Table IV. Summary of the Best-Fit Sizes of Metal Ions, according to Coordination Geometry, into Different Conformers of 12-aneN₄, 13-aneN₄, and 14-aneN₄^a

ligand	square-planar geometry			square-pyramidal geometry			octahedral geometry		
	favored conformer ^b	best-fit size	comments	favored conformer	best-fit size	comments	favored conformer	best-fit size	comments
12-aneN ₄	++++ (trans-I)	2.11	flat <i>U</i> vs. <i>r</i> curve; tolerance to variation in metal ion size high; found in [Ni(Me ₄ -12-aneN ₄)] ²⁺ ; Ni-N = 1.94 Å ²⁷	++++ (trans-I)	2.11	found in [Cu(12-aneN ₄ -NO ₃)] ⁺ ; Cu-N = 2.02 Å; Cu 0.51 Å out of plane ⁷	(+ + - -)	(1.81)	+ + - - only possible form, too highly strained to be observed; only cis-V folded form likely
13-aneN ₄	+ + - - (trans-III planar)	1.92	found in [Ni(Me ₂ -13-aneN ₄)] ²⁺ ; Ni-N = 1.88 Å ⁵	++++ (trans-I)	2.03	found in [Cu(13-aneN ₃ O-Br)] ⁺ ; Cu-N = 2.02 Å; Cu 0.47 Å out of plane (this work)	+ + - - (trans-III planar)	1.92	only small ions such as Co(III); larger ions have folded form
14-aneN ₄	+ + - - (trans-III planar)	2.05	found in [Cu(14-aneN ₄)] ²⁺ ; Cu-N = 2.04 Å ²⁹	+ + - - (out of plane)	1.98	metal ion must lie well out of plane	+ + - - (trans-III planar)	2.05	found in: [Ni(14-aneN ₄)X ₂], X = Cl, NO ₃ , Ni-N = 2.06 Å; ¹⁴ [Ru(14-aneN ₄)-Cl ₂], Ru-N = 2.08 Å ³⁸
				++++ (trans-I)	2.00	found in [Hg(14-aneN ₄ -Cl)] ⁺ ; Hg-N = 2.37 Å; Hg is 0.8 Å out of plane ³⁰	+ - + - (cis-V folded)	2.15	folding favored as M-N length exceeds 2.09 Å

^aCalculated by using molecular mechanics, as described in text. For ligand abbreviation, see Figure 1. ^bFor an explanation of the nature of the conformers, see Figures 2 and 11. ^cUnits are Å.

repulsion between atoms joined to the same atom has not been included. Our ideal Ni-N bond length of 2.10 Å thus ignores N-N repulsion, and would be shorter if N-N non-bonded repulsion were included separately. This is seen for Co(III) in a new parameterisation developed by Snow,³³ where repulsions between adjacent donor atoms are included as separate terms, with the result that the new ideal Co-N length is shorter at 1.90 Å than that of 1.925 Å used previously.¹⁶ In future work non-bonded repulsions between adjacent donor atoms will be included as an attempt to reproduce the shorter Ni-N bond lengths found in association with oxygen donors.

(2) Whether one views the effect as one of steric packing or rehybridization, lengthening of the axial Ni-O (or Ni-Cl) bonds in [Ni(14-aneN₄)X₂] complexes should lead to shortening of the in-plane Ni-N bonds. The question then is what causes the lengthening of the axial bonds? The answer is already largely given in Figure 6, where we saw close approach of the oxygen from the nitrate to some of the aliphatic hydrogen atoms of the macrocyclic ring. This interpretation is confirmed by MM calculations on [Ni(14-aneN₄)(H₂O)₂], which give, using an ideal Ni-N of 2.07 Å, a final Ni-N of 2.065 Å, in good agreement with the observed 2.055 (6) Å. More important, an axial Ni-O bond length of 2.16 Å is predicted, in excellent agreement with the observed length of 2.17 Å. If this lengthening of the axial Ni-O bond leads to any shortening of the in-plane Ni-N bonds, the effect here is small. For [Ni(14-aneN₄)Cl₂] the elongation of the Ni-Cl bonds at 0.15 Å over normal Ni-Cl bond lengths¹⁴ is considerably greater than the elongation in [Ni(14-aneN₄)(NO₃)₂], which is only some 0.08 Å. It seems likely, therefore, that for the chlorocomplex, elongation of the Ni-Cl bonds plays a more important part in

shortening the in-plane Ni-N bonds.

A recent extreme example³⁴ of distortion produced by steric hindrance at the axial site on octahedral 14-aneN₄ complexes is found in [Ni(14-aneN₄)I]_n, which has Ni-I bond lengths of 3.34 Å, with correspondingly shortened Ni-N bond lengths of 1.94 Å.

G. The Folding of [M(14-aneN₄)(H₂O)₂]ⁿ⁺ Complexes. In Figure 12 is seen a plot of *U* vs. *r* for both the trans-III-planar and cis-V-folded form of the [M(14-aneN₄)(H₂O)₂]ⁿ⁺ complex. It is seen that a steep curve results for the trans-III conformer, with a flatter curve for the folded cis-V form, in agreement with the greater flexibility expected for the latter. The dotted lines cross at a M-N length of 2.09 Å. The octahedral metal ions with M-N lengths above this size should thus exist in predominantly the cis-folded form. We find that Cr(III) and Rh(III) with ideal M-N lengths of 2.07 Å exist in both cis and trans forms,^{35,36} and Cr(III) in solution exists as a mixture of the two forms.³⁵ Co(III) with an M-N of 1.92 Å is far from the crossover point of the two curves. It is possible to synthesize the cis form, but it rapidly isomerizes in solution to the trans form.³ Ni(II), with an Ni-N length of 2.055 Å in planar [Ni(14-aneN₄)(NO₃)₂] fits exactly into the trans-III form, but there should from Figure 12 be about 20% of the folded form present. Experiments with the folded form, which can be generated in solution from [Ni(cyclam)(en)]²⁺ by stripping the en off with acid, suggest the presence of a small percentage of the cis form.³⁷ This was estimated to be presented only to the extent of about 1% by comparison of the log *K*₁ values for the binding of en to the cis form of [NiL(H₂O)₂]²⁺ where L

(34) Prasad, L.; McCauley, A. *Acta Crystallogr., Sect. C* **1983**, C39, 1175-1177.

(35) Swisher, R. G.; Brown, G. A.; Smiercak, R. C.; Blinn, E. L. *Inorg. Chem.* **1981**, 20, 3947-3951.

(36) Bhattacharya, P. K. *J. Chem. Soc., Dalton Trans.* **1980**, 810-812.

(37) Billo, E. *J. Inorg. Chem.* **1981**, 20, 4019-4021.

(33) Hambley, T. W.; Searle, G. H.; Snow, M. R. *Aust. J. Chem.* **1982**, 35, 1285-1295.

is 14-aneN₄, to the case where L is trien. As pointed out,³⁶ this must be regarded as a lower limit because of the severe steric interactions which 14-aneN₄ produces for additional coordinated ligands, which is confirmed in our MM calculations.

H. Conclusions. In Table IV we have attempted to summarize the results of our MM calculations. The following general conclusions can be drawn:

(1) Trans-I (++++) forms are much more flexible than trans-III (+ + - -) forms; they are not readily able to accommodate octahedral coordination geometry, and they tend to cause the metal ion to lift out of the plane of the donor atoms. For 12-aneN₄ the trans-I is so much more stable than the trans-III configuration that the latter is unlikely to occur. For 13-aneN₄ the trans-I and trans-III are of about the same stability, while for 14-aneN₄ the trans-III is the most stable except at high (M-N > 2.29 Å) and low (M-N < 1.90 Å) bond lengths.

(2) van der Waals repulsions mean that ligands coordinated axially to the planar trans-III forms will experience considerable steric hindrance.

(3) Folding of 14-aneN₄ to give the cis-V structure will be favored for octahedral metal ions with M-N above 2.09 Å.

(4) The ideal bond length of Ni(II), and probably other metal ions, can vary as nitrogens are replaced by other donor atoms such as oxygen, as well as in response to gross distortion of coordination geometry, such as the tetragonal distortion present in [Ni(14-aneN₄)Cl₂]

Acknowledgment. We thank the Senate and Council Research Grants Committee of the University of the Witwatersrand and the Council for Scientific and Industrial Research for financial support. Jon Albain is thanked for carrying out the crystallographic data collection.

Registry No. [Cu(13-aneN₃O)Br]Br, 91711-59-0; [Ni(14-aneN₄)(NO₃)₂], 91711-60-3.

Supplementary Material Available: Table of temperature factors and observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

(38) Walker, D. D.; Taube, H. *Inorg. Chem.* **1981**, *20*, 2828-2834.

(39) Johnson, C. K. "ORTEP"; Oak Ridge National Laboratory: Oak Ridge, TN, 1965; Report No. ORNL-3794.

MO Theory of Ease of Formation of Carbocations Derived from Nonalternant Polycyclic Aromatic Hydrocarbons

John P. Lowe*[†] and B. D. Silverman[‡]

Contribution from the Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802, and IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598. Received January 6, 1984

Abstract: The energy required for carbocation formation from diol epoxide derivatives of polycyclic aromatic hydrocarbons (PAHs) is of interest in understanding molecular carcinogenicity. Here we examine the effects upon such (computed) energies of changing from alternant to nonalternant PAHs. Quantum chemical calculations indicate that the presence of an external unsaturated five-membered ring on an otherwise alternant PAH makes "bay-region" carbocation formation more difficult. However, the presence of a saturated external five-membered ring has the opposite effect. A "peninsular" ring can undergo ionization in either of two ways, the resulting ions often having significantly different stabilities. Simple interactive-fragment frontier-orbital models are found to rationalize all of these results and to offer predictive shortcuts.

There is currently strong interest in relative stabilities of carbocations formed from polycyclic aromatic hydrocarbons (PAHs). A great deal of experimental evidence¹⁻⁶ supports the notion that, when certain PAHs undergoing metabolism in the body lead to cancer, the transition state for the reaction with DNA has carbocation character. (See Figure 1.) Quantum chemical calculations of relative ion stabilities by many groups indicate a general tendency for the most carcinogenic PAHs to be those with greatest computed ion stability,⁶⁻²⁴ relative to the diol epoxide precursor. This correlation between experimental carcinogenicity and computed ease of ion formation is imperfect, which is hardly surprising when we consider the involved nature of the overall biochemical process. Still, it is widely felt that knowledge of relative carbocation stability is one of the chief ingredients needed to rationalize or predict relative PAH carcinogenicities.

Our goal, in this and earlier papers,¹³⁻¹⁸ is to understand and predict relative ease of carbocation formation. That is, if carbocation A is computed to be easier to form from a diol epoxide than carbocation B, what factors are responsible? Could we have predicted in advance that A is more easily formed? If it is also true that the PAH associated with carbocation A is more carcinogenic than that associated with B, then perhaps our explanation

of the computed relative ease of ion formation is also an explanation for the relative experimental carcinogenicities. If the

(1) Arcos, J. C.; Argus, M. F. "Chemical Induction of Cancer"; Academic Press: New York, 1974.

(2) Conney, A. H. *Cancer Res.* **1982**, *42*, 4875-4917.

(3) Borgen, A.; Darvey, H.; Castagnoli, N.; Crocker, T. T.; Rasmussen, R. E.; Yang, I. Y. *J. Med. Chem.* **1973**, *16*, 502.

(4) Sims, P.; Grover, P. L.; Swaisland, A.; Pal, K.; Hewer, A.; *Nature (London)* **1974**, *252*, 326.

(5) Harvey, R. G. *Acc. Chem. Res.* **1981**, *14*, 218-226.

(6) Jerina, D. M.; Lehr, R. E.; Yagi, H.; Hernandez, O.; Dansette, P. M.; Wislocki, P. G.; Wood, A. W.; Chang, R. L.; Levin, W.; Conney, A. H. In "In Vitro Metabolic Activation and Mutagenesis Testing"; DeSerres, F. J., Fouts, J. R., Bend, J. R., Philpot, R. M., Eds.; Elsevier: Amsterdam, 1976; pp 159-177.

(7) Lehr, R. E.; Jerina, D. M. *J. Toxicol. Environ. Health* **1977**, *2*, 1259-1265.

(8) Jerina, D. M.; Lehr, R. E. In "Microsomes and Drug Oxidation"; Ullrich, V., Roots, I., Hildebrandt, A. G., Estabrook, R. W., Conney, A. H., Eds.; Pergamon: Oxford, 1977; pp 709-720.

(9) Smith, I. A.; Berger, G. D.; Seybold, P. G.; Servē, M. P. *Cancer Res.* **1978**, *38*, 2968-2977.

(10) Loew, G. H.; Sudhindra, B. S.; Ferrell, J. E., Jr. *Chem.-Biol. Interact.* **1979**, *26*, 75.

(11) Loew, G. H.; Wong, J.; Phillips, J.; Hjelmeland, L.; Pack, G. R. *Cancer Biochem. Biophys.* **1978**, *2*, 123.

(12) Loew, G. H.; Phillips, J.; Hjelmeland, L.; Pack, G. R. *Cancer Biochem. Biophys.* **1978**, *2*, 113.

* The Pennsylvania State University.

† IBM Thomas J. Watson Research Center.