is apparent that the expression for K_p has units of volume per mole (geometrically, the volume involved is that of the "reaction zone"); thus, transposition of this expression into a 2D system gives

$$^{2D}K_p = 2\pi NR\delta R \tag{15}$$

and the 2D expression analogous to eq 13 is

$$^{2D}k_{ex} = k_{et}{}^{2D}K_p \tag{16}$$

In view of eqs 12-16, the relationship between k_{ex} and $^{2D}k_{ex}$ can be expressed by eq 17. Assuming a literature value of R (7.6 Å) for the ferrocene/ferrocenium precursor complex,[20] we obtained $k_{ex} = 6.4 \times 10^7$ M^{-1} s^{-1} as an expected value of the electron-transfer rate constant, which would lead to D_e equal to the lowest D observed in our experiments at the air/water interface. A literature value for the ferrocene/ferricenium rate constant in acetonitrile is 9.1×10^6 M^{-1} s^{-1}.[21] Direct comparison of these values is complicated by uncertainties stemming from solvent effects and other phenomena that cannot be evaluated precisely for the C_{18}Fc system at the air/water interface. However, it is not surprising that the present measurements appear to reflect solely translational diffusion. Since the measurements of the electron transfer rate constant involving sites at the air/water interface could shed some light on solvation effects and reveal, potentially, orientational dependence of the electron transfer kinetics, we are currently pursuing various strategies aimed at restricting the rate of lateral diffusion in these types of systems in order to experimentally access the kinetics of electron self-exchange.

$$k_{ex} = {}^{2D}k_{ex}2R \tag{17}$$

Conclusions

The main conclusions of this report can be summarized in the following points:

1. We have developed a microband electrode that can be used in electrochemical experiments at the air/water interface and demonstrated the application of electrochemical techniques in the measurements of the dynamics of 2D lateral diffusion in Langmuir monolayers.
2. Lateral diffusion of C_{18}Fc at the air/water interface, alone and in mixtures with $C_{18}OH$, obeys a simple free area model in a broad range of surface concentrations, in which the diffusing molecules can be treated as hard disks with the surface area equal to the projected area of their head groups.
3. Above approximately 25 °C, the C_{18}Fc monolayer remains fluid and does no exhibit phase transitions in the range of free areas of ca. 5-100 Å^2/molecule.
4. The magnitude of the C_{18}Fc lateral diffusion coefficient of ca. 2×10^{-7} cm^2/s measured at the highest surface concentration attainable in these studies is sufficiently high as to eliminate any contribution to the lateral current due to electron hopping in this 2D network of the redox sites.

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[21] Nielson, R. M.; McManis, G. E.; Safford, L. K.; Weaver, M. J. *J. Phys. Chem.* **1989**, *93*, 2152.

Comparative Molecular Mechanics Study of the Low-Spin Nickel(II) Complexes of an Extended Series of Tetraaza Macrocycles

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Abstract: Molecular mechanics calculations of metal complex structures are often not straight forward because of uncertainties concerning the appropriate force-field parameters for structural elements involving the metal. A systematic study aimed at extending the Allinger MM2 force field for use with N_4-macrocyclic complexes of low-spin Ni(II) is reported. Although molecular mechanics investigations of particular low-spin Ni(II) complexes of tetraaza macrocycles have been performed previously, no calibration of the force field for such complexes with a wide range of compounds of this type has been reported. X-ray data for twenty low-spin Ni(II) complexes incorporating solely sp^3 nitrogen donors and six complexes also containing sp^2 nitrogens have been used in the calibration of the extended force field. Inclusion of an out-of-plane bending term, which restricts the degree to which the Ni(II) atom can deviate from the least-squares plane of the donor atoms, was generally beneficial in modeling the respective coordination planes. The application of the extended force field to the re-examination of the configurational isomers of [Ni(cyclam)]$^{2+}$ and their N,N,N,N-tetramethylated derivatives is reported.

Since the introduction of the molecular mechanics procedure for organic molecules,[1] there has been continuing development of the method toward the modeling of other types of compounds,[2] including transition-metal complexes.[3,4] For example, much attention has been given to the conformational analysis of the

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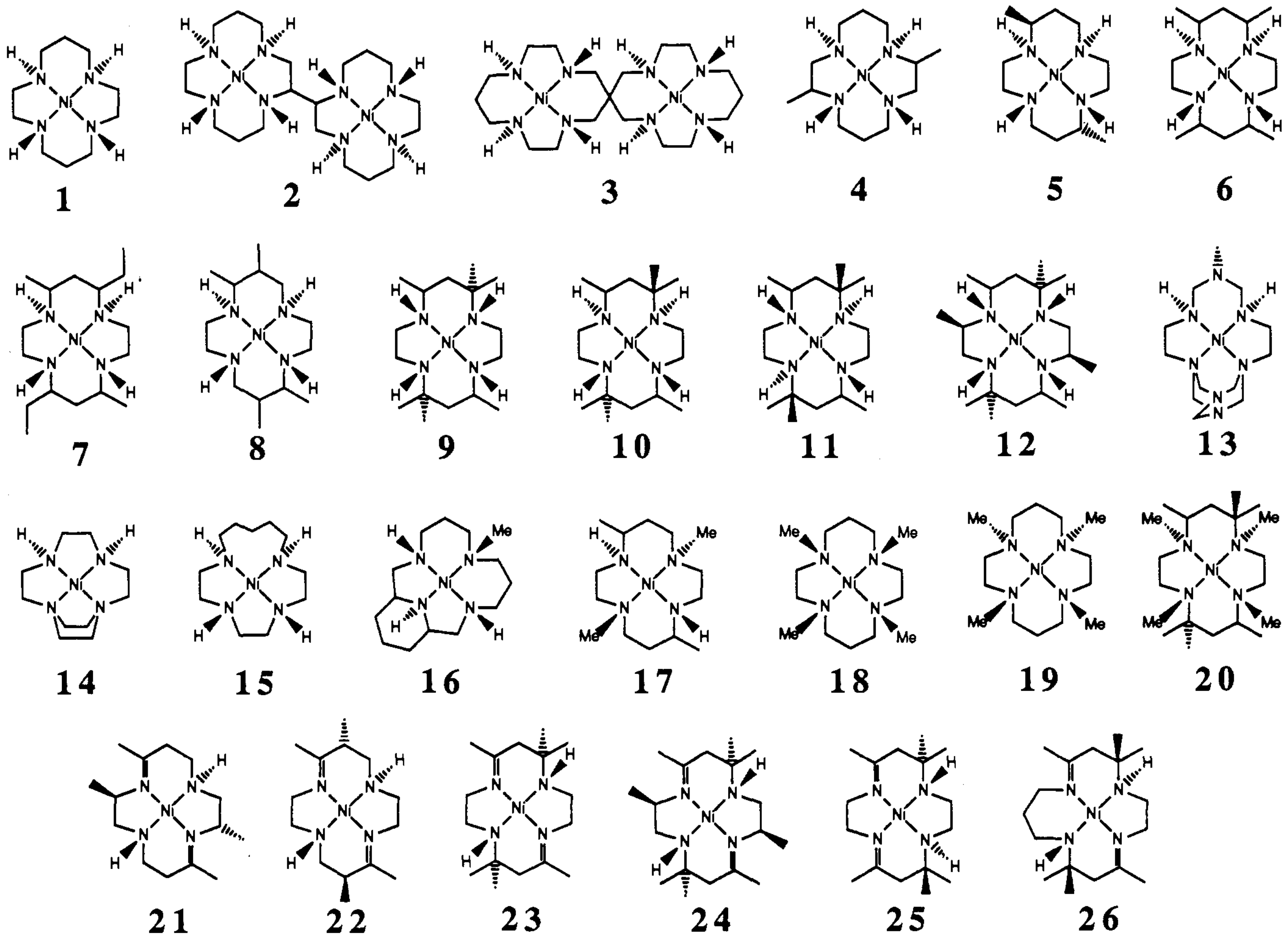
[1] Allinger, N. L. *Adv. Phys. Org. Chem.* **1976**, *13*, 1. Burkert, U.; Allinger, N. L. *Molecular Mechanics*; American Chemical Society: Washinton, DC, 1982; p 1ff and references therein. Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127.

[2] Weiner, S. J.; Kollman, P. A.; Case, D. A.; Singh, U. C.; Ghio, C.; Alagona, G.; Proteta, S.; Weiner, P. *J. Am. Chem. Soc.* **1984**, *106*, 765. Grootenhuis, P. D. J.; Kollman, P. A. *J. Am. Chem. Soc.* **1989**, *111*, 2152, 4046. Andreetti, G. D.; Ori, O.; Ugozzoli, F.; Alfieri, C.; Pochini, A.; Ungaro, R. J. *Incl. Phenom.* **1988**, *6*, 523. Kollman, P. *Acc. Chem. Res.* **1985**, *18*, 105 and references therein.

0002-7863/91/1513-3346$02.50/0

Chart I



1 **2** **3** **4** **5** **6** **7** **8** **9** **10** **11** **12** **13** **14** **15** **16** **17** **18** **19** **20** **21** **22** **23** **24** **25** **26**

complexes of open-chain polydentate ligands.[5,6] Many of these latter studies have involved complexes of Co(III) for which a generally satisfactory set of parameters has been derived. The molecular mechanics procedure has also been applied increasingly to the study of macrocyclic ligand complexes of heavy metals.[7,8] However, although many of these studies have been quite informative, they nevertheless tend to be somewhat fragmentary with, for example, a single structure (or small number of similar structures) being modeled with little indication that the force field used has general applicability. It has been our experience that a single structure may be fitted equally well with several different parameter sets; it is only by testing the parameters over a considerable number (and range) of structures that it is possible to decide between alternative sets. In view of the continuing interest in macrocyclic complexes of the type mentioned above,[9] there remains a clear need for a broadly calibrated set of force-field parameters for use with such species.

In the present study, the previously published X-ray data for 26 low-spin Ni(II) complexes of tetraaza macrocyclic ligands incorporating solely sp^3 nitrogen donors,[10-28] and in some cases

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(3) Busch, D. H.; DeHayes, L. J. *Inorg. Chem.* **1973**, *12*, 1505. Martin, L. Y.; DeHayes, L. J.; Zompa, L. J.; Busch, D. H. *J. Am. Chem. Soc.* **1974**, *96*, 4046.

(4) Brubaker, G. R.; Johnson, D. W. *Coord. Chem. Rev.* **1984**, *53*, 1.

(5) See for example: Gollogly, J. R.; Hawkins, C. J. *Inorg. Chem.* **1969**, *8*, 1168. Buckingham, D. A.; Maxwell, I. E.; Sargeson, A. M.; Snow, M. R. *J. Am. Chem. Soc.* **1970**, *92*, 3617. Snow, M. R. *J. Am. Chem. Soc.* **1970**, *92*, 3610. Geue, R. J.; Snow, R. *J. Chem. Soc. A* **1971**, 2981. Hambley, T. W.; Searle, G. H. *Acta Crystallogr.* **1984**, *C40*, 383. Bond, A. M.; Hambley, T. W.; Snow, M. R. *Inorg. Chem.* **1985**, *24*, 1920. Hambley, T. W.; Snow, M. R. *Inorg. Chem.* **1986**, *25*, 1378. Hambley, T. W. *Inorg. Chem.* **1988**, *27*, 1073. Comba, P.; Hambley, T. W.; Zipper, L. *Helv. Chim. Acta* **1988**, *71*, 1875.

(6) Buckingham, D. A.; Sargeson, A. M. *Top. Stereochem.* **1971**, *6*, 219.

(7) Hancock, R. D. *Prog. Inorg. Chem.* **1989**, *37*, 187. Hancock, R. D. *Acc. Chem. Res.* **1990**, *23*, 253 and references therein.

(8) See for example: Searle, G. H.; Dwyer, M. *Inorg. Chim. Acta* **1981**, *52*, 251. Boeyens, J. C. A.; Hancock, R. D.; Thom, V. J. *J. Cryst. Spectrosc.* **1984**, *14*, 261. Brubaker, G. R.; Johnson, D. W. *Inorg. Chem.* **1984**, *23*, 1591. Adam, K. R.; Brigden, L. G.; Henrick, K.; Lindoy, L. F.; McPartlin, M.; Mimnagh, B.; Tasker, P. A. *J. Chem. Soc., Chem. Commun.* **1985**, 710. Drew, M. G. B.; Yates, P. C.; Murphy, B. P.; Nelson, J.; Nelson, S. M. *Inorg. Chim. Acta* **1986**, *118*, 37. Drew, M. G. B.; Yates, P. C. *J. Chem. Soc., Dalton Trans.* **1987**, 2563. Hancock, R. D.; Dobson, S. M.; Boeyens, J. C. A. *Inorg. Chim. Acta* **1987**, *133*, 221. Schwarz, C. L.; Endicott, J. F. *Inorg. Chem.* **1989**, *28*, 4011. Endicott, J. F.; Kumar, K.; Schwarz, C. L.; Perkovic, M. W.; Lin. W. K. *J. Am. Chem. Soc.* **1989**, *111*, 7411. Hancock, R. D.; Weaving, J. S.; Marques, H. M. *J. Chem. Soc., Chem. Commun.* **1989**, 1176. Hancock, R. D.; Wade, P. W.; Ngwenya, M. P.; de Sousa, A. S.; Damu, K. V. *Inorg. Chem.* **1990**, *29*, 1968.

(9) Lindoy, L. F. *The Chemistry of Macrocyclic Ligand Complexes*; Cambridge University Press: Cambridge, U.K., 1989.

(10) Prasad, L.; McAuley, A. *Acta Crystallogr.* **1983**, *C39*, 1175.

(11) Barefield, E. K.; Cheung, D.; van Derveer, D. G.; Wagner, F. *J. Chem. Soc., Chem. Commun.* **1981**, 302.

(12) McAuley, A.; Subramanian, S.; Whitcombe, T. W. *J. Chem. Soc., Chem. Commun.* **1987**, 539.

(13) Urbanczyk-Lipkowska, Z.; Krajewski, J. W.; Gluzinski, P.; Parkanyi, L. *Pol. J. Chem.* **1983**, *57*, 85.

(14) Krajewski, J. W.; Urbanczyk-Lipkowska, Z.; Gluzinski, P. *Bulletin de l'Academie Polonaise de Sciences, Serie des Sciences Chimiques* **1977**, *25*, 853.

(15) Hay, R. W.; Jeragh, B.; Ferguson, G.; Kaitner, B.; Ruhl, B. L. *J. Chem. Soc., Dalton Trans.* **1982**, 1531.

(16) Krajewski, J.; Urbanczyk-Lipkowska, Z.; Gluzinski, P. *Bull. Acad. Pol. Sci., Sci. Chim.* **1977**, *25*, 939.

(17) Krajewski, J. W.; Urbanczyk-Lipkowska, Z.; Gluzinski, P. *Pol. J. Chem.* **1978**, *52*, 1513.

(18) Curtis, N. F.; Swann, D. A.; Waters, T. N. *J. Chem. Soc., Dalton Trans.* **1973**, 1963.

(19) Ito, T.; Toriumi, K. *Acta Crystallogr.* **1981**, *B37*, 88.

(20) Ito, H.; Ito, T.; Toriumi, K. *Acta Crystallogr.* **1981**, *B37*, 1412.

Table I. Force-Field Parameters for Low-Spin Ni(II) Complexes of N$_4$-Donor Macrocycles

Nonbonded Parameters[a]

atom	r^*/Å	ϵ/kJ mol^{-1}
Ni(II)	2.30	0.711

Bond-Stretching Parameters and Bond Moments

bond type	r_0/Å	k_r/mdyn Å^{-1} molecule^{-1}	μ/D
Ni–N(sp^3)	1.89	2.65	–0.027
Ni–N(sp^2)	1.84	1.70	–0.300
N(sp^3)–C(sp^3)	1.47	4.20	0.027
N(sp^2)–C(sp^2)	1.26	5.00	0.040
N(sp^2)–C(sp^3)	1.47	4.20	0.200

Bond Bending Parameters

bond angle	θ_0/deg	k_θ/mdyn Å rad^{-2} molecule^{-1}
H–N(sp^3)–Ni	109.5	0.50
N(sp^3)–Ni–N(sp^2)	90.0	0.50
N(sp^3)–Ni–N(sp^2)	90.0	0.50
N(sp^2)–Ni–N(sp^2)	90.0	0.50
C(sp^3)–N(sp^3)–Ni	109.5	0.50
C(sp^2)–N(sp^3)–Ni	120.0	0.45
C(sp^2)–N(sp^2)–C(sp^3)	112.0	0.70

Out-of-Plane Bending Term

atom	plane	k_{opb}/mdyn Å^{-1} molecule^{-1}
Ni(II)	N$_4$-donor	1.10

Torsional Constants

torsion	V_1/kJ mol^{-1}	V_2/kJ mol^{-1}	V_3/kJ mol^{-1}
C(sp^3)–C(sp^3)–N(sp^2)–Ni	–0.84	3.05	3.35
C(sp^3)–C(sp^3)–N(sp^3)–Ni	–0.84	3.05	3.35
C(sp^3)–C(sp^2)–N(sp^2)–Ni	–0.42	62.8	0.0
H–C(sp^3)–N(sp^3)–Ni	0.0	0.0	2.18
H–C(sp^3)–N(sp^2)–Ni	0.0	0.0	2.18

[a] The same values were used by Drew et al. (Drew, M. G. B.; Rice, D. A.; Silong, S. B.; Yates, P. C. *J. Chem. Soc., Dalton Trans.* **1986**, 1081.).

also sp^2 nitrogen donors,[29-34] have been used as a basis for the modification and extension of Allinger's MM2 "organic" parameters. The structures are given in Chart I **1–26**.

Experimental Section

The molecular mechanics calculations reported in the present study were undertaken with use of the MOLMEC suite of computer programs written at James Cook University.[35]

X-ray structures were selected for use in the study on the basis of accuracy, and an arbitrary upper limit for the R factor of 0.08 was used to make the selection.[36] Of the 14-membered-ring structures containing a symmetric arrangement of their chelate rings it is noted that **1–8**, **10**, **17**, **19**, and **20** have configurations corresponding to the trans-III form[37] of [Ni(cyclam)]$^{2+}$, **9**, **12**, and **18** have configurations corresponding to the trans-I form, while **11** has a configuration of the trans-V type (see Figure 1).

Parametrization of the Force Field. Allinger's widely tested MM2[1] force field (together with extensions to the field which cover aliphatic amines[38] and aromatic systems[39]) was used unchanged for the present study apart from the modifications discussed below.

With use of a trial and error process, force-field parameters for the parts of the structure involving Ni(II) were derived that gave the best overall match to the reported X-ray geometries of the 26 structures designated **1–26**. These and other parameters derived during the present study are listed in Table I. Initial estimates of the "ideal" bond lengths (r_0) for Ni–N(sp^3) and Ni–N(sp^2) were made from inspection of similar bonds in simple noncyclic systems in which steric influences were at a minimum. The Ni–N bond distances in these structures were assumed to be only slightly longer than the required "ideal" Ni–N distances; the initial estimates were then further refined, in terms of structures **1–26**, to yield the final values listed in Table I. Estimates of the stretching constants (k_r) for Ni–N(sp^3) and Ni–N(sp^2) bonds were also made and refined.[40]

Allinger's N(sp^3)–C(sp^3) bond stretching parameters were also modified to account for coordination of the nitrogen. Best fits across the structures were obtained when the ideal bond length was increased slightly, from 1.45 to 1.47 Å, and the force constant reduced from 5.1 to 4.2 mdyn Å^{-1}.[41] The N(sp^2)–C(sp^3) and N(sp^2)–C(sp^2) bond stretching parameters were treated similarly. An adjustment was required to the Allinger bond moments when they involved a donor atom to allow for coordination; they were arbitrarily reduced by one-third. An approximation, required by a lack of empirical data, was used when assigning bond moments for the Ni-donor bonds; these were made equal to the values used for the corresponding carbon-donor bonds. Bond angle parameters for H–N–C and C–N–C, taken from the MM2 force field,

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(21) Suh, M. P.; Shin, W.; Kim, H.; Koo, C. H. *Inorg. Chem.* **1987**, *26*, 1846.

(22) Hancock, R. D.; Dobson, S. M.; Evers, A.; Wade, P. W.; Ngwenya, M. P.; Boeyens, J. C. A.; Wainwright, K. P. *J. Am. Chem. Soc.* **1988**, *110*, 2788.

(23) Sugimoto, M.; Fugita, J.; Ito, H.; Toriumi, K.; Ito, T. *Inorg. Chem.* **1983**, *22*, 955.

(24) Alcock, N. W.; Moore, P.; Omar, H. A. A. *J. Chem. Soc., Dalton Trans.* **1986**, 985.

(25) Miyamura, K.; Kohzuki, M.; Narushima, R.; Saburi, M.; Gohshi, Y.; Tsuboyama, S.; Tsuboyama, K.; Sakurai, T. *J. Chem. Soc., Dalton Trans.* **1987**, 3093.

(26) Hambley, T. W. *J. Chem. Soc., Dalton Trans.* **1986**, 565.

(27) Barefield, E. K.; Freeman, G. M.; Van Derveer, D. G. *Inorg. Chem.* **1986**, *25*, 552.

(28) Lee, T.-Y.; Hsieh, M.-Y.; Lee, T.-J.; Chen, J.-W.; Chung, C.-S. *Acta Crystallogr.* **1986**, *C42*, 1001.

(29) Krajewski, J. W.; Urbanczyk-Lipkowska, Z.; Gluzinski, P. *Rocz. Chem.* **1977**, *51*, 2385.

(30) Ferguson, G.; Restivo, R. J.; Hay, R. W. *Acta Crystallogr.* **1979**, *B35*, 159.

(31) Hanic, F.; Miklos, D. *J. Cryst. Mol. Struct.* **1972**, *2*, 115.

(32) Swann, D. A.; Waters, T. N.; Curtis, N. F. *J. Chem. Soc., Dalton Trans.* **1972**, 1115.

(33) Kilbourn, B. T.; Ryan, R. R.; Dunitz, J. D. *J. Chem. Soc. A* **1969**, 2407.

(34) Curtis, N. F.; Gainsford, G. J. *Aust. J. Chem.* **1986**, *39*, 1509.

(35) The following is a brief description of each program in the package: (a) MOLMIN minimizes the molecular geometry of a structure, using a quasi-Newton minimization algorithm and a BFGS update method with analytical first derivatives (Wright, M. H. *Practical Optimisation*; Academic Press: London, 1983; p 116.). For molecules of the type studied, about 300 variables were involved in the minimization process. (b) ANAL analyzes a structure in terms of its component elements of strain. It produces a listing of the bond lengths, bond angles, van der Waals' interactions, dipole–dipole interactions, out-of-plane distances, and torsional force constants. Strain energy contributions from each of these interactions and the total strain energy of the structure are also listed. (c) COMPAR compares two structures containing the same number and types of atoms. It lists the respective bond lengths, bond angles, out-of-plane angles, and torsion angles as well as the differences between them. Such a listing is useful for estimating the match (or otherwise) between an X-ray structure and the corresponding calculated structure after minimization with MOLMIN. (d) ADATOM scans a file of atom coordinates for a structure and adds H atoms or lone pairs of electrons to C, N, O, or S atoms when required. This program is useful for adding H atoms to X-ray structures that are often not reported in the literature. (e) HOLPLN calculates the hole size of the ligand cavity for a given structure and also least-squares planes and atom deviations from the calculated planes.

(36) Certain structures were eliminated on grounds other than R factor (such as the presence of disorder, apparently anomalous bond distances in the respective backbones of the macrocycles, or particular intermolecular hydrogen-bonding patterns which are unable to be treated by MOLMEC). Structures in this category are described in the following references: Prasad, L.; Nyburg, S. C.; McAuley, A. *Acta Crystallogr.* **1987**, *C43*, 1038. Crick, I. S.; Gable, R. W.; Hoskins, B. F.; Tregloan, P. A. *Inorg. Chim. Acta* **1986**, *111*, 35. Coates, J. H.; Hadi, D. M. M. A.; Hambley, T. W.; Lincoln, S. F.; Rodgers, J. R. *Cryst. Struct. Commun.* **1982**, *11*, 815. Lu, T.-H.; Lee, T.-J.; Lee, T.-Y.; Liang, B.-F.; Chung, C.-S. *Proc. Nat. Sci. Counc. A, ROC* **1984**, *8*, 217. Ito, T.; Toriumi, K.; Ito, H. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1096. An otherwise important structure in this latter category was *trans*-V [Ni(cyclam)]$^{2+}$ (see ref 51). Although this structure has a satisfactory R factor, it contains apparently anomalous C–C distances in the organic backbone of the ligand. Nevertheless, the Ni–N distances were adequately modeled with use of our extended force field.

(37) Bosnich, B.; Poon, C. K.; Tobe, M. L. *Inorg. Chem.* **1965**, *4*, 1102.

(38) Profita, S.; Allinger, N. L. *J. Am. Chem. Soc.* **1985**, *107*, 1907.

(39) Beckhaus, H.-D. *Chem. Ber.* **1983**, *116*, 86.

(40) A different set of values for r_0 and k_r might be expected for the Ni–tertiary nitrogen bonds found in **16–20**, in practice no difference in the force constants was needed.

(41) These (small) changes are in the expected direction, since the carbon–nitrogen bond will normally be weakened upon coordination.

Table II. Comparison of the X-ray and Calculated Structures for the Low-Spin Ni(II) Structures of N_4-Donor Macrocycles

structure	bond distances rms differences/Å	bond angles rms differences/deg	torsion angles[a] rms differences/deg	R factor[b]	ref no.
1	0.0233	1.41	1.19	0.055	10
2	0.0144	1.35	4.02	0.056	11
3	0.0205	1.57	2.86	0.049	12
4	0.0108	1.27	3.02	0.043	13
5	0.0159	1.78	4.07	0.033	14
6	0.0150	1.68	2.48	0.036	15
7	0.0495	1.77	5.72	0.042	16
8	0.0175	1.73	5.78	0.033	17
9	0.0217	2.08	4.92	0.039	18
10[c]	0.0142	1.71	2.67	0.031	19
11	0.0285	2.37	5.64	0.071	18
12	0.0206	2.92	8.33	0.034	20
13	0.0235	1.11	4.30	0.049	21
14	0.0178	1.34	3.64	0.018	22
15	0.0529	2.66	8.74	0.048	23
16	0.0290	1.96	5.34	0.056	24
17	0.0161	1.59	1.30	0.034	25
18	0.0235	2.27	3.56	0.052	26
19	0.0126	0.97	1.36	0.042	27
20	0.0171	1.70	3.65	0.047	28
21	0.0174	1.44	4.91	0.027	29
22	0.0147	1.39	2.16	0.039	30
23	0.0208	2.96	18.13[d]	0.030	31
24	0.0199	2.55	5.64	0.080	32
25	0.0225	2.15	4.03	0.062	33
26	0.0222	2.58	6.86	0.046	34

[a] Torsional angles involving N–Ni–N angles above 170° were not included in the analysis, since they incorporate an unrealistically high error. [b] Published crystallographic R factor. [c] A corresponding analysis of a duplicate structure determination of this complex cation (Drew, M. G. B.; Mok, K. F. *Acta Crystallogr.* **1987**, *C43*, 666) also gave a satisfactory (although marginally poorer) fit for each of the parameters listed in the table. [d] Minimization gave a slightly different conformation to that found in the X-ray structure, leading to the higher rms value in this case. This difference is likely due to crystal packing forces; these forces are not accounted for in the present MM2 calculations.

were modified to account for the more "tetrahedral" geometry that the sp^3 nitrogen atoms would be expected to adopt on coordination. Parameters for H–N–Ni and C–N–Ni were then derived by analogy with these (taking nickel to be approximately equivalent to carbon).

In addition to the out-of-plane bending terms already in the MM2 force field for sp^2 C and N, an out-of-plane bending term involving the mean plane through the Ni(II) and donor set was also found to aid the modeling of the Ni-donor plane.[42] For this purpose a term was introduced involving a Hooke's law harmonic potential where k_{opb} is the

$$E_{opb} = {}^1\!/_2 k_{opb} d^2$$

restoring constant (in mdyn $Å^{-1}$) and d is the distance (in Å) of the deviation of the metal atom from the least-squares plane of the donor atoms. Using trial and error, a value for the restoring constant (k_{opb}) of 1.1 mdyn $Å^{-1}$ yielded the best fit across all systems, although, of course, the inclusion of such a term had no effect on those structures for which the metal is already strictly in the donor plane. Where possible, the H–C–N–Ni and C–C–N–Ni torsions were taken to be analogous to the corresponding torsions in which Ni(II) is replaced by C and were assigned the corresponding MM2 values;[43] in other cases the values listed in Table I were employed. The torsional force constants for the atom sequences X–N–Ni–N (where X = C or H) were all set to zero, as is common practice.[44] The modifications and additions to the MM2 parameters employed in the present study are given in Table I. In all cases, the starting coordinates used for the minimizations were the actual X-ray structure coordinates.

Results and Discussion

Discussion of the Structures. The overall success of the new force field in modeling the 26 low-spin structures is illustrated by the comparisons given in Table II. In general, the hydrocarbon backbone of the respective ligands was adequately modeled by the unmodified MM2 force field. Consequently, the following discussion will focus on those parts of the respective structures directly influenced by the metal ion. Of principal interest is the good agreement between the observed and calculated Ni-donor bond distances (overall rms difference in bond lengths, 0.016 Å) and angles about the Ni(II) (overall rms difference in bond angles, 1.07°) as well as the observed and calculated out-of-plane displacement in each complex (Table III). Other structural elements, such as the C–N–Ni and C–N–C angles, were also generally adequately modeled.[45] Inspection of the nickel-to-nitrogen bond lengths confirmed that there is a tendency for these distances to be extended when *N*-methyl substitution is present; these extensions often appear to reflect interaction between adjacent axial *N*-methyl groups and/or van der Waals' repulsions between the latter groups and the central metal ion.[46]

Table III lists the X-ray and calculated macrocyclic hole sizes of the respective complexes. As observed previously,[47] hole size expansion is not a simple function of alkyl substitution, even when a given ligand conformation is maintained.

In our initial attempts at modeling complexes of the present type there was a tendency, in particular calculated structures, for the metal ion to deviate too greatly from the donor atom plane. The inclusion of the out-of-plane bending term mentioned previously was beneficial in more accurately fitting structures of the latter type. For those 14-membered-ring structures that approximate a trans-III configuration and contain symmetric arrangements (6,5,6,5) of the chelate rings, the coordination plane is usually relatively unstrained and the Ni(II) atom tends to lie in the plane. While 15 out of the 26 structures fall into this category, the remaining 11 structures exhibit varying degrees of displacement of the metal from the donor plane. A comparison of the X-ray and calculated out-of-plane displacement of the Ni(II)

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(42) It seemed intuitively reasonable to include such a term for low-spin Ni(II) complexes in view of the usual preference of this metal for a well-defined square-planar-coordination geometry.

(43) Drew, M. G. B.; Hollis, S.; Yates, P. C. *J. Chem. Soc., Dalton Trans.* **1985**, 1829.

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

(45) Crystal packing forces have not been incorporated in the MM2 calculations. Such forces mainly tend to influence torsional angles involving bonds on the periphery of the respective structures.

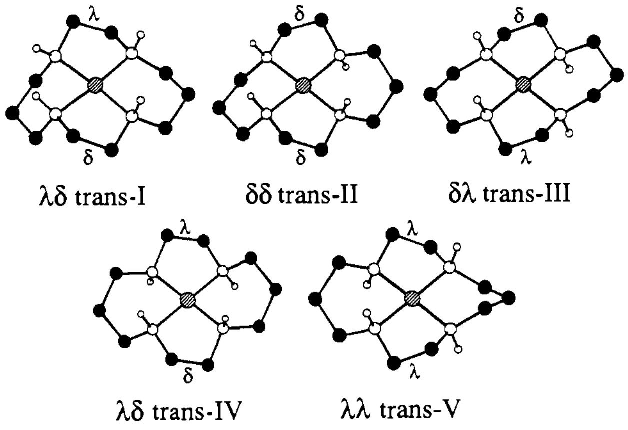
(46) Alkyl substitution on the carbon framework of the macrocycle adjacent to the nitrogen donors also results in bond length extension in some cases but no systematic pattern was evident.

(47) Henrick, K.; Tasker, P. A.; Lindoy, L. F. *Prog. Inorg. Chem.* **1985**, *33*, 1.

Table III. Observed and Calculated Ni(II) Out-of-Plane Distances and Macrocyclic Hole Sizes for the 26 Low-Spin Ni(II) Structures

structure		dist of Ni(II) atom from the mean N_4 plane/Å		hole size[a]/Å	
		X-ray	calcd	X-ray	calcd
1		0.00	0.00	1.95	1.94
2	Ni 1	0.00	0.00	1.95	1.94
	Ni 2	0.00	0.00	1.95	1.94
3	Ni 1	0.01	0.00	1.93	1.94
	Ni 2	−0.01	0.00	1.95	1.94
4		0.00	0.00	1.95	1.94
5		0.00	0.00	1.93	1.94
6		0.00	0.00	1.97	1.95
7		0.00	0.00	1.99	1.96
8		0.00	0.00	1.94	1.94
9		0.01	0.03 (0.09)[b]	1.93	1.92
10		0.00	0.00	1.96	1.96
11		0.05	0.02 (0.07)	1.90	1.93
12		0.06	0.04 (0.16)	1.93	1.91
13		0.03	0.03 (0.08)	1.92	1.93
14		0.15	0.14 (0.46)	1.86	1.87
15		0.11	0.07 (0.34)	1.91	1.91
16		0.06	0.09 (0.26)	1.93	1.93
17		0.00	0.00	1.97	1.96
18		0.01	0.03 (0.10)	1.98	2.00
19		0.00	0.00	1.99	2.00
20		0.00	0.00	2.01	2.04
21		0.00	0.00	1.92	1.92
22		0.00	0.00	1.93	1.92
23		0.03	0.02 (0.10)	1.90	1.92
24		0.04	0.04 (0.09)	1.91	1.91
25		0.00	0.00	1.91	1.91
26		0.02	0.04 (0.05)	1.90	1.90

[a] Radius of macrocyclic cavity calculated as reported previously (see ref 47). [b] Values in parentheses correspond to minimization without the out-of-plane bending term.



λδ trans-I δδ trans-II δλ trans-III

λδ trans-IV λλ trans-V

Figure 1. Conformations of the five trans isomers of $[Ni(cyclam)]^{2+}$.

Table IV. Relative Strain Energies[a] (kJ mol^{-1}) of the Five Configurational Isomers[b] of $[Ni(cyclam)]^{2+}$

isomer	Billo et al.[c]	this work
trans-I	1.3	0.0
trans-II	5.4	6.4
trans-III	0.0	1.1
trans-IV	32.4	42.9
trans-V	9.9	14.4

[a] Relative to the lowest energy isomer of $[Ni(cyclam)]^{2+}$ taken as zero energy. [b] See Figure 1. [c] From ref 50.

Table V. Relative Strain Energies[a] (kJ mol^{-1}) of the Isomers of $[Ni(N,N,N,N\text{-}Me_4\text{-cyclam})]^{2+}$

isomer	previous calculations[b]	this work
18 trans-I (without o.p.b.t.[c])	0.0	0.0
19 trans-III (without o.p.b.t.)	11.2	10.3
18 trans-I (with o.p.b.t.)		30.8
19 trans-III (with o.p.b.t.)		0.0

[a] Relative to the lowest energy isomer of $[Ni(cyclam)]^{2+}$ taken as zero energy. [b] From ref 26. [c] o.p.b.i. = out-of-plane bending term.

atom in each complex after inclusion of the out-of-plane term is given in Table III; satisfactory agreement is present in each case.[48]

The extended force field has been used to calculate the strain energies of the configurational isomers of selected Ni(II) complexes.

The Five Configurational Isomers of $[Ni(cyclam)]^{2+}$. Of the five possible configurational isomers of $[Ni(cyclam)]^{2+}$ (Figure 1), it has long been supposed that the trans-III configuration is the most stable. Bosnich et al. made a qualitative estimate of the strain energy of each of the isomers from models.[37] Whimp et al. revised this early non-quantitative estimate by a semi-quantitative estimate.[49] Billo et al.[50] published the calculated strain energies of the above isomers using a modified version of Allinger's MM2 force field [but not including an out-of-plane bending term for Ni(II)]. In a parallel study to that of Billo et al.,[50] the present force field was applied to the calculation of the five possible configurations of $[Ni(cyclam)]^{2+}$. The starting coordinates for the trans-III and trans-V configurations of $[Ni(cyclam)]^{2+}$ were obtained from the respective X-ray structure determinations.[10,51] The starting coordinates for the complexes having the remaining configurations, trans-I, trans-II, and trans-IV, were obtained by the manipulation of the coordinates for the complex with the trans-III configuration.[52] The relative strain energies for each of the five configurations derived in the present study are listed in Table IV.. For comparison, the energies calculated by Billo et al. are also included in the table.

It is evident that for this system both force fields give quite similar results. The difference in strain energy between the trans-I and trans-III isomers using either force-field is too small to be significant; both studies thus indicate that the trans-I and trans-III isomers are approximately equal in energy.

The Two Configurational Isomers of $[Ni(N,N,N,N\text{-}Me_4\text{-cyclam})]^{2+}$. There has been considerable interest in the low-spin Ni(II) complex of N,N,N,N-Me_4-cyclam.[26,53-55] In the initial studies it was assumed that the trans-III configuration is the lowest energy structure and that the trans-I configuration, **18**, forms because it is favored kinetically.[53,54] It was also demonstrated that, in the presence of coordinating solvents, an equilibrium is established between the trans-I and trans-III species with the trans-I species being favored in strongly coordinating solvents.[54] More recently, a molecular mechanics investigation has been performed on this system. These calculations indicated that the trans-I isomer should be favored over the trans-III isomer if four-coordinate low-spin species are involved.[26] Morever, the calculations indicated that if six-coordinate species are present then the stabilities would be reversed.

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(48) In general, the reason for any out-of-plane displacement tends to be obscure but, at least in some instances, it is associated with the presence of strain in the coordinated macrocyclic ring.

(49) Whimp, P. O.; Bailey, M. F.; Curtis, N. F. *J. Chem. Soc. A* **1970**, 1956.

(50) Connolly, P. J.; Billo, E. J. *Inorg. Chem.* **1987**, *26*, 3224.

(51) Barefield, E. K.; Bianchi, A.; Billo, E. J.; Connolly, P. J.; Paoletti, P.; Summers, J. S.; van Derveer, D. G. *Inorg. Chem.* **1986**, *25*, 4197.

(52) For each configuration obtained in this way there were two possible combinations for the conformations of the two five-membered chelate rings. They may either be δδ or λδ (or the corresponding mirror images λλ or δλ). No similar complication arises with the six-membered rings, which simply adopt chair conformations whenever possible. In practice, both structural possibilities for the five-membered rings were used as starting points for the respective calculations and the structure that yielded the lowest strain energy was the one listed in Table IV (and shown in Figure 1).

(53) D'Aniello, M. J.; Mocella, M. T.; Wagner, F.; Barefield, E. K.; Paul, I. C. *J. Am. Chem. Soc.* **1975**, *97*, 192.

(54) Moore, P.; Sachinidis, J.; Willey, G. R. *J. Chem. Soc., Chem. Commun.* **1983**, 522.

(55) Moore, P.; Sachinidis, J.; Willey, G. R. *J. Chem. Soc., Dalton Trans.* **1984**, 1323.

The results of our molecular mechanics calculations on these square-planar isomers are shown in Table V; results from the previous calculations are also included for comparison.[26] In contrast to the latter results, the (low-spin) trans-III isomer was calculated to be the lower energy isomer in the present study, a result largely attributable to the presence of the out-of-plane bending term in the force field. That is, our calculations suggest that the trans-III isomer is favored over the trans-I isomer as originally proposed. While it remains difficult to decide on the "correct" order from the present study, the results do illustrate the sensitivity of the method to the nature of the force field employed.[56] Clearly, in studies of the present type, appropriate caution should be exercised when using the molecular mechanics procedure for predicting the relative energies of isomeric metal complexes.

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(56) It needs to be emphasized that the present force field has been optimized only in terms of geometry and that the associated energy terms have not been "calibrated"—especially with respect to those parts of the structures influenced by the central metal.

The Pentafluoroxenate(IV) Anion, XeF_5^-: The First Example of a Pentagonal Planar AX_5 Species

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Abstract: Xenon tetrafluoride forms stable 1:1 adducts with $N(CH_3)_4F$, CsF, RbF, KF, and NaF and an unstable 1:1 adduct with FNO. All these adducts are ionic salts containing pentagonal planar XeF_5^- anions as shown by a crystal structure determination of $N(CH_3)_4^+XeF_5^-$, Raman and infrared spectra, and ^{19}F and ^{129}Xe NMR spectroscopy. The X-ray crystal structure of $N(CH_3)_4^+XeF_5^-$ was determined at -86 °C. This compound crystallizes in the orthorhombic system, space group *Pmcn*, with four molecules in a unit cell of dimensions a = 6.340 (2) Å, b = 10.244 (3) Å, and c = 13.896 (4) Å with R = 0.0435 for 638 observed $[I > 3\sigma(I)]$ reflections. In addition to four $N(CH_3)_4^+$ cations, the structure contains four pentagonal planar XeF_5^- anions per unit cell with D_{5h} symmetry. The Xe-F distances are 1.979 (2)-2.034 (2) Å with F-Xe-F angles of 71.5 (4)-72.3 (4)°. The D_{5h} structure of the XeF_5^- anion is highly unusual and represents the first example of an AX_5E_2 (E = valence electron lone pair) species in which all six atoms are coplanar. The results from the crystal structure determination and a normal coordinate analysis show that the XeF_5 plane of XeF_5^- is considerably more rigid than that in the fluxional IF_7 molecule due to the increased repulsion from the xenon free valence electron pairs. Local density functional calculations were carried out for XeF_5^- and XeF_4 with a double-numerical basis set augmented by polarization functions and confirm the experimentally observed geometries and vibrational spectra. It is shown that the bonding in XeF_5^- closely resembles that in XeF_4. In a valence bond description, it can be visualized as the two axial positions being occupied by two sp-hybridized free valence electron pairs and the equatorial fluorines being bound by two Xe 5p electron pairs through semiionic multicenter four-electron bonds.

Introduction

Recent work in our laboratories has shown that anhydrous $N(CH_3)_4F$[4] holds great potential for the synthesis and characterization of novel, high oxidation state, complex fluoro anions.[5-7] An area of special interest to us is the problem of maximum coordination numbers and their influence on the steric activity of free valence electron pairs. For example, it was shown that nitrogen(V) cannot accommodate five fluorine ligands,[8] whereas the iodine in IF_6^-, which had long been thought to have a distorted octahedral structure,[9,10] has recently been confirmed to possess a sterically active lone valence electron pair.[10] In contrast, the central atom free valence electron pairs in the smaller ClF_6^- and BrF_6^- anions become sterically inactive due to space limitations, as demonstrated in very recent vibrational[6,10] and single-crystal X-ray structure studies.[11]

In this context, the likely structures of the XeF_5^- and XeF_6^{2-} anions posed an interesting problem, since both anions contain two free valence electron pairs on the xenon central atom. Therefore, they are representatives of the novel AX_5E_2 and AX_6E_2 geometries, respectively, where E stands for a free valence electron pair. Whereas no reports have been published on the existence or possible structure of XeF_5^- or any other AX_5E_2 species, Kiselev and co-workers[13-15] recently reported the synthesis of M_2XeF_6 salts (M = Cs, Rb, K, Na) from XeF_4 and MF. On the basis of vibrational spectra, they surprisingly assigned an octahedral structure to XeF_6^{2-}. However, a closer inspection of their published

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(1) Rockwell International, Rocketdyne Division.
(2) E. I. du Pont de Nemours and Company, Inc.
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(4) Christe, K. O.; Wilson, W. W.; Wilson, R. D.; Bau, R.; Feng, J. *J. Am. Chem. Soc.* **1990**, *112*, 7619.
(5) Wilson, W. W.; Christe, K. O. *Inorg. Chem.* **1989**, *28*, 4172.
(6) Christe, K. O.; Wilson, W. W.; Chirakal, R. V.; Sanders, J. C. P.; Schrobilgen, G. J. *Inorg. Chem.* **1990**, *29*, 3506.
(7) Wilson, W. W.; Christe, K. O.; Feng, J.; Bau, R. *Can. J. Chem.* **1989**, *67*, 1988.
(8) Christe, K. O.; Wilson, W. W.; Schrobilgen, G. J.; Chirakal, R. V.; Olah, G. A. *Inorg. Chem.* **1988**, *27*, 789.
(9) Klamm, H.; Meinert, H.; Reich, P.; Witke, P. *Z. Chem.* **1968**, *8*, 469.
(10) Christe, K. O.; Wilson, W. W. *Inorg. Chem.* **1989**, *28*, 3275 and references cited therein.
(11) Mahjoub, A. R.; Hoser, A.; Fuchs, J.; Seppelt, K. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1526.
(12) Reference deleted in proof.
(13) Spitzin, V. I.; Kiselev, Yu. M.; Fadeeva, N. E.; Popov, A. I.; Tchumaevsky, N. A. *Z. Anorg. Allg. Chem.* **1988**, *559*, 171.
(14) Kiselev, Yu. M.; Goryachenkov, S. A.; Martynenko, L. I.; Spitsyn, V. I. *Dokl. Akad. Nauk SSSR* **1984**, *278*, 881.
(15) Kiselev, Yu. M.; Fadeeva, N. E.; Popov, A. I.; Korobov, M. V.; Nikulin, V. V.; Spitsyn, V. I. *Dokl. Akad. Nauk SSSR* **1987**, *295*, 378.

0002-7863/91/1513-3351$02.50/0