Study of amino- and pyridyl-containing zinc(II) and cadmium(II) complexes by molecular mechanics using a force field based on the Gillespie—Kepert model

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A new approach combining the molecular mechanics (MM) method and the Gillespie—Kepert model was applied to calculate the geometry and strain energy of zinc(II) and cadmium(II) complexes with amino- and pyridyl-containing ligands. High accuracy of calculations of the geometry was demonstrated for more than 20 complexes of these metals. Typical r.m.s. deviations between the calculated and experimental values (X-ray diffraction analysis) were 0.02 Å for bond lengths, 2° for bond angles, and 4° for torsion angles. The size-match selectivity of several macrocycles and polydentate open-chain ligands was studied. Correlations between the calculated strain energies of metal complexes and the experimental values of their stability constants and enthalpies of formation are discussed.

Key words: molecular mechanics; the Gillespie—Kepert model; zinc(II) complexes; cadmium(II) complexes.

Molecular mechanics (MM) is a recognized method used for theoretical investigations in the field of coordination chemistry.[1] With the aid of this method the structure and properties of a wide variety of complexes[2] have been studied, and the molecular design of new reagents[3] has successfully been performed. However, the commonly used version of the method has drawbacks associated with the "idealization" of the coordination geometry of the compound under study. Hence, the structures of metal complexes with strongly distorted coordination polyhedra as well as reorganizations of the polyhedra are poorly reproduced. It is possible to adequately describe the geometry of complexes of a metal with various coordination numbers only if individual parameters are used for each species. In this connection, interest in improving the routine of the MM method has grown among researchers in recent years.

Previously,[4] we suggested "incorporating" the Gillespie—Kepert model, well known in qualitative stereochemistry, into the MM method. The force field (a set of calculated parameters) of complexes of iron(II) and nickel(II) with amino- and pyridyl-containing ligands has been successfully used to describe properties of several transition metal complexes. In this work, the force field parameters were determined on the basis of the Gillespie—Kepert model in the framework of the MM method (MMGK) and the structure and properties of several zinc(II) and cadmium(II) complexes with ligands containing donor atoms of amine and pyridyl nitrogen were studied. Zinc is one of the most important biometals; in many cases the mechanism of the action of zinc-containing biologically active substances (for instance, human carboanhydraze) includes changes in the coordination number of zinc. The version of the MM method presented in this work and tested on 17 zinc(II) complexes makes it possible to calculate the geometry of metal complexes with various coordination numbers. We particularly emphasize that the structures of zinc(II) complexes with coordination numbers 4, 5, and 6 were calculated with the same set of parameters.

As far as we know, attempts to study zinc complexes by the MM method have mostly been undertaken with the aim of elucidating the mechanism of the action of various zinc-containing proteins and enzymes (for instance, human carboanhydraze (HCA II)[5—7] *etc.*), whereas little attention has been paid to problems of the adequacy of parametrization. The authors of Ref. 7 fitted parameters only for zinc complexes with monodentate ligands; however, even for these substances the calculated and experimental structural data were not compared. In Ref. 5 the parameters for calculations by the MM method were fitted for only one structure, HCA II. In a number of works,[8,9] calculations of zinc and cadmium complexes with low-molecular ligands by the MM method have been described; however, the parameters used in those works were tested only for two compounds, Zn([16]aneN$_4$) [8] and Cd(L^3) (L^3 is a macrocycle with the O$_2$N$_4$-donor set).[9] The parametrization we present adequately reproduces the geometry of 17 zinc(II) and 6 cadmium(II) complexes (Table 1).

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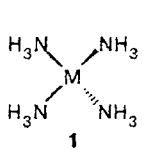
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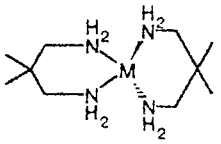
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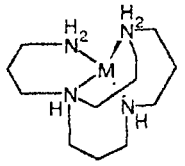
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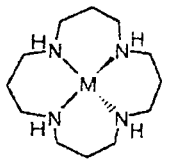
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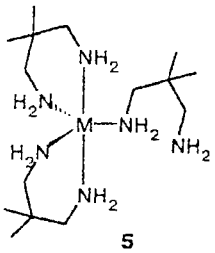
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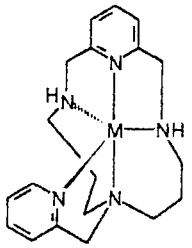
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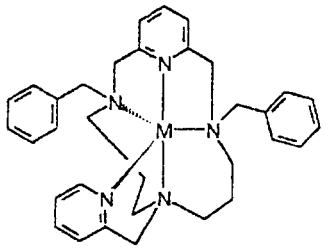
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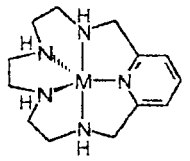
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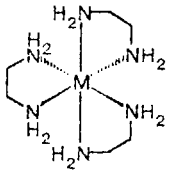
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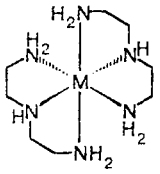
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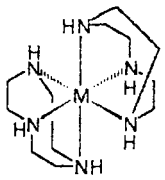
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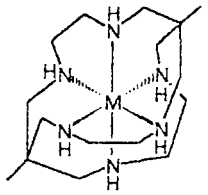
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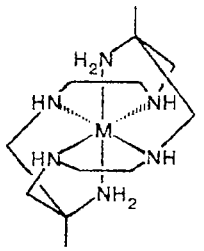
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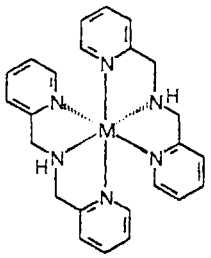
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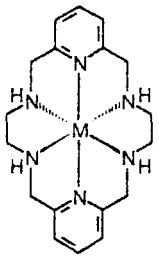
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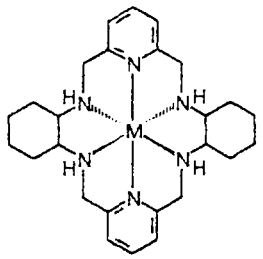
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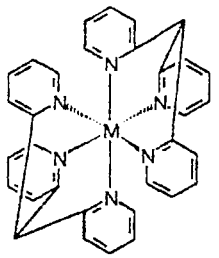
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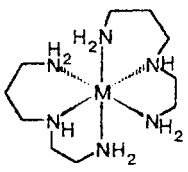
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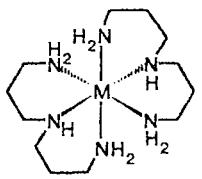
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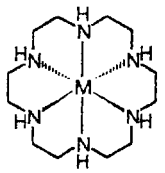
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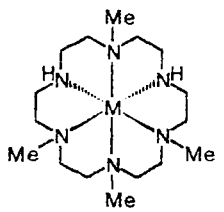
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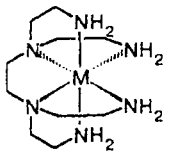
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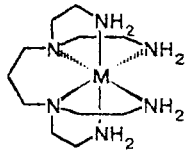
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M = Zn (**1**—**8**, **10**, **13**, **17**); M = Zn, Cd (**9**, **11**, **12**, **14**—**16**, **18**, **19**); M = Zn, Cd, Ni, Co (**20**, **21**); M = Zn, Cd, Ni, Co, Mn (**22**, **23**)

Table 1. The calculated and experimental geometries of zinc(II) and cadmium(II) complexes (**1**—**23**, M = Zn (**a**), Cd (**b**))

Compound	M—N bond length/Å		N—M—N Bond angle/deg		D	Reference
	X-ray analysis	Calculation	X-ray analysis	Calculation		
1a	2.05	2.04	90.0, 180.0	90.0, 180.0	0.0, 0.0	12
2a	2.04	2.02	97.6, 115.7	98.4, 115.3	*	13
3a	2.00	1.98	104.8, 118.2	107.2, 113.9	*	14
4a	2.00	1.98	103.1, 123.1	104.7, 119.4	3.2, 6.0	8
5a	2.08 (e), 2.21 (a)	2.13 (a), 2.19 (e)			*	13
6a	2.20, 2.18, 2.09 (am) 2.01, 2.02 (arom)	2.18, 2.17, 2.11 (am) 2.03, 2.04 (arom)	78.9, 84.5, 91.5, 93.5, 107.8, 104.2, 130.4, 146.5	79.3, 83.2, 93.2, 96.4, 103.0, 105.0, 125.6, 151.2	2.0, 5.3	15
7a	2.07, 2.26, 2.30 (am) 2.01, 2.06 (arom)	2.10, 2.22, 2.23 (am) 2.07, 2.07 (arom)	77.7, 83.9, 99.2, 93.8, 100.2, 102.6, 142.4, 133.4, 155.2	76.5, 82.0, 96.5, 97.6, 102.6, 103.9, 138.2, 139.5, 153.0	2.2, 4.4	16
8a	2.08, 2.25 (am) 2.00 (arom)	2.08, 2.23 (am) 2.06 (arom)	77.9, 83.7, 88.2, 114.2, 135.9, 155.9	75.9, 85.1, 89.5, 115.5, 135.3, 151.9	1.7, 2.4	17
9a	2.22	2.22	81.2, 93.2, 92.9, 171.5	83.0, 91.9, 93.7, 172.6	*	18
10a	2.15, 2.24, 2.26	2.15, 2.23, 2.26	79.8, 80.8, 87.5, 90.5, 97.7, 98.1, 101.9, 159.6, 177.5	81.9, 82.4, 85.7, 89.9, 95.2, 99.0, 100.8, 162.6, 176.4	2.5, 6.2	19
11a	2.17	2.18			*	20
12a	2.19	2.18			*	21
13a	2.10, 2.21	2.12, 2.21	78.9, 81.1, 86.8, 93.3, 98.4, 101.6, 177.3, 178.7	81.5, 85.9, 88.4, 91.7, 93.9, 98.7, 175.4, 179.7	2.9, 4.7	22
14a	2.15 (am), 2.15 (arom)	2.18 (am), 2.13 (arom)	80.4, 87.0, 93.0, 99.6, 180.0	80.7, 85.3, 94.6, 99.3, 180.0	1.4, 8.0	23
15a	2.21 (am), 2.11 (arom)	2.22 (am), 2.11 (arom)	75.1, 82.5, 104.9, 105.3, 150.2, 180.0	75.7, 84.4, 104.3, 102.7, 151.4, 180.0	1.3, 1.7	24
16a	2.22 (am), 2.08 (arom)	2.22 (am), 2.08 (arom)	75.1, 82.5, 104.9, 105.3, 150.2, 180.0	76.3, 84.3, 103.7, 102.3, 152.5, 179.9	1.9, 3.6	25
17a	2.13	2.13	85.4, 93.5, 180.0	85.3, 93.6, 180.0	0.8, 1.7	26
9b	2.37	2.39	75.1, 93.9, 96.2, 166.6	77.8, 95.9, 93.8, 167.6	4.1, 6.2	27
11b	2.36	2.34			*	28
12b	2.30	2.28			*	21
14b	2.34 (am), 2.35 (arom)	2.36 (am), 2.36 (arom)			*	23
15b	2.38 (am), 2.31 (arom)	2.36 (am), 2.31 (arom)	71.6, 78.2, 108.4, 113.7, 143.2, 174.8	71.3, 80.4, 108.7, 111.9, 142.5, 179.9	1.9, 2.2	29
16b	2.38 (am), 2.26 (arom)	2.36 (am), 2.26 (arom)			*	25

Note. D is the r.m.s. deviation between the calculated and experimental values (over all bond and torsion angles, respectively); e, a, am, and arom denote the equatorial, axial, amine, and aromatic N atom, respectively.
* Experimental data are incomplete or erroneous.

The force field

The total conformational energy of a molecule is described by the expression[4]

$$E_{conf} = \Sigma(E_b + E_{GK} + E_a + E_t + E_{NB} + E_{imp}),$$

where $E_b = 0.5K_b(r - r_0)^2$ is the energy of bond deformation, $E_{GK} = A_{ij}/R_{ij,eff}^6$ is the energy of "bond repulsion", $E_a = 0.5K_a(\theta - \theta_0)^2$ is the energy of deformation of the bond angle, $E_t = 0.5V_0(1 + \cos(n\phi + \delta))$ is the torsional energy, $E_{NB} = A/R^{12} - B/R^6$ is the energy of nonbonding interactions, $E_{imp} = 0.5K_{imp}\psi^2$ is the energy of the out-of-plane deviations (for conjugated systems).

The force field for computing metal complexes consists of two parts: the "organic" part, corresponding to the ligands, and the "metal-dependent" part, which in-

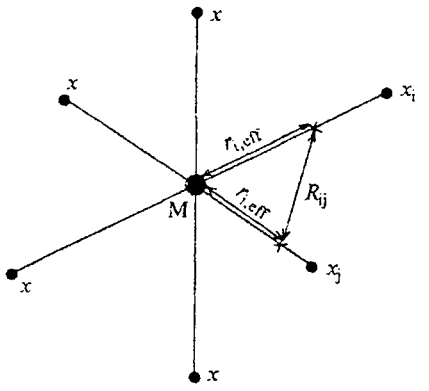

Fig. 1. "Repulsion of bonds" in the coordination sphere of the metal.

cludes a set of parameters for the coordination sphere of the metal.

Parameters for the "organic" moiety of metal complexes. To describe the geometry of the "organic" component of metal complexes, the known CHARMM[10,11] force field supplemented by several parameters for the pyridyl fragment was used.

Parameters for the coordination sphere. The Gillespie—Kepert model was used to describe the deformations of the bond angles at the metal atom; the arrangement of the donor atoms around the metal ion was assumed to be caused by mutual repulsion of all metal—ligand bonds (M—L). The ratio:

$$d_i = r_{eff,i}/r_i.$$

was used to determine the position of the effective center of the repulsion of bond i (Fig. 1).

The potential of the repulsion of bonds i and j was defined as

$$E_{GK,ij} = A_{ij}/R_{ij,eff}^6,$$

where $R_{ij,eff}$ is the distance between the effective centers of repulsion (Fig. 1) related to the angle i—M—j between bonds i and j by the relationship

$$R_{ij,eff}^2 = r_{eff,i}^2 + r_{eff,j}^2 + 2r_{eff,i}r_{eff,j}\cos(iMj);$$

A_{ij} is a constant ($A_{ij} = 1$ was taken as a first approximation; in this case only coefficients d_i and d_j[4] are parameters of the model). The total energy of bond repulsion in the coordination sphere of the metal is obtained by the summation $E_{rep} = \Sigma E_{rep,ij}$.

To describe deformations of the lengths of the metal—donor atom bonds, we used a harmonic potential: $E_b = 0.5K_b(r - r_0)^2$, where r_0 is the "ideal", and r is the real value of the bond length. It is natural that the repulsion of the donor atoms in the coordination sphere of the metal should cause the lengthening of the metal—ligand bonds. Hence, the "ideal" bond lengths were changed (shortened) as compared to those commonly used in routine calculations.

Calculation Procedures

To determine the optimal size of the metal ion for one or another macrocycle or for an open-chain polydentate reagent, we calculated complexes with central ions of various sizes (variable r_0 for coordination bonds) to clarify how the conformational energy changed. Since the conformational energy of an ideal MN_6 polyhedron in the adopted model differs from zero and is equal to the minimum energy of the "repulsion" of coordination bonds, its value (individual for each metal) was subtracted from the calculated energy of the complex.

The K_r, A_i, and d_i values were kept constant (equal to those for zinc) in the course of calculations, so that only r_0 was varied. A preliminary test showed that in this case the general pattern of the dependence of the energy on the ion size was not essentially different from that obtained by a more rigorous procedure (with an individual set of all parameters for each metal). The calculated strain energy E_{conf} was represented as a dependence of the metal—nitrogen bond lengths in the complexes under study.

Parameters for the coordination sphere of the metal were fitted so that they could best reproduce the geometry of the reference structures. The following values were found:

Metal	Bond	K_r/kcal mol^{-1}	r_0/Å	$d_{i,eff}$
Zn(II)	M—N_{am}	30.0	1.78	0.243
	M—N_{arom}	30.0	1.86	0.271
Cd(II)	M—N_{am}	30.0	2.20	0.250
	M—N_{arom}	30.0	2.30	0.305

The structures of seventeen Zn(II) complexes and six Cd(II) complexes were used for calibration (see Table 1). The experimental and calculated geometric parameters of the complexes are listed in Table 1. As can be seen, the structures are reproduced with high accuracy. The deviations in the lengths of coordination bonds are equal to ~0.02 Å, those in the angles are equal to 2—3°. The r.m.s. deviations between the calculated and experimental values for zinc and cadmium complexes are:

Deviation	Zn(II)	Cd(II)
in bond lengths/ Å	0.02	0.02
in bond angles/deg	1.8	3.0
in torsion angles/deg	4.0	4.2

The above approach makes it possible to describe the geometry of complexes containing not only amine or pyridyl nitrogen atoms, but also that of complexes with a mixed coordination sphere using only one set of parameters for each metal. Such a description is difficult within the framework of a conventional approach, so one has to introduce additional parameters. For instance, in Ref. 12 the "ideal" values of the bond lengths r_0 for the amine and pyridyl complexes of nickel(II) were taken to be equal to 2.090 and 2.025 Å for the Ni—N_{am} and Ni—N_{arom} bonds, respectively, whereas for complexes with a mixed coordination sphere r_0(Ni—N_{am}) was reduced to 2.050 Å. In our work the r_0(M—N_{am}) and r_0(M—N_{arom}) values are independent of the composition of the coordination sphere.

One more advantage of the model lies in its ability to adequately calculate the geometry of metal complexes with different coordination numbers using the same set of parameters. In particular, adequate results for tetra-, penta-, and

hexacoordinated complexes of Zn were obtained, which was impossible with the routine method.

Results and Discussion

Despite the great difference in the ionic radii of the metals ($R_i(Zn^{2+})$ = 0.75 Å, $R_i(Cd^{2+})$ = 0.95 Å),[32] the stabilities of most zinc(II) and cadmium(II) complexes are known[31] to be usually nearly the same (discrepancies within the limits of one logarithmic unit). This made it more interesting to study the reasons for the appreciable distinctions in the stabilities of the zinc and cadmium complexes with some ligands. Additionally, quantitative studies of the stereochemical effect on one or another property of complexes of different metals (derivation of various correlations) take on particular meaning; this is also important for the subsequent molecular design of new reagents.

Geometry and conformational energies of zinc(II) and cadmium (II) complexes with several triamines

As can be seen from the data listed below, the stability of the Zn^{2+} and Cd^{2+} complexes with three open-chain N_3-ligands is approximately the same, whereas the zinc complex with triazacyclononane is much more stable than the cadmium complex.

Metal	$\log\beta_2$			
	10	**18**	**19**	**11**
Zn(II)	14.0	12.4	10.3	21.7
Cd(II)	13.5	11.5	9.5	17.9

The latter is in good agreement with the results of calculations of the size-match selectivity of bis-complexes of triazacyclononane;[1] according to these calculations, complexes of metals with small ionic radii are the least sterically strained. However, it was of interest to compare changes in the steric energies with differences in the stabilities of considered compounds for the whole series of above-mentioned ligands.

We calculated the strain energies for the zinc and cadmium bis-complexes with these ligands. The dependence of $\Delta\log\beta_2 = \log\beta_2(ZnL) - \log\beta_2(CdL)$ on $\Delta E_{conf} = E_{conf}(ZnL) - E_{conf}(CdL)$ was considered.

The correlation found is given below; as can be seen, the results of calculations (ΔE_{conf}) are in agreement with the experimental data ($\Delta\log\beta_2$).

Complex	ΔE_{conf} /kcal mol^{-1}	$\Delta\log\beta_2$
10	−3.1	0.5
18	−3.4	0.9
19	−0.9	0.8
11	−10.3	3.8

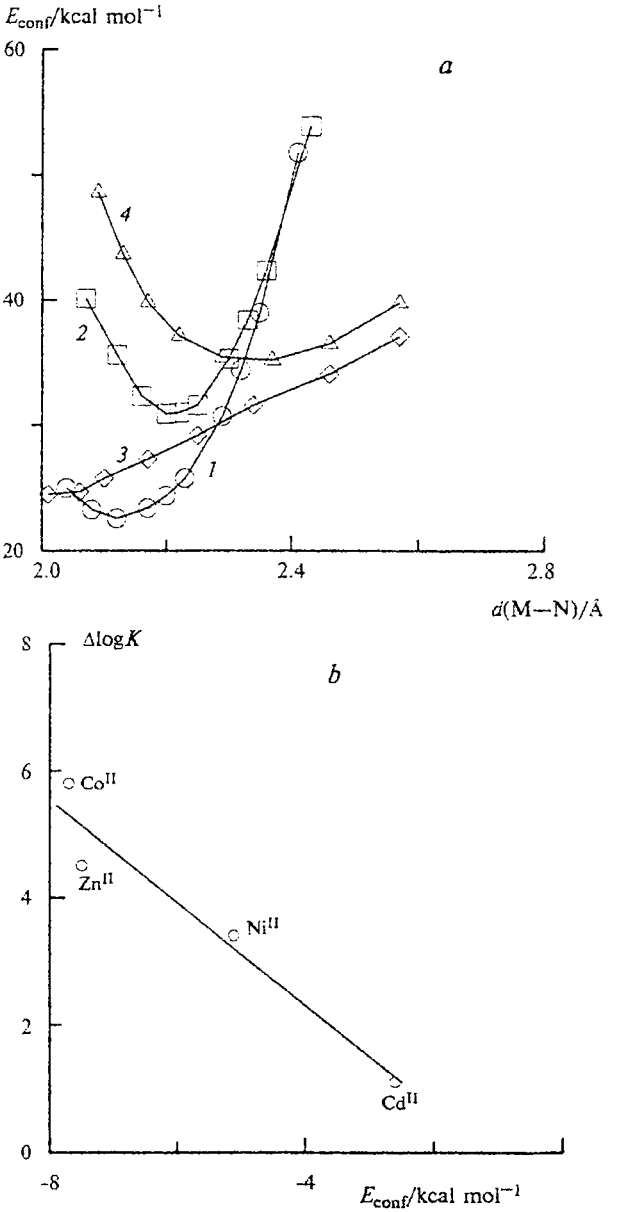

Fig. 2. Metal complexes M(18N$_6$) and M(tm18N$_6$): *a*, curves of the size-match selectivity for M(18N$_6$) (*1*, *3*) and M(tm18N$_6$) (*2*, *4*): facial(*1*, *2*) and meridional (*3*, *4*) isomers; *b*, dependence of stability on the strain energy in the complexes.

Metal complexes with 1,4,7,10,13,16-hexaazacyclooctadecane (M(18N$_6$) (20)) and 1,4,7,13-tetramethyl-1,4,7,10,13,16-hexaazacyclooctadecane (M(tm18N$_6$) (21))

One more example of an "abnormally" great difference in the stability of zinc(II) and cadmium(II) complexes is in their compounds with the azamacrocycle

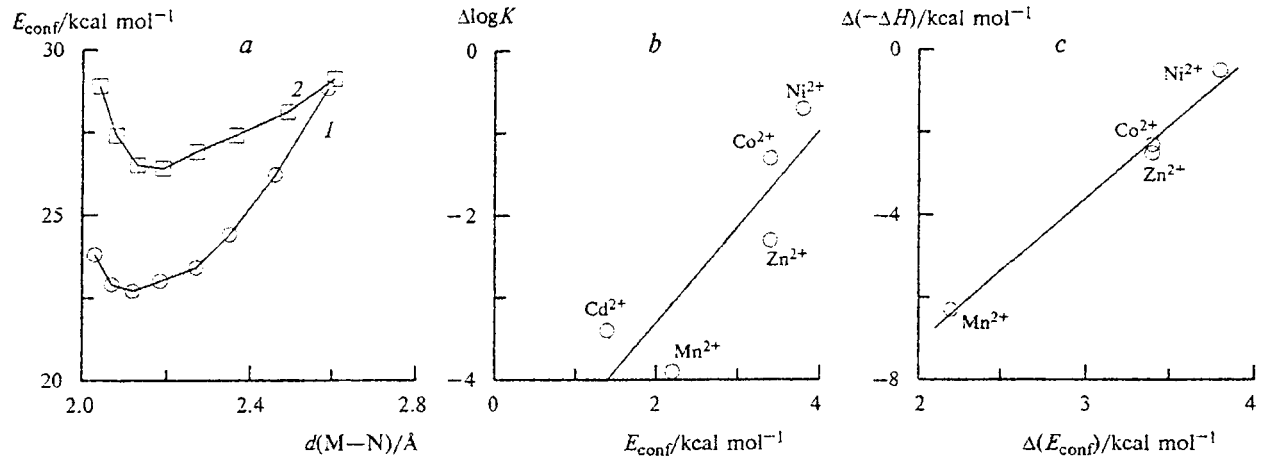

Fig. 3. Metal complexes M(taen) and M(tatn): *a*, curves of the size-match selectivity: *1* — M(taen), 2 — M(tatn); *b*, correlation between stability and the strain energy in the complexes; *c* — correlation between ΔH and the strain energies in the complexes.

tm18N_6. As far as we know, this is virtually the only ligand for which the complex with Cd is much more stable than that with Zn (log$K$ = 16.8 and 13.3, respectively). However, the stability of complexes with nonmethylated 18N_6 is almost the same (log$K$ = 17.9 and 17.2 for CdL and ZnL, respectively). It is interesting that a sharp decrease in stability is observed on going from 18N_6 to tm18N_6 not only in the case of Zn and Cd complexes but also for complexes of other metals. This is likely due to steric hindrances caused by the four methyl substituents. We attempted to quantitatively estimate the magnitude of this drop in stability. For this purpose, we determined the optimal size of the metal ion for the complex with 18N_6 and as well as for that with tm18N_6.

Metal complexes with 18N_6 exist in two isomeric forms, facial and meridional.[33] Since no structural information on these complexes of zinc and cadmium has been reported in the literature, we studied the size preferences for both forms (the isomer with minimum energy was selected from six meridional isomers of tm18N_6).

The obtained curves of the size-match selectivity are shown in Fig. 2. The dependence of the change in the logarithm of the stability constant [$\Delta\log K$ = log$K$(M(18N_6)) − log$K$(M(tm18N_6))] on the increment in the strain energy [ΔE_{conf} = E_{conf}(M(18N_6)) − E_{conf}(M(tm18N_6))] on going from the metal complexes with 18N_6 to those with tm18N_6 is presented below and in Fig. 2.

Metal	ΔE_{conf} /kcal mol^{-1}	$\Delta\log K$
Cd(II)	−2.6	1.1
Ni(II)	−5.1	3.4
Zn(II)	−7.5	4.5
Co(II)	−7.7	5.8

As can be seen, the sharp change in the stability of the complexes is well reproduced by the calculations.

Complexes of *N,N,N′,N′*-tetra-(2-aminoethyl)ethylenediamine (M(taen) (22)) and 2,2′,2″,2‴(trimethylenedinitrile)tetrakis(ethylamine) (M(tatn) (23))

The two ligands, taen and tatn, differ only in the bridge between the tertiary nitrogen atoms. This bridge is ethylenediamine for compound **22** and trimethylenediamine for compound **23**. However, this small change in the structure of the reagent has a rather strong effect on the stability of its complexes. We studied this effect by the MM method.

The dependences of the strain energies on the metal—nitrogen bond lengths in the complexes (*i.e.*, the profiles of the size-match selectivity) were plotted. As can be seen from Fig. 3, the changes in the calculated strain energies correlate well with the changes in the stability constants and the enthalpies of formation on going from M(taen) to M(tatn). Note that in this case we had an opportunity to compare the calculated and experimental data not only on the stability constants, but also on the enthalpies of formation. As can be seen, the latter dependence is more pronounced (by and large, it is more reasonable to compare the energies calculated by the MM method with ΔH). Unfortunately, data on the enthalpies of formation of the complexes are scarce in the literature, therefore, only stability constants were used for comparison in the above cases.

Metal	ΔE_{conf} /kcal mol^{-1}	$\Delta\log K$	$\Delta(-\Delta H)$ /kcal mol^{-1}
Cd(II)	1.4	−3.4	—
Mn(II)	2.2	−3.9	−6.3
Zn(II)	3.4	−1.3	−2.5
Co(II)	3.4	−2.3	−2.3
Ni(II)	3.8	−0.7	−0.5

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