426 *Inorg. Chem.* **1989**, *28*, 426–431

ration of about 75 mV at a scan rate of 50 mV/s. The voltammogram has been attributed to the $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ couple. The formal potential of the couple, calculated from the voltammogram, is more positive than the potential for chlorine evolution from the tetrachloroaluminate ion in the melt. Thus, ferricyanide is thermodynamically unstable, but the homogeneous reaction is too slow to produce any observable catalytic anodic current under our experimental conditions. The couple undergoes a quasi-reversible faradaic reaction that is diffusion controlled. No electroactivity of the couple was observed in neutral or basic melt, as the couple is insoluble.

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Registry No. $(Bu_4N)_3Fe(CN)_6$, 14589-06-1; $(Bu_4N)_4Fe(CN)_6$, 53682-43-2; 1-methyl-3-ethylimidazolium chloride, 65039-09-0; aluminum chloride, 7446-70-0; tetrachloroaluminate, 17611-22-2; potassium ferricyanide, 13746-66-2.

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Coordination Geometries of Hexaamine Cage Complexes

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The structures of all six important conformers of the first-row transition-metal hexaamine cage complexes $M(sar)^{n+}$ (sar = 3,6,10,13,16,19-hexaazabicyclo[6.6.6]eicosane) have been computed by strain energy minimization calculations with fixed M–N distances between 1.90 and 2.36 Å. The excellent agreement between calculated and experimental structural parameters supports the force field used, which involves replacing metal–donor atom angle deformation terms by nonbonded interactions between the donor atoms. From the analysis of the total strain energy in dependence of M–N for all conformers considered, the following points emerge: (i) For small M–N distances (M–N < 2.0 Å) five conformers have similar strain energies; viz., their relative stability is dependent on environmental factors (crystal lattice, solution media, etc.), and this is in agreement with experimental data. (ii) With increasing number of oblique en-type chelate five rings (*ob* conformations) the stability decreases with increasing size of the metal centers. *lel*$_2$*ob*, *ob*$_2$*lel*, and *ob*$_3$ conformations are unstable vs the *lel*$_3$ conformations for M–N > 2.0, 2.10, and 2.2 Å, respectively. Qualitatively, this was already assumed from experimental data; however, it has not been quantified yet. (iii) Above ~2.2 Å there exists only one conformation with D_3*lel*$_3$ geometry. This conformation is different from the D_3*lel*$_3$ conformation observed for smaller M–N distances (e.g. cobalt(III) cages), and it has not been identified before. (iv) The analysis of the structural parameters of $M(sar)^{n+}$ in dependence on M–N indicates that the unsteady course of the twist angle ϕ vs M–N is the result of conformational changes. Metal-centered electronic effects in relation to these structural factors are also briefly discussed.

Introduction

Molecular-mechanics calculations are now relatively well established in coordination chemistry.[1] A large part of the studies deals with cobalt(III) hexaamines, and it is often tedious and difficult to get accurate force field parameters for other systems. With the recent improvement[2] of the widely used force field for cobalt(III) hexaamines,[3] the only metal-dependent force field parameters are the two parameters (k and r_0) that describe the metal center–ligand atom (M–N) breathing mode. One aim of the present study was to test the quality of these changes based on a large amount of experimental data. Furthermore, for a recently started project, which involves the design by molecular mechanics calculations of ligands used for stereoselective ligand exchange on chiral matrices,[4–6] it was also important to test these recently proposed changes.

A large number of transition-metal hexaamine cage complexes with sar-type ligand systems are known (sar = 3,6,10,13,16,19-hexaazabicyclo[6.6.6]eicosane; for atom labeling, see Figure 1). The most prominent structural variation in the whole series is the trigonal twist angle ϕ, which varies from about 25 to roughly 60° (for definitions of structural parameters, see also Figure 1). In a recent publication we have analyzed the variation of the twist angle ϕ based on a ligand field model.[7] I am now presenting metal center independent strain energy minimization calculations of all six important conformers of $M(sar)^{n+}$. Minimized strain energies and structural parameters are analyzed as a function of the M–N bond length ("blowing up" of the cages), and the calculated parameters are compared with experimental data. This analysis is discussed in relation to the quality of the presently used force field, to the possible evaluation of force field parameters for metal centers other than cobalt(III), and to the question of the influence of metal-centered electronic effects toward the structure of the cage complexes.

Experimental Section

In the molecular-mechanics formalism the structure of a complex is calculated by strain energy minimization. The total strain energy (conformational energy) is parametrized into bond length (E_b), valence angle (E_θ), torsion angle deformation (E_ϕ), and nonbonded interaction energies (E_{nb}):

$$U_{total} = \sum(E_b + E_\theta + E_\phi + E_{nb}) \qquad (1)$$

$$E_b = \tfrac{1}{2}A_b(r - r_0)^2 \qquad (2)$$

$$E_\theta = \tfrac{1}{2}A_\theta(\theta - \theta_0)^2 \qquad (3)$$

$$E_\phi = \tfrac{1}{2}A_\phi(1 + \cos 3\phi) \qquad (4)$$

$$E_{nb} = A_{nb}[\exp(-Bd)] - C/d^6 \qquad (5)$$

All strain energy minimization calculations have been performed with the Fortran program MOMEC85.[8] It involves a modified Newton–Raphson technique that allows for simultaneous variations in all coordinates. All calculations are based on a recently developed force field parametrization,[2] which is widely used for cobalt(III) hexaamines. As usual, the strain energy minimized structures and all strain energies are the result of the optimized structures of the "naked" complex ion; viz., environmental effects such as solvation, ion pairing, and crystal lattice effects are not included.

The force field used involves representing valence angle bending terms between the metal center and two ligating atoms (N–M–N) by nonbonded interactions between the ligating atoms N. Therefore, the only metal center dependent parameters are related to the M–N breathing mode (M–N–X angle functions are assumed to be metal center M independent). The M–N dependent structural parameters and strain en-

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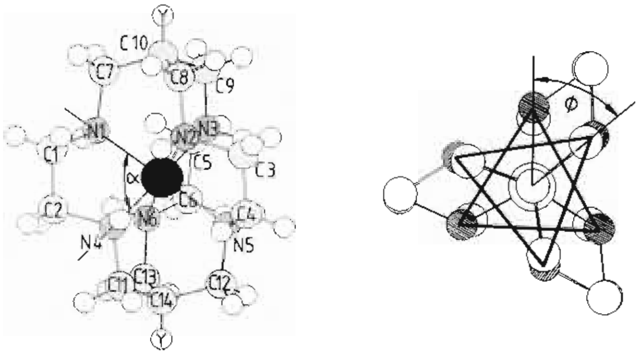

Figure 1. Structure and atom labeling of the cage ligands (Y = H, sar; Y = NH_2, diamsar; Y = NH_3^+, di(amH)sar^{2+}; Y = NH_2OH^+, di-(NH_2OH)sar^{2+}; C10, C14 = N, sep).

Table I. Minimized Strain Energies of the Co(sar)$^{3+}$ Conformers (kJ mol^{-1})

	energies				
conformer	E_b	E_{nb}	E_θ	E_ϕ	$U_{(total)}$
D_3lel_3	16.88	74.66	26.45	37.16	155.16
C_3lel_3	17.92	75.97	23.15	35.22	152.27
C_2lel_2ob	18.10	77.05	20.75	35.10	150.99
C_2ob_2lel	16.43	79.15	17.48	38.61	151.66
D_3ob_3	14.00	79.57	17.90	43.81	155.28

ergies have been calculated by using the cobalt(III) hexaamine force field with fixed M–N distances between 1.90 and 2.36 Å with 0.02-Å steps (bond length deformation energies involving the metal center M are not included in the interaction list; viz., they are constant and set to zero). The atomic coordinates of the five identified conformers of Co(sar)$^{3+}$, calculated by strain energy minimization, have been used as the first set of input coordinates. The (fixed) M–N distances have then be varied for all conformers between 1.90 and 2.36 Å ("blowing up" of the cages). In the region 2.04–2.16 Å a reduced step of 0.01 Å was used. For the sixth conformer (see Results) a series of calculations with decreasing bond lengths between 2.18 and 2.00 Å (step of 0.01 Å) was performed. No symmetry restrictions have been imposed during the minimization procedures. In all cases the total strain energies minimized to true potential energy minima. A series of additional parameters (twist angles ϕ, distance of the two trigonal planes d, bite angles α, etc.) have been calculated from the output coordinates at the end of each energy minimization procedure.

The plots of the structures of the calculated molecules have been performed with the graphics package ORCHIDEE.[9]

Results

Conformations. The six possible conformations for sar-type M^{n+} cage complexes (D_3lel_3, $D_3lel'_3$, C_3lel_3, C_2lel_2ob, C_2ob_2lel, D_3ob_3) are shown in Figure 2. The nomenclature is based on the orientation of the en-type chelate five rings (parallel (*lel*) or oblique (*ob*) with respect to the (pseudo) C_3 axis) and on the orientation of the caps (catoptric or same chirality of both caps), which defines together with the orientation of the en-type chelate rings the overall (pseudo) symmetry (D_3, C_3, C_2). The $D_3lel'_3$ conformation has not been identified before. The two conformers with D_3lel_3 symmetry are different with respect to a set of torsion angles (see Figure 2 and Table III, and see below); i.e., the D_3lel_3 structure has caps that are more eclipsed than the ones of the $D_3lel'_3$ conformer. Theoretically, the same possibilities (D_3, D'_3, and C_3 symmetries) would exist for the ob_3 conformation. However, this does not lead to additional stable conformers (see below), and these possibilities are therefore not included in our calculations. In principle, there exists an additional set of conformers with the N–H protons at opposit trigonal faces syn (and not anti as in Figure 2).[10] However, such conformers have not yet been isolated, and they are not included in the present analysis. Although no symmetry restrictions have been imposed during the strain energy minimization, the resulting structures have, in contrast to the experimental data, pure D_3, C_3, or C_2 symmetry. The deviation from this high symmetry in the experimental structures is clearly the result of environmental effects.

Table II. Structural Parameters of the Strain Energy Minimized Structures of the Co(sar)$^{3+}$ Conformers

conformer	twist angle,[a] deg	bite angle,[a] deg	torsion angle (en),[b] deg	torsion angle (cap),[c] deg
D_3lel_3	53.4	86.7	172.8	119.8
			172.8	119.8
	53.4	86.7	172.8	119.8
			172.8	119.8
	53.4	86.7	172.8	119.8
			172.8	119.8
C_3lel_3	48.2	84.7	162.0	150.5
			162.0	150.5
	48.2	84.7	162.0	150.5
			178.2	108.3
	48.2	84.7	178.2	108.3
			178.2	108.3
C_2lel_2ob	59.0	84.9	88.4	159.7
			165.1	144.7
	42.1	84.4	175.8	137.2
			88.4	159.7
	42.1	84.4	175.8	137.2
			165.1	144.7
C_2ob_2lel	57.2	85.3	95.5	161.4
			87.8	160.3
	57.2	85.3	167.3	143.0
			87.8	160.3
	42.9	84.8	95.5	161.4
			167.3	143.0
D_3ob_3	57.4	86.1	94.6	159.8
			94.6	159.8
	57.4	86.1	94.6	159.8
			94.6	159.8
	57.4	86.1	94.6	159.8
			94.6	159.8

[a] For atom labeling, see Figure 1. [b] E.g. C2–C1–N1–C7; for atom labeling, see Figure 1. [c] E.g. C10–C7–N1–C1; for atom labeling, see Figure 1.

Energy Minimization of Co(sar)$^{3+}$ Conformers. The five conformations of Co(sar)$^{3+}$ (see Figure 2 and also ref 11; the sixth conformation, $D_3lel'_3$, does not exist for Co(sar)$^{3+}$ (see below)) have been calculated. Minimized strain energies and structural parameters for all conformers of Co(sar)$^{3+}$ are presented in Tables I and II, respectively. The torsional angle data (Table II) indicate that the N–C_{en} torsion angle is a valuable indicator for *lel* vs *ob* conformation, while the N–C_{cap} torsion angle is very sensitive in terms of the conformation of the cap. The conformational analysis of the data of M(sar)$^{n+}$ cages is largely based on these torsion angles.

Energy Minimization of M(sar)$^{n+}$ Conformers. The minimized strain energies and structures of the six conformers of M(sar)$^{n+}$ have been calculated by variation of the (fixed) M–N bond lengths between 1.90 and 2.36 Å with 0.02- or 0.01-Å steps.[12] A selection

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(12) A similar approach based on strain energy minimization of coordination compounds (Co(sep)$^{2+/3+}$ and Co(en)$_3^{2+/3+}$) with variable whole size was recently used to evaluate the contribution of the Franck–Condon term in electron-transfer rates.[13] As in the present study metal donor bending terms have been assumed to be metal center independent (but not zero as in this work). Although the approach and the ligand systems investigated are very similar (but not identical in the latter case; see Results) a quantitative comparison is restricted: (i) The force fields used are different, and a comparison of strain energy terms is therefore not warranted.[1] This is supported by a comparison of the cited study with recently published strain energy minimizations of the same system (Co(sep)$^{2+/3+}$) produced by using the same force field that I am using.[11] Not only the strain energies but also the relative stabilities are different. (ii) Only about one-third of the possible interactions have been taken into account in ref 13. (iii) Only one of the three possible *lel* conformations has been included in the earlier work. (iv) Due to the possible comparison with 14 X-ray structures of M(sar)$^{n+}$ (only 2 in the case of Co(sep)$^{n+}$) the M–N range has now been extended to 1.90–2.36 Å. The main message of ref 13 in relation to the present results is that upon "blowing up" of the cages there are substantial (coupled) changes of angle, nonbonded, and torsional strain. Although quantitatively there are some differences, this is in full agreement with my results.

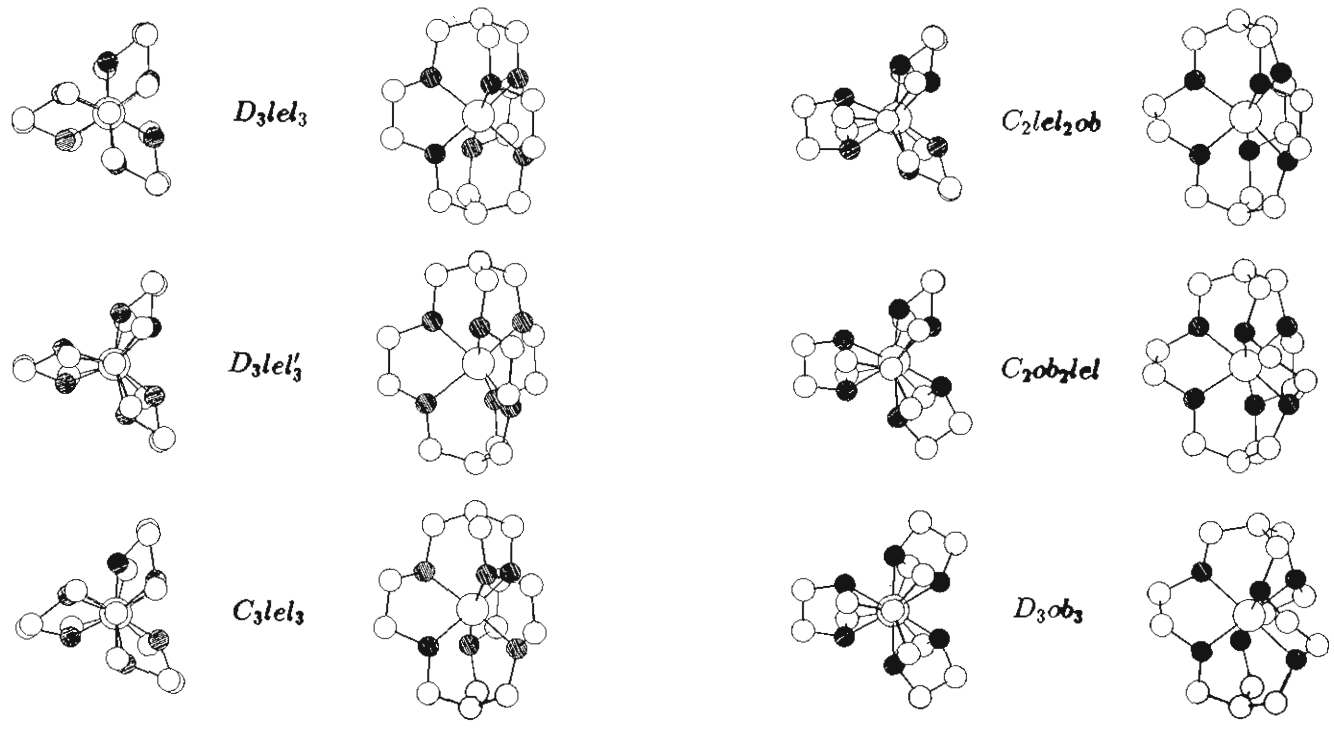

Figure 2. Conformations of M(sar)$^{n+}$. The structures shown are energy minimized with M-N = 2.06 Å.

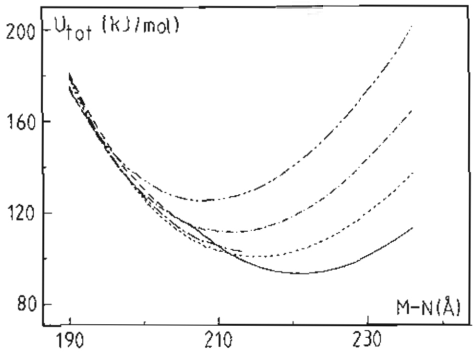

Figure 3. Minimized strain energies of M(sar)$^{n+}$ as a function of the M-N bond length: (--) D_3lel_3; (—·—) C_3lel_3; (—) $D_3lel'_3$; (- -) C_2lel_2ob; (-·-·-) C_2ob_2lel; (- - -) D_3ob_3.

of minimized total strain energies and structural parameters as a function of the M-N bond length are presented in Table III (the complete data are presented as supplementary material). For all conformers the dependence of the minimized total strain energies U_{total} and of the twist angles ϕ on the M-N distance are presented in Figures 3 and 4, respectively. Experimental structural parameters, which are presented in Table IV, are also included in Figure 4. For the comparison of experimental structural parameters with the calculated data I have to recall two important facts:[7,14] (i) The doubly deprotonated cage ligand in V^{IV}di(amH)sar-2H[10,15] and the sepulchrates (sep) are virtually different from sar-type ligand systems.[7] For that reason the vanadium(IV) complex is omitted from our discussion, and all sepulchrates are specifically labeled in Table IV and Figure 4. (ii) It has been demonstrated that the influence of the substituents on the caps of the cage ligands (Y in Figure 1) on the electronic and structural properties of the cage complexes is negligible.[7,14]

The relative importance of the various contributions to the total strain energy of each structure depends on the conformer and on the M-N bond length. The bonding interactions are generally not decisive in terms of conformer stability. Their contribution to the total strain energy is quite small, and it increases in the order $D_3lel'_3 < D_3lel_3 < C_3lel_3 < C_2lel_2ob < C_2ob_2lel < D_3ob_3$ over the whole M-N bond length region. The nonbonded interaction terms are for all conformers very large for small ions and become unimportant for large M-N bonds. They are again rather unimportant in terms of conformer stability. The torsion angle deformation energy is roughly independent on the M-N bond length. It is generally larger for *ob* than for *lel* conformations and it is increasing in the order $D_3lel'_3 < D_3lel_3 < C_3lel_3 < C_2lel_2ob < C_2ob_2lel < D_3ob_3$. Also the angle deformation energy is decisive in terms of the most stable conformer. For small metal ions *ob* conformations are preferred, and for large ones *lel* conformations result in minimum angle deformations. Bond length (excluding M-N bonds), nonbonded, valence angle and torsional terms are increasing with increasing M-N (all conformers), are decreasing with increasing M-N (all conformers), have a energy minimum at 2.15, 2.15, 2.02, 2.04, 2.00, and 1.96 Å for D_3lel_3, $D_3lel'_3$, C_3lel_3, C_2lel_2ob, C_2ob_2lel, and D_3ob_3 conformations, respectively, and have an energy minimum at 2.18, 2.18, 2.02, 2.08, 2.00, and 1.90 Å for D_3lel_3, $D_3lel'_3$, C_3lel_3, C_2lel_2ob, C_2ob_2lel, and D_3ob_3 conformations, respectively.

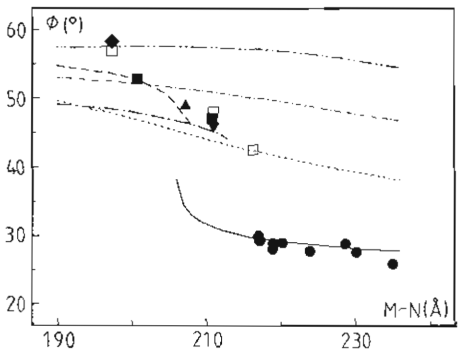

Figure 4. Calculated twist angle ϕ of M(sar)$^{n+}$ and experimental data (see Table IV) as a function of the M-N bond length: (--, ■) D_3lel_3; (—·—, ▲) C_3lel_3; (—, ●) $D_3lel'_3$; (- -, ▼) C_2lel_2ob; (-·-·-) C_2ob_2lel; (- - -, ◆) D_3ob_3; open symbols are for sepulchrate structures. For the two conformers with C_2 symmetry, where the twist angle is not well defined, the average of the three trigonal angles has been considered.

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Table III. Selected Minimized Total Strain and Torsion Angle Deformation Energies and Structural Parameters of all Conformers of $\mathrm{M(sar)}^{n+\,a}$

M–N dist, Å	U_{total}, kJ mol^{-1}	E_ϕ, kJ mol^{-1}	twist angle,[b] deg	torsion angle (en),[c] deg	torsion angle (cap),[d] deg
			D_3lel_3		
1.90	181.27	37.61	54.6	174.9	119.1
2.00	130.22	37.03	52.7	172.1	120.4
2.05[e]	116.74	36.60	50.3	171.2	123.5
			$D_3lel'_3$		
2.10[f]	104.85	27.58	31.7	172.5	151.4
2.20	93.15	28.73	29.0	169.6	153.0
2.30	100.84	32.37	28.0	166.0	152.0
2.35	110.71	34.85	27.8	164.2	151.1
			C_3lel_3		
1.90	179.83	36.21	49.1	163.9, 179.6	150.6, 108.9
2.00	126.85	34.98	47.9	161.4, 177.7	150.4, 108.2
2.10[g]	104.94	34.65	45.5	159.5, 176.1	150.5, 109.9
			C_2lel_2ob		
1.90	178.40		60.1, 44.3, 44.3	90.7, 166.1, 177.5	158.9, 143.9, 135.7
2.00	125.57		58.3, 41.3, 41.3	87.5, 164.7, 175.2	160.0, 145.0, 137.8
2.10	102.92		55.7, 38.2, 38.2	84.6, 163.5, 172.6	161.5, 145.7, 140.4
2.20	102.64		53.1, 35.5, 35.5	81.6, 162.2, 169.2	162.3, 144.9, 142.7
2.30	119.74		50.8, 33.5, 33.5	78.4, 160.6, 164.5	162.1, 142.1, 144.6
2.35	133.71		49.8, 32.5, 32.5	76.9, 159.6, 161.7	161.7, 140.0, 145.6
			C_2ob_2lel		
1.90	175.31		57.3, 57.3, 44.0	98.5, 90.3, 168.2	162.7, 161.5, 144.0
2.00	127.88		57.0, 57.0, 42.1	94.4, 86.4, 166.9	161.1, 159.5, 142.8
2.10	111.47		56.2, 56.2, 40.2	89.8, 82.5, 165.1	160.0, 157.6, 141.4
2.20	118.33		54.9, 54.9, 38.3	84.9, 78.8, 162.7	159.4, 155.6, 139.8
2.30	142.95		53.3, 53.3, 36.6	79.5, 75.3, 159.6	159.0, 153.4, 137.7
2.35	160.93		52.4, 52.4, 35.8	76.5, 73.5, 157.9	158.7, 152.3, 136.5
			D_3ob_3		
1.90	173.69		57.3	97.3	161.5
2.00	134.12		57.4	92.6	158.7
2.10	125.47		57.3	87.3	155.9
2.20	140.14		56.7	81.6	153.2
2.30	172.64		55.5	76.0	150.9
2.35	194.12		54.6	73.1	149.9

[a] Complete list of parameters is given as supplementary material. [b] For atom labeling see Figure 1. [c] E.g. C2–C1–N1–C7; for atom labeling see Figure 1. [d] E.g. C10–C7–N1–C1; for atom labeling, see Figure 1. [e] For M–N ≥ 2.07 Å, change to C_3lel_3 conformation. [f] For M–N ≤ 2.05 Å, change to C_3lel_3 conformation. [g] For M–N ≥ 2.14 Å, change to $D_3lel'_3$ conformation.

Table IV. Experimental Structural Parameters of Transition-Metal Hexaamine Cage Complexes[b]

compd[a]	conformation	M–N$_{\mathrm{av}}$, Å	twist angle$_{\mathrm{av}}$, deg
$[\mathrm{Co^{III}sep(NO_3)_3}$	D_3lel_3	1.974	56.7]
$\mathrm{Co^{III}di(NH_2OH)sarCl_5.4H_2O}$	D_3ob_3	1.974	58.3
$\mathrm{Fe^{III}sar(NO_3)_3}$	D_3lel_3	2.007	52.8
$\mathrm{Cr^{III}diamsarCl_3{\cdot}H_2O}$	C_3lel_3	2.073	49.0
$\mathrm{Ni^{II}di(amH)sar(NO_3)_4{\cdot}H_2O}$	D_3lel_3	2.110	47.1
$\mathrm{Ni^{II}di(amH)sarCl_4{\cdot}H_2O}$	C_2lel_2ob	2.111	45.7
$[\mathrm{Ni^{II}sep(ClO_4)_2}$		2.111	48.0]
$[\mathrm{Co^{II}sepS_2O_6{\cdot}H_2O}$	D_3lel_3	2.164	42.4]
$\mathrm{Cu^{II}di(amH)sar(NO_3)_4{\cdot}H_2O}$	$D_3lel'_3$	2.169	29.8
$\mathrm{Co^{II}di(amH)sar(NO_3)_4{\cdot}H_2O}$	$D_3lel'_3$	2.170	29.0
$\mathrm{Mg^{II}di(amH)sar(NO_3)_4{\cdot}H_2O}$	$D_3lel'_3$	2.188	27.8
$\mathrm{Zn^{II}di(amH)sar(NO_3)_4{\cdot}H_2O}$	$D_3lel'_3$	2.190	28.6
$\mathrm{Fe^{II}di(amH)sar(NO_3)_4{\cdot}H_2O}$	$D_3lel'_3$	2.202	28.6
$\mathrm{Mn^{II}di(amH)sar(NO_3)_4{\cdot}H_2O}$	$D_3lel'_3$	2.238	27.6
$\mathrm{Ag^{II}di(amH)sar(NO_3)_4{\cdot}H_2O}$	$D_3lel'_3$	2.286	28.8
$\mathrm{Cd^{II}di(amH)sar(NO_3)_4{\cdot}H_2O}$	$D_3lel'_3$	2.30	27.4
$\mathrm{Hg^{II}di(amH)sar(NO_3)_4{\cdot}H_2O}$	$D_3lel'_3$	2.35	25.8

[a] For atom labeling, see Figure 1. [b] The experimental data are from ref 7; sepulcharate structures are in brackets.

Table V. Minimized Total Strain Energies and Structural Parameters of the Metal Free Cage Ligand sar

conformer	U_{total}, kJ mol^{-1}	torsion angle (en),[a] deg	torsion angle (cap),[b] deg
D_3lel_3	58.29	178.1	151.2
C_2lel_2ob	72.68	88.9, 169.1, 179.7	162.0, 147.6, 148.4
C_2ob_2lel	88.73	91.9, 88.9, 169.8	160.5, 159.5, 145.8
D_3ob_3	104.68	93.7	158.6

[a] E.g. C2–C1–N1–C7; for atom labeling, see Figure 1. [b] E.g. C10–C7–N1–C1; for atom labeling, see Figure 1.

From Figures 3 and 4 and Table III, it emerges that the D_3lel_3 conformation exists in the M–N region of 1.90–2.07 Å, $D_3lel'_3$ exists from 2.06 to 2.36 Å, and C_3lel_3 exists between 1.90 and 2.13 Å; viz., D_3lel_3 and C_3lel_3 conformations are coexisting over a large M–N range, whereas the region of coexistance of $D_3lel'_3$ and C_3lel_3 is considerably smaller and that of D_3lel_3 and $D_3lel'_3$ is rather narrow. It follows that there is a conformational lability of the three structures with lel_3 symmetry in the M–N region of roughly 2.07 Å. The scattered strain energy and structural data in that bond length region are the result of very flat energy minima, and it indicates that conformational isomerization does not necessarily and does not immediately lead to a global energy minimum. The data also imply that the jump of the trigonal angle ϕ in the region of 2.14 Å is due to a relaxation of torsion angle deformation (see Discussion).

Energy Minimization of Some Conformers of the Free Ligand sar. Energy-minimized structures and strain energies of the metal-free ligand sar have been calculated on the basis of the conformations of $\mathrm{M(sar)}^{n+}$ (see Figure 2). The calculations have been performed with starting coordinates from $\mathrm{M(sar)}^{n+}$ conformers with M–N of 1.97 and 2.34 Å. The refined structural and energy parameters are identical for both sets of input coordinates, and the resulting conformers represent true minima. The data are given in Table V. Clearly, these are not all possible conformers, and structures such as the additional ones mentioned in the Discussion and above, the intermediates of transition-metal complexes of sar where the metal is on the way out of the cage,[16]

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(16) Sargeson, A. M. *Pure Appl. Chem.* **1984**, *56*, 1603.

and others would also have to be considered in a comprehensive analysis of the free cage ligands.

Discussion

$Co(sar)^{3+}$. D_3lel_3 conformation has been observed in the cobalt(III) and cobalt(II) complexes of sepulchrate,[17,18] whereas both the cobalt(III)-di(NH_2OH)sar[19] (di(NH_2OH)sar = 1,8-dihydroxyaminosar) and the monodeprotonated cobalt(III) dinosar complexes[17] (dinosar = 1,8-dinitrosar) adopt D_3ob_3 geometry (the influence of the substituents on caps of the sar-type cage ligands is negligible; the sepulchrates are structurally a slightly different ligand system; see Results). This indicates that the total strain of the various conformers of $Co(sar)^{3+}$ is quite similar; viz., it is a function of structural subtleties within the sar and sepulchrate framework and of environmental effects. The latter argument is further supported by the two structures of the nickel(II) di(amH)sar cage complex (see Table IV).

It is important to remember the above facts with respect to the limits of molecular mechanics calculations in general. Specifically, I note that a comparison of the results for the sar-type cage complexes presented herein with those for other hexaamine complexes is only warranted with great care. Furthermore, a direct comparison of strain energies is only warranted for isomers (same number and type of interactions) that have the same chromophore (same electronic effects).

With these limitations in mind it might be illustrative to compare the present data with a recent conformational analysis of cobalt(III) sepulchrates[11] based on the same force field (see also footnote 12). Under certain conditions and with a number of restrictions, it is possible within a set of isomers or conformers to calculate the distribution of the species (relative ΔG) from total strain energies.[4] The calculated free energies at 298 K (ΔG_{rel}, kJ mol^{-1}) for the five conformers of cobalt(III) sepulchrate (3.8, 5.0, 0.0, 1.1, and 10.3 for D_3lel_3, C_3lel_3, C_2lel_2ob, C_2ob_2lel, and D_3ob_3, respectively) are of the same order of magnitude as the ones of the cobalt(III)-sar cages (6.9, 4.0, 0.0, 0.7, and 7.0 for D_3lel_3, C_3lel_3, C_2lel_2ob, C_2ob_2lel, and D_3ob_3, respectively). As for the sepulchrates, the sar-type cages with asymmetrical (mixed *lel/ob* conformations) seem to accommodate the cobalt(III) ion best. Again, the D_3ob_3 conformation seems to have (relative to the other conformers) a too small cavity for cobalt(III) (compression in the direction of the C_3 axis; see also below). However, the energy differences are smaller than in the case of sepulchrates, and this might be explained by the relatively flat cap of the sepulchrates. The inversion of the order of stability of the two conformers with lel_3 geometry might be a result of the same effect (the cavity of the C_3lel_3 conformer is slightly compressed compared with the cavity of the D_3lel_3 confomer). However, in view of the error limits of molecular mechanics calculations in general (see above) a discussion of such small effects does not necessarily seem to be warranted.

$M(sar)^{n+}$. In the six conformations considered (see Figure 2) all coordinated N atoms adopt either *R* or *S* configuration (the configurations shown in Figures 1 and 2 are all *R*). Clearly, cages with different configurations are also possible (e.g. *RRRSSS*, etc.[10]), but they have not been observed yet and are not further discussed in this paper. Of the six conformations considered, all but one (C_2ob_2lel) have been found experimentally. Most of the $M(sar)^{n+}$ cages have experimentally $D_3lel'_3$ conformation, and (pseudo) symmetry lower than D_3 seems not to be usual (see Table IV). In the strain energy minimizations the fixed M-N bond lengths have been varied for each calculation in the range 1.90-2.36 Å for all six conformers (see Experimental Section and Results).[12] Clearly, the assumption of a fixed M-N bond length (six identical M-N bonds) is only strictly correct for structures with D_3 symmetry. However, apart from Jahn-Teller-active species, the experimentally observed deviation from a mean M-N bond length is very small.[7] Therefore, the error resulting from imposing a fixed M-N bond length on C_3lel_3, C_2lel_2ob and C_2ob_2lel conformers is negligible.

Cage complexes with one or more en-type chelate five rings in ob conformation are only observed for metal centers with small M-N bonds (see Table IV). It was argued that this is the result of a compressed cavity imposed by ob conformations.[14] This interpretation has now been quantified. From Figures 2 and 3 it emerges that up to about 2.05 Å only five conformers are existent. Up to M-N bond lengths of ~1.98 Å, all these five conformers have similar stabilities. Above ~2.0, ~2.1, and ~2.2 Å D_3ob_3, C_2ob_2lel, and C_2lel_2ob conformations, respectively, become unstable. Above ~2.20 Å there exists only one stable conformer, $D_3lel'_3$.

There is a dependence of the trigonal angle ϕ from the conformation of the sar-type cage complexes, and from Figure 4 and Tables II and III it emerges that the preference for octahedral coordination ($\phi \sim 60°$) is decreasing with an increasing number of *lel* conformations and for lel_3 conformers from D_3lel_3 to C_3lel_3 to $D_3lel'_3$. This is also apparent from Figure 2; viz., the horizontal projection of the N-N distance within an en-type chelate five ring, e.g. N1-N4 (which is related to the trigonal angle ϕ), is for structural reasons decreasing in the order *ob*-, D_3lel-, C_3lel-, and D_3lel'-type en ring. This together with the fact that the cavity size of the cages is increasing (longer M-N bonds) with decreasing trigonal angle[7] is obviously the reason for the fact that $D_3lel'_3$ conformation is not observed for small M-N bonds and that $D_3ob'_3$ conformations are not observed at all (see Results).

In general, strain energy minimization calculations with MOMEC85 do not directly lead to a global energy minimum; i.e., usually there is no conformational rearrangement. However, in the present case in the M-N bond length region of ~2.07 Å, the three conformers with lel_3 geometry have very flat minima and this allows for conformational rearrangement. Relaxation of torsional strain within the caps seems to be the major driving force for these rearrangements. At 2.06 Å, where all three conformations with lel_3 geometry have been refined, the torsional strains imposed by the 12 torsions about C-N bonds are 3.74, 3.00, and 2.61 kJ mol^{-1} for D_3lel_3, C_3lel_3, and $D_3lel'_3$, respectively. Near the transition state between two conformations the species seem to rearrange to the structure with the least torsional strain (steepest decent), even if the total strain energy does not become minimal.

One of the most prominent structural features of the sar type cages with a variety of transition-metal centers (see Table IV) is the trigonal twist angle ϕ (apart from the M-N bond lengths, which, where data are available, are as expected from analogous transition-metal hexaamines.[7] In an earlier analysis,[7,14] we have noted that there is a series of largely high-spin weak ligand field complexes with quite constant geometries, which are in between the trigonal-prismatic and the octahedral limits ($\phi \sim 28°$). The twist angles ϕ of the other complexes (largely low spin and stronger ligand field) vary between this geometry and the octahedral limit. It was assumed that all structures are the result of a compromise between ligand preferences (largely steric effects) and metal center preferences (electronic effects), and the more trigonal-prismatic structures are the result of ligand preference while the almost octahedral geometries reflect largely metal center preference. One of the reasons to invoke metal-centered electronic effects in a compromise with steric effects was the fact that the dependence of the twist angle ϕ from the M-N bond length is not a smooth function as could have been expected,[20,21] but there is a jump in the region of M-N ~ 2.14 Å (see Figure 4). On the basis of a relatively simple ligand field model, it was possible to calculate the trigonal twist angles ϕ within ~5°.[7,14]

With the discussed molecular-mechanics calculations I am now presenting a different analysis of the coordination geometries of

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transition-metal hexaamine cage complexes. On the basis of the identification of a new conformer (it was observed but not identified before) and on the basis of the conformational lability of the cage complexes (quantified by our calculations), the twist angle jump at M–N ~ 2.14 Å is no longer unexpected. The strain energy minimized structures are in general and in specific in terms of the trigonal twist angle ϕ in excellent agreement with the experimental data.

Obviously, with both models, viz. with the earlier proposed ligand field model[7,14] and with the strain energy minimizations presented herein, the geometries of the cage complexes can be calculated with high accuracy. Whereas in the ligand field model metal-centered electronic effects are important in terms of the structural result, in the strain energy minimization calculations with the force field used the N–M–N angle is represented by pure repulsion and the electronics of the metal center are reduced to the M–N bonding interaction. Is that a contradiction, viz. does one of the models accidentally lead to correct structural predictions, or is the parametrization of one or both of the models used such that, in terms of the coordination geometry, both models are equivalent? There have been and still are arguments about the force field parametrization for molecular-mechanics calculations in relation to experimental physical parameters (e.g. arguments on C–H and N–H bonds,[2,22] consideration of torsional angle deformation *and* 1,4-repulsion, inclusion of 1,3-interactions,[23] etc.), and there have been proposals of force field parametrizations replacing bond angle and torsion angle deformations by two body central forces between atoms (pure central force field approach).[24] The fact that the only metal center M dependent parameters in our calculations (which lead to good agreement between experimental and calculated parameters) are related to the M–N bond deformation implies that it is rather improbable that the electronic influence extends to the geometry of the chromophore in terms of N–M–N angles. If the similarity of the results based on ligand field and molecular mechanics calculations is not accidental and the applied force field does not include metal-centered electronic effects, it emerges that the similar structural result with both models implies that the electronic ground state of transition-metal complexes is the result of the structural environment and not vice versa. The ligand field model and parametrization used in our earlier study clearly is based on that aspect.

The remaining uncertainity clearly implies that, even with the good agreement between experimental and calculated (molecular mechanics) structural data, the results of strain energy minimizations have to be considered with great care.[25] The good agreement between experimental and calculated structural data confirms the applicability of the currently used force field, specifically for hexaamines and the transition-metal centers involved in Table IV and with some caution in an even more general way. This is clearly of great importance for some of our present studies.[4-6] The main advantage of the currently used force field, in terms of its applicability in coordination chemistry, is the representation of the valence angle bending modes involving the metal center and two ligand atoms by nonbonded interactions. Therefore, the only metal center dependent force field parameters are the force constant k and the zero bond length r_0 describing the M–N bond (M–N–X angle functions are assumed to be metal center M independent). With the results of the energy minimizations of the whole set of transition-metal hexaamine cages in all possible conformations and with the large amount of experimental data for comparison, based on the "metal ion independent" force field, it might be possible to calculate (at least approximately) otherwise inaccessible force field parameters for a whole set of metal centers.

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Registry No. $Co^{III}(sar)^{3+}$, 85664-13-7; $Co^{III}sep(NO_3)_3$, 88228-11-9; $Co^{III}di(NH_2OH)sarCl_5$, 96164-48-6; $Fe^{III}sar(NO_3)_3$, 96164-44-2; $Cr^{III}diamsarCl_3$, 96164-39-5; $Ni^{II}di(amH)sar(NO_3)_4$, 96164-51-1; $Ni^{II}di(amH)sarCl_4$, 96193-88-3; $Ni^{II}sep(ClO_4)_2$, 88229-09-8; $Co^{II}sepS_2O_6$, 96193-87-2; $Cu^{II}di(amH)sar(NO_3)_4$, 96164-54-4; $Co^{II}di(amH)sar(NO_3)_4$, 72560-65-7; $Mg^{II}di(amH)sar(NO_3)_4$, 96164-36-2; $Zn^{II}di(amH)sar(NO_3)_4$, 96164-57-7; $Fe^{II}di(amH)sar(NO_3)_4$, 96164-47-5; $Mn^{II}di(amH)sar(NO_3)_4$, 96164-42-0; $Ag^{II}di(amH)sar(NO_3)_4$, 92096-45-2; $Cd^{II}di(amH)sar(NO_3)_4$, 96164-60-2; $Hg^{II}di(amH)sar(NO_3)_4$, 96164-63-5; sar, 64189-50-0.

Supplementary Material Available: Tables 1–6, giving minimized total strain energies and structural parameters as a function of the M–N bond length (0.2- or 0.1-Å steps) for all six conformers (6 pages). Ordering information is given on any current masthead page.

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(25) Although it might seem that some of the earlier criticism[7] to pure repulsion models[26] is made relative by the present strain energy minimizations, it seems to be dangerous (and unnecessary) to further simplify an already very crude and simple method for structural calculations.

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