197. Interaction of Ca^{2+} and Mg^{2+} with Ionophores Studied by Using a Pair-Potential Model Based on *Ab Initio* Calculations

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Summary

Atom pair potentials are obtained from *ab initio* SCF-LCAO-MO calculations for model complexes of Mg^{2+} and Ca^{2+} with N,N-dimethylacetamide, N,N-dimethylbutyramide and malonamide. The SCF-LCAO-MO interaction energies for 271 complexes of Mg^{2+} and 271 complexes of Ca^{2+} with these amides were fitted with a simple analytical potential by a least-square procedure. Interaction energies and optimal ion locations obtained by pair-potential calculations are compared with values obtained by *ab initio* calculations for some related amides. The application of the atom pair potentials to the structure of the Mg^{2+}-complex $[MgCl_2(C_3H_7ON)_6]$ of N-methylacetamide is discussed.

In view of a design of ionophores with selectivity for Mg^{2+} a quantitative treatment of the energy of interaction of ions with ligands is most relevant [1] [2]. Although classical calculations of such interaction energies have given useful hints [1–4], obviously more fundamental computations are necessary for a deeper insight into features of the molecular design [5]. *Ab initio* computations have been successfully applied to assess the interaction of small molecules with various cations [6–8]. For large molecules, *e.g.* realistic ionophores, approximations have been used, which are based on *ab initio* calculations on small molecules [9] [10]. In such an approach ion-ionophore interaction energies have been estimated by an additive procedure as a sum of atom-ion interactions [11] [12] and successfully applied to ionophores such as crown ethers and N,N,N',N'-tetracyclohexyl-3-oxapentandiamide [13]. Here we report on the derivation and use of such pair potentials for the interaction of Mg^{2+} and Ca^{2+} with amides acting as carriers for group Ia and IIa cations [14] [15].

For fixed coordinates of all ligand atoms, pair potentials were derived from interaction energies calculated using the SCF-LCAO-MO approximation for different positions of the ion in the space around the ionophore moiety. The basis sets [16] as applied in previous calculations [11] [12] were used for H-, C-, N- and O-atoms. For Mg^{2+} and Ca^{2+} those published in [17] were used.

The above interaction energies I (L, M) (L: ligand, M: ion) were fitted using the *Equation 1* [10] [18–20]:

$$I(L,M) = \sum_i \left(-A_{iM}/r_{iM}^6 + B_{iM}/r_{iM}^{12} + C_{iM}\, q_i\, q_M/r_{iM}\right) \tag{1}$$

where A_{iM}, B_{iM}, and C_{iM} are adjustable constants, r_{iM} is the distance between an atom i on the ligand and M, q_M and q_i are the net charges of M and the atom i calculated for the isolated species. The r^{-12}-term represents the repulsion between the atom i and the ion, the r^{-6}-term a repulsive or attractive interaction (depending on the sign of A_{iM}) and the r^{-1}-term the point charge-point charge interaction, attractive or repulsive depending on the sign of q_i. B_{iM} was constrained to be grater or equal 10^3 and C_{iM} grater or equal zero.

Table 1. *Atomic codes and coordinates* (in pm) *of* N,N-*dimethylbutyramide*. The geometrical parameters of N,N-dimethylacetamide, methyl propyl ether [11] and propionic acid [21] were used. Total energy: -362.680108 E_h.

Nr.	Code	X	Y	Z
1	H1C1	11.415	−253.376	0.000
2	C1	116.375	−218.181	0.000
3	N	118.843	−71.302	0.000
4	C2	247.278	0.000	0.000
5	H1C2	330.238	−73.301	0.000
6	H2C2	254.261	63.555	90.373
7	H3C2	254.261	63.555	−90.373
8	H2C1	167.924	−256.006	−90.373
9	H3C1	167.924	−256.006	90.373
10	C3	0.000	0.000	0.000
11	O	−4.355	122.427	0.000
12	C4	−124.199	−86.763	0.000
13	C5	−254.415	−4.563	0.000
14	C6	−379.409	−94.505	0.000
15	H1C6	−470.355	−31.384	0.000
16	H2C6	−378.930	−158.440	−90.373
17	H3C6	−378.930	−158.440	90.373
18	H1C5	−257.811	59.284	90.373
19	H2C5	−257.811	59.284	−90.373
20	H1C4	−124.612	−150.700	−90.373
21	H2C4	−124.612	−150.700	90.373

Atoms of the same kind in similar chemical environments (all α- and β-neighbors having the same atom number and the same hybridization [13]) were grouped in the same classes and have the same constants. The geometries of the molecules for which SCF-LCAO-MO calculations were performed are given in *Tables 1* (N, N-dimethylbutyramide) and 2 (malonamide) as well as in *Table 4* of [11] (N, N-dimethylacetamide). The corresponding structures are depicted in *Figure 1* together with the atom symbols, class numbers and the net atomic charges. To obtain the pair potentials for the interaction of Mg^{2+} and Ca^{2+} with the atoms of the three
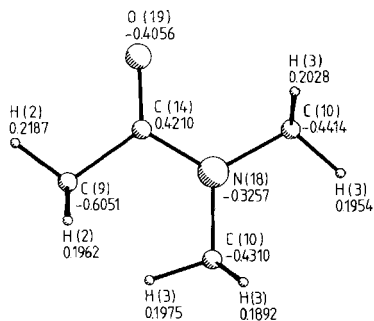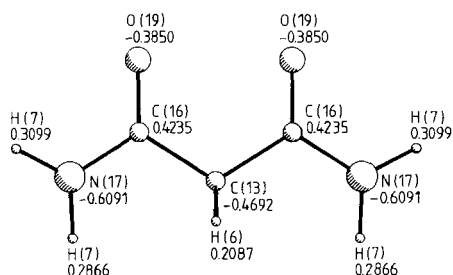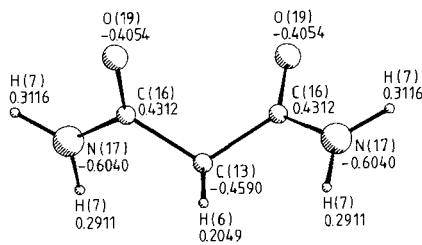
N,N–DIMETHYL ACETAMIDE
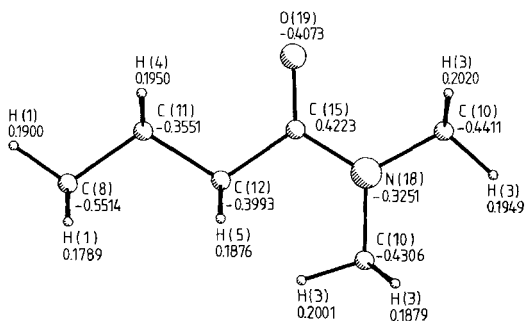
N,N–DIMETHYL BUTYRAMIDE

MALONAMIDE, $\theta_{OCCC} = 0°$

MALONAMIDE, $\theta_{OCCC} = 45°$

Fig. 1. *The four structures* (two of them different conformations of malonamide) *studied for deriving pair potentials for* Mg^{2+} *and* Ca^{2+} *complexes, atomic symbols, class numbers* (in parenthesis) *and net atomic charges*

Table 2. *Atomic codes and coordinates* (in pm) *of malonamide in the planar conformation* (left; $\theta(OCCC)=\theta(CCCO)=0°$, total energy: -374.369123 E_h.) *and in the non-planar conformation* (right; $\theta(OCCC)=\theta(CCCO)=45°$, total energy: -374.370918 E_h.). The geometrical parameters of acetamide [22] and 1-butene (synperiplanar C-skeleton) [23] were used.

| Nr.	Code	X	Y	Z	X	Y	Z
1	H1N1	−335.056	−26.595	0.000	−313.914	6.463	−94.736
2	N1	−244.486	−73.944	0.000	−224.749	−43.083	−88.438
3	C1	−127.969	0.000	0.000	−127.969	0.000	0.000
4	H2N1	−240.206	−176.055	0.000	−207.259	−124.537	−147.635
5	O1	−128.820	121.997	0.000	−144.966	96.751	72.350
6	C2	0.000	−81.839	0.000	0.000	−81.839	0.000
7	C3	127.969	0.000	0.000	127.969	0.000	0.000
8	O2	128.820	121.997	0.000	144.966	96.751	−72.350
9	N2	244.486	−73.944	0.000	224.749	−43.083	88.438
10	H1N2	335.056	−26.595	0.000	313.914	6.463	94.736
11	H2N2	240.206	−176.055	0.000	207.259	−124.537	147.635
12	H1C2	0.000	−148.347	86.988	0.000	−148.347	86.988
13	H2C2	0.000	−148.347	−86.988	0.000	−148.347	−86.988
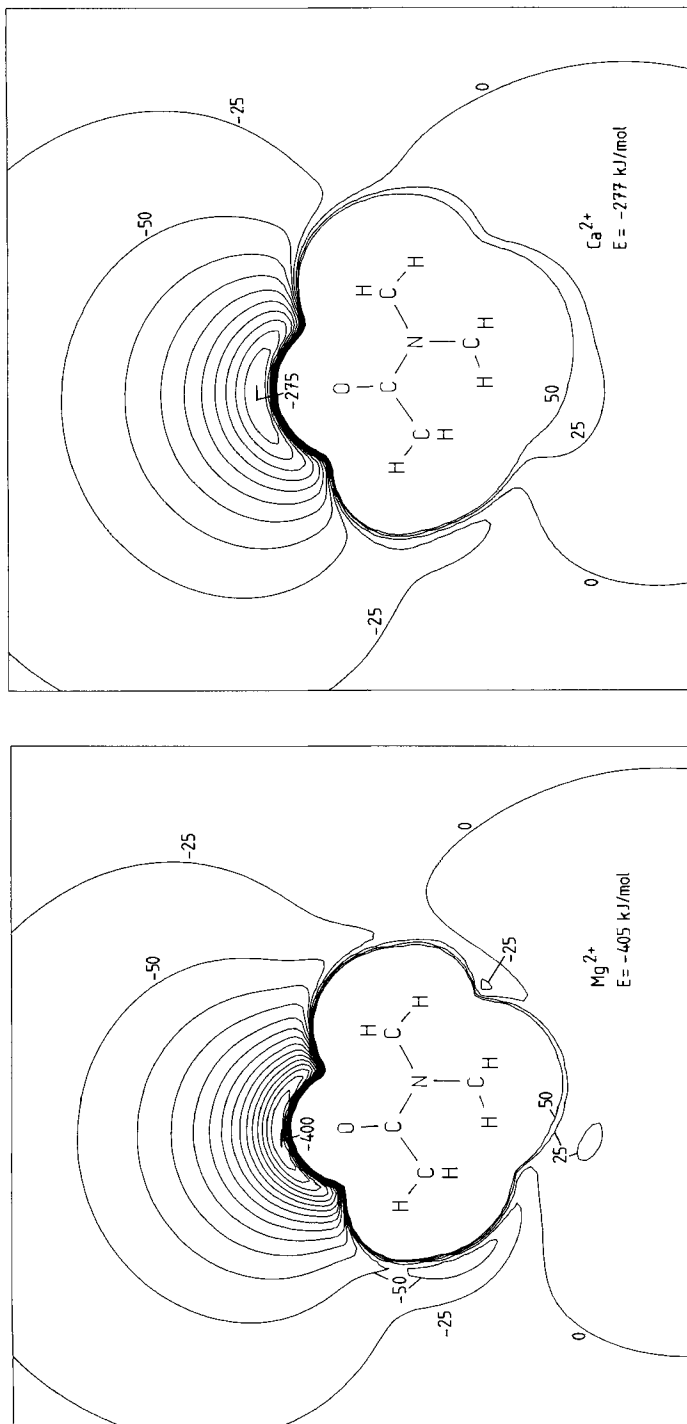
Fig. 2. *Isoenergy contour diagrams for the interaction of* Mg^{2+} *(left) and* Ca^{2+} *(right) with N,N-dimethyl-acetamide in the symmetry plane of the molecule* ($z = 0$ *pm*). The contour-to-contour interval is 25 kJ mol^{-1}. The figure maps an area of 1800 pm square.

Table 3. *Fitting constants for the atomic pair potentials for the interaction of Mg^{2+} with 19 classes of atoms studied (see also Fig. 1) and mean net charges of the atoms belonging to the individual classes[a])*

Atom	Group	Nr.	Code	A	B	C	Charge
H	CH3	1	HC(H2C)	0.16039471E+04	0.25420166E+05	0.56070685E−03	0.1826
		2	HC(H2C*)	0.11838410E+04	0.10793968E+05	0.15829639E+04	0.2037
		3	HC(H2N)	0.64344912E+03	0.83488108E+04	0.65868707E+03	0.1960
H	CH2	4	HC(HC2)	0.47333516E+04	0.92309571E+05	0.19317752E+03	0.1950
		5	HC(HCC*)	0.18948385E+04	0.33047124E+05	0.	0.1876
		6	HC(HC*2)	0.21958585E+04	0.17003733E+05	0.16348130E+04	0.2068
H	NH2	7	HN(HC*)	−0.50865361E+03	0.14794982E+05	0.11904366E+04	0.2998
C	CH3	8	CH3 C(H2C)	−0.71482191E+04	0.23978548E+05	0.12011504E+03	−0.5514
		9	CH3 C*(=ON)	0.21196094E+05	0.45581292E+07	0.22841207E+04	−0.6051
		10	CH3 N(CC*)	0.11745218E+05	0.19882029E+07	0.63715453E+03	−0.4360
C	CH2	11	CH2 C(H3) C(H2C*)	−0.33829079E+04	0.11992919E+07	0.31744084E−02	−0.3551
		12	CH2 C(H2C) C*(=ON)	0.16811627E+05	0.33181748E+07	0.55578863E+03	−0.3993
		13	CH2 C*(=ON) C*(=ON)	−0.12182399E+05	0.14066462E+06	0.39822767E+04	−0.4641
C	C*	14	C* C(H3) N(C2)=O	0.57266973E+04	0.23718824E+06	0.39666747E+04	0.4210
		15	C* C(H2C) N(C2)=O	0.11762684E+05	0.48753681E+06	0.34301496E+04	0.4223
		16	C* C(H2C*) N(H2)=O	0.33758351E+04	0.14602575E+06	0.39427092E+04	0.4273
N	NH2	17	NH2 C*(=OC)	0.10661362E+05	0.36232426E+06	0.13867868E+04	−0.6066
N	N	18	N C(H3) C(H3) C*(=OC)	−0.48435106E+03	0.19202144E+06	0.15704710E+04	−0.3254
O	O*	19	O* =C(CN)	−0.10543587E+04	0.37372652E+05	0.25261112E+04	−0.3990

[a]) The interaction energy $I(L, Mg)$ is obtained according to *Equation 1* in kJ mol⁻¹ if A, B and C are used as given in the table; the unit of r_{LM} is [Å] and that of the net charges is e (atomic unit of electron charge). A pure *Coulomb* interaction corresponds to a value of $C = 1389.354$. The code contains the atomic symbols of the atoms (see column 1) followed by the atomic symbols of all α- and β-neighbors (β-neighbors in parenthesis). X^* and $=X$ designate atoms participating in double bonds.

Table 4. *Fitting constants for the atomic pair potentials for the interaction of* Ca^{2+} *with 19 classes of atoms studied (see also Fig. 1) and mean net charges of the atoms belonging to the individual classes*[a])

Atom	Group	Nr.	Code	A	B	C	Charge
H	CH3	1	HC(H2C)	0.13209518E+03	0.86627720E+05	0.15032460E−02	0.1826
		2	HC(H2C*)	0.62928916E+03	0.61857754E+05	0.15094100E+04	0.2037
		3	HC(H2N)	−0.97388649E+02	0.10000000E+04	0.13241031E+04	0.1960
H	CH2	4	HC(HC2)	0.66433109E+04	0.27360213E+06	0.24989022E+03	0.1950
		5	HC(HCC*)	−0.22685345E+04	0.85656503E+05	0.62915987E−02	0.1876
		6	HC(HC*2)	0.42390168E+04	0.19729383E+06	0.10783285E+04	0.2068
H	NH2	7	HN(HC*)	0.43186353E+04	0.65173846E+06	0.12021852E+04	0.2998
C	CH3	8	CH3 C(H2C)	0.21951919E+05	0.74365125E+07	0.49420133E+02	−0.5514
		9	CH3 C*(=ON)	0.15596090E+05	0.72818586E+07	0.22762369E+04	−0.6051
		10	CH3 N(CC*)	0.76149487E+04	0.52968469E+07	0.17410043E+04	−0.4360
C	CH2	11	CH2 C(H3) C(H2C*)	−0.21749254E+05	0.11706824E+07	0.	−0.3551
		12	CH2 C(H2C) C*(=ON)	0.51539587E+05	0.86873320E+07	0.58970843E+03	−0.3993
		13	CH2 C*(=ON) C*(=ON)	−0.24442900E+05	0.55289078E+06	0.33469235E+04	−0.4641
C	C*	14	C* C(H3) N(C2) =O	0.86271720E+04	0.10160226E+07	0.43343097E+04	0.4210
		15	C* C(H2C) N(C2) =O	−0.20534723E+04	0.51517495E+06	0.36207779E+04	0.4223
		16	C* C(H2C*) N(H2) =O	0.31393268E+05	0.62692364E+07	0.42060293E+04	0.4273
N	NH2	17	NH2 C*(=OC)	0.28479565E+05	0.42389119E+07	0.14757465E+05	−0.6066
N	N	18	N C(H3) C(H3) C*(=OC)	0.29413821E+04	0.12819185E+07	0.11411287E+04	−0.3254
O	O*	19	O* =C(CN)	−0.78867903E+04	0.15639239E+06	0.27317838E+04	−0.3990

a) The interaction energy $I(L, Ca)$ is obtained according to *Equation 1* in kJ mol^{-1} if A, B and C are used as given in the table; the unit of r_M is [Å] and that of the net charges is e (atomic unit of electron charge). A pure *Coulomb* interaction corresponds to a value of $C = 1389.354$. The code contains the atomic symbols of the atoms (see column 1) followed by the atomic symbols of all α- and β-neighbors (β-neighbors in parenthesis). X* and =X designate atoms participating in double bonds.
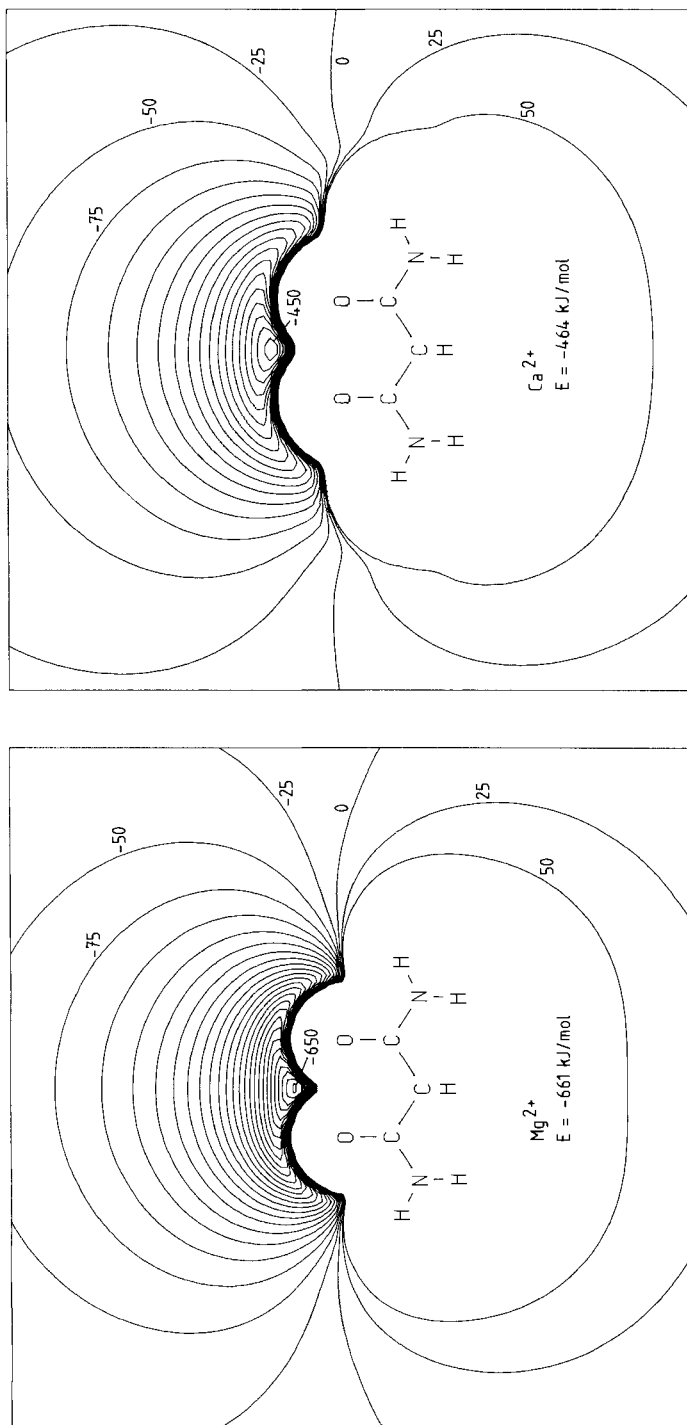
Fig. 3. *Isoenergy contour diagrams for the interaction of* Mg²⁺ *(left) and* Ca²⁺ *(right) with malonamide* (θ(OCCC) = θ(CCCO) = 0°) *in the symmetry plane of the molecule* (z = 0 pm). *The contour-to-contour interval is 25 kJ mol⁻¹. The figure maps an area of 1800 pm square.*

Table 5. *Number of SCF-LCAO-MO calculations performed for each structure (see Fig. 1) and standard deviation of the interaction energies approximated by* Equation 1 *with the parameters of* Table 3 *and* 4 *for* Mg^{2+} *and* Ca^{2+}, *respectively*

Structure	Number of complexes (SCF-LCAO-MO calculations)		Standard deviation [kJ mol^{-1}]	
	Mg^{2+}	Ca^{2+}	Mg^{2+}	Ca^{2+}
N, N-Dimethylacetamide	95	92	13.0	12.6
N, N-Dimethylbutyramide	80	84	13.1	13.6
Malonamide θ (OCCC)=θ (CCCO) = 0°	83	83	20.1	11.1
Malonamide θ (OCCC)=θ (CCCO) = 45°	13	12	17.4	8.9
Total	271	271	15.8	12.4

molecules (four structures) a total of 271 complexes with interaction energies lower than 120 kJ mol^{-1} were considered for each ion. The fit by *Equation 1* led to the parameters presented in *Tables 3* and *4*. For the entire set of 271 calculations the least-square standard deviation was 15.8 and 12.4 kJ mol^{-1} for Mg^{2+} and Ca^{2+}, respectively (see *Table 5*), which corresponds to 2.3–4.3% relative to the total interaction energy in the complexes of optimal ion location (see *Table 6*). In this table interaction energies derived by *ab initio* and pair-potential computations are compared. Entries A and B correspond to an optimization of the ion location by pair-potential and *ab initio* techniques, respectively.

Using the pair potentials given in *Tables 3* and *4* isoenergy contour diagrams were calculated for the energy of Mg^{2+} and Ca^{2+} in the field of N, N-dimethylacetamide *(Fig. 2)*, malonamide *(Fig. 3)* and N, N, N', N'-tetramethylsuccinamide *(Fig. 4*, see also [24]). In contrast to the preferred location of Na$^+$ and Mg^{2+} in the approximate direction of the O-lone-pairs of N-methylacetamide as obtained by

Table 6. *Comparison of the interaction energies and optimal ion location derived by* ab initio $(E_{ab\ initio})$ *and pair potential* (E_{ABC}) *computations for the four structures studied for deriving pair potentials (fixed ligand geometry). A and B correspond to an optimization of the ion location by pair potentials respectively* ab initio *techniques.*

Structure		Mg^{2+}				Ca^{2+}			
		$E_{ab\ initio}$ kJ mol^{-1}	E_{ABC} kJ mol^{-1}	Optimal ion coordinates pm	d^a) Mg-O pm	$E_{ab\ initio}$ kJ mol^{-1}	E_{ABC} kJ mol^{-1}	Optimal ion coordinates pm	d^a) Ca-O pm
N, N-Dimethyl-	A	− 420	− 405	− 18/296/0	175	− 286	− 277	− 24/340/0	219
acetamide	B	− 421	− 404	− 22/299/0	177	− 286	− 277	− 26/339/0	218
N, N-Dimethyl- butyramide	A	− 431	− 420	− 5/296/0	174	− 294	− 287	2/340/0	218
Malonamide θ(OCCC)=	A	− 670	− 661	0/250/0	181	− 483	− 464	0/304/0	223
θ(CCCO) = 0°	B	− 675	− 657	0/258/0	187	− 483	− 464	0/306/0	225
Malonamide θ(OCCC)= θ(CCCO) = 45°	A	− 429	− 418	− 110/262/123 110/262/− 123	176/ 361	− 325	− 324	0/273/0	240

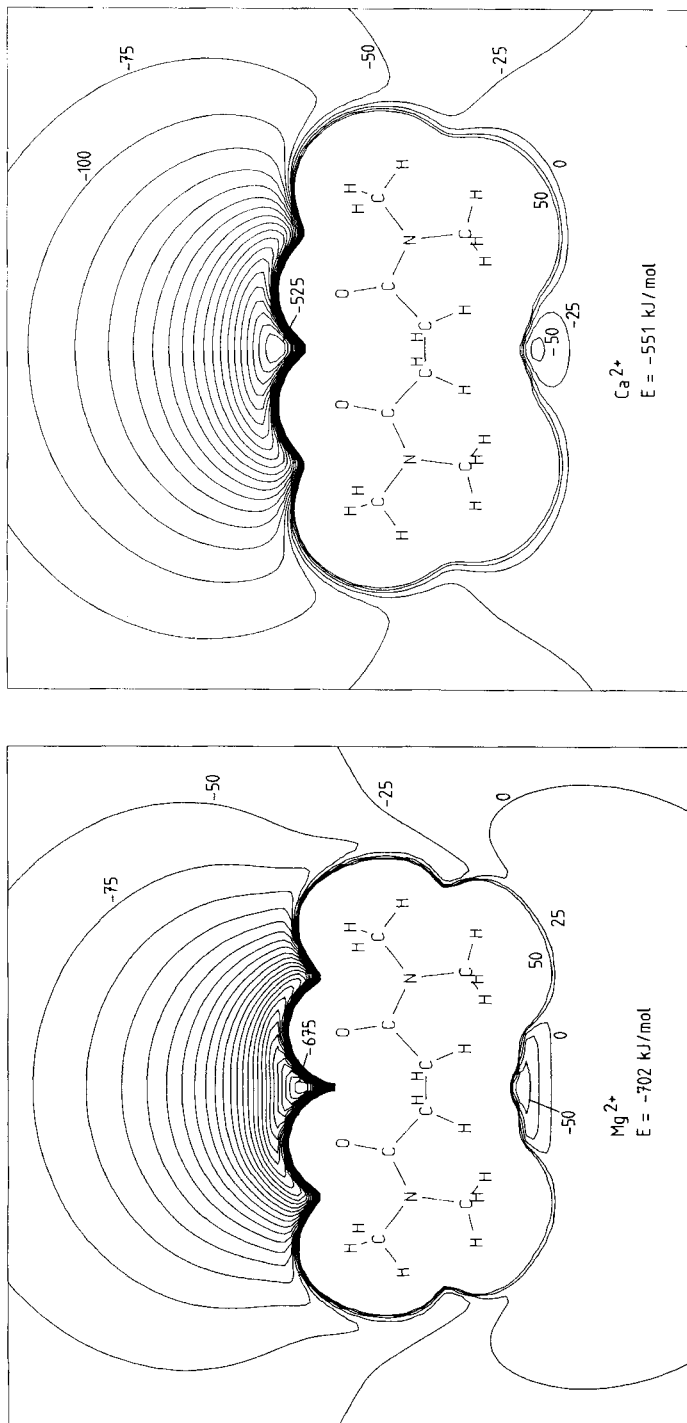^{a}) Optimal ion-oxygen distances.

Fig. 4. *Isoenergy contour diagrams for the interaction of* Mg^{2+} *(left) and* Ca^{2+} *(right) with N,N,N',N'-tetramethylsuccinamide* (θ(OCCC) = θ(CCCO) = 60°, θ(CCCC) = –90°). The plane of the diagrams is defined by the carbonyl-C-atoms and the C_2-axis of the molecule in this conformation. The contour to contour interval is 25 kJ mol^{-1}. The figure maps an area of 1800 pm square.

Table 7. *Comparison of the ion-ligand interaction energies obtained by the pair-potential method with* ab initio *results for some structures* (fixed ligand geometry). For *N*-methylacetamide geometrical parameters of [22] [31] were used. The geometries of the remaining structures were fixed using the same parameters as for the four structures studied for deriving pair potentials (see *Table 1, 2* and *Table 4* of [11]). The net charges were determined by a *Mulliken* population analysis [32] for each structure.

Structure	Mg²⁺				Ca²⁺			
	$E_{ab\ initio}$ kJ mol⁻¹	E_{ABC} kJ mol⁻¹	d[a])	Optimal ion location a, θ[b])	$E_{ab\ initio}$ kJ mol⁻¹	E_{ABC} kJ mol⁻¹	d[a])	Optimal ion location a, θ[b])
Malonamide	−270	−316	177	a(CO1Mg) = 160° θ(NCO1Mg)= 0°	−165	−233	219	a(CO1Ca) = 166° θ(NCO1Ca)= 0°
θ(O1CCC)= 0° θ(O2CCC)= 180°	−443	−533	173	a(CO2Mg) = 173° θ(NCO2Mg)= 180°	−305	−403	212	a(CO2Ca) = 176° θ(NCO2Ca)= 180°
N-Methyl-acetamide	[c]) −414	−417	174	a(COMg) = 179° θ(NCOMg) = 180°	−283	−222	220	a(COCa) = 175° θ(NCOCa) = 180°
θ(CNCO)=0°	[d]) −414	−376	175	a(COMg) = 178° θ(NCOMg) = 180°	−283	−297	217	a(COCa) = 179° θ(NCOCa) = 0°
N, N, N', N'-Tetramethyl-malonamide θ(OCCC)= θ(CCCO)=0°	[e]) −691	−721	182	on C₂-axis	−492	−515	224	on C₂-axis
N, N, N', N'-Tetramethyl-succinamide θ(OCCC)= θ(CCCO)= 60° θ(CCCC)= −90°	−705	−702	180	on C₂-axis	−510	−551	224	on C₂-axis

[a]) d: Optimal ion-oxygen distances in pm.
[b]) a: Optimal angle C=O....Mg, C=O.....Ca respectively; θ: Optimal dihedral angle N−C=O...Mg, N−C=O...Ca respectively.
[c]) N-atom described by class 18.
[d]) N-atom described by class 17.
[e]) Carbonyl-C-atoms described by class 16.

semiempirical methods (CNDO/2) [25] and to the results found for the interaction of Na⁺ and K⁺ with *N*-methylacetamide and methyl acetate as obtained by *ab initio* computations [26], the results in *Figure 2* document a nearly colinear position relative to the carbonyl group. This is in agreement with recent findings for the interaction of Li⁺, Na⁺, K⁺, Be²⁺, and Mg²⁺ with alkyl-substituted acetamide [27] and the Li⁺-complexes of formamide [28] and R_2CO (R = NH₂, CH₃, OH, H, F) [29] [30].

For some structures not used in the derivation of the pair potentials the interaction energy for the optimal ion location (as obtained by the pair-potential method) is compared with values obtained by *ab initio* techniques for the same ion location *(Table 7)*. Considering the fact that unsatisfactory atom classes [13] were used throughout the differences in the energies are, except for malonamide, acceptable (0.4 to 21.5%). For malonamide formally suitable atom classes are given in *Tables 3* and *4*; however, they do not cover the influence of a H-bond probably
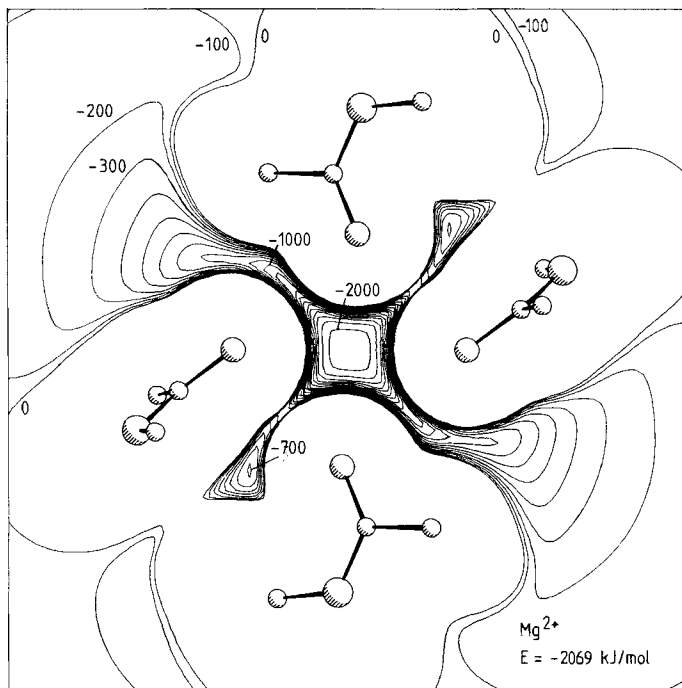
Fig. 5. *Isoenergy contour map for the interaction of six* N-*methylacetamide molecules in octahedral arrangement with* Mg^{2+} (two molecules are not depicted). The arrangement of the ligands corresponds to the structure of the Mg^{2+}-complex of *N*-methylacetamide $[MgCl_2(C_3H_7ON)_6]$ [33] (see text). The net atomic charges calculated for a single *N*-methylacetamide molecule were used. The N-atoms were described by class 18. The plane of the diagram is defined by the four O-atoms (and the optimal location of the Mg^{2+}-ion. The contour-to-contour interval is 100 kJ mol^{-1}. The figure maps an area of 1200 pm square.

present in the conformation considered. If the assignment in atom classes as specified earlier [13] is accepted, this poses a clear limitation of the model used. The data presented in *Table 7* for *N*-methylacetamide document, however, that the ion location can be predicted nicely even if less than perfectly suited atom classes are used (see also [13]).

Based on the structure of the Mg^{2+}-complex of *N*-methylacetamide [MgCl₂ $(C_3H_7ON)_6$] [33] the location of Mg^{2+} has been calculated by the pair-potential technique. The coordinates of all atoms other than H-atom for the six ligands were taken from X-ray structure analyses [33]. The positions of the H-atoms were calculated according to data published in [22] [31]. They do not agree with those available from [34], which are incomplete and partly erroneous. The isoenergy contour map for the interaction of the six *N*-methylacetamide ligands with Mg^{2+} is depicted in *Figure 5*. The location of the computed energy minimum agrees to better than 0.01 pm with the experimental value. The Mg^{2+} is neither located colinearly with the carbonyl group nor is it in the plane of the heavy atoms of the

ligand. The mean Mg-O distance is 206 pm in the array of six ligands and 174 pm in the 1:1-complex (see also *Fig. 13* in [33]). Therefore Mg^{2+} is located differently relative to a single ligand than to an array of ligands. A transfer of ion locations obtained from X-ray analysis of a 1:n-complex as optimal to a 1:1-complex is therefore problematic.

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