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Crystal and Molecular Structures of Alkali- and Alkaline-Earth-Metal Complexes of *N*,*N*-Dimethylformamide

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Structures of lithium, sodium, magnesium, and calcium complexes of *N*,*N*-dimethylformamide (DMF) have been investigated by X-ray crystallography. Complexes with the formulas $LiCl \cdot DMF \cdot {}^1/_2H_2O$, $NaClO_4 \cdot 2DMF$, $CaCl_2 \cdot 2DMF \cdot 2H_2O$, and $Mg(ClO_4)_2 \cdot 6DMF$ crystallized in space groups $P2_1/c$, $P2/c$, $P\bar{1}$, and $P2_1/a$, respectively, with the following cell dimensions: Li complex, a = 13.022 (7) Å, b = 5.978 (4) Å, c = 17.028 (10) Å, β = 105.48 (4)°, Z = 8; Na complex, a = 9.297 (4) Å, b = 10.203 (3) Å, c = 13.510 (6) Å, β = 110.08 (4)°, Z = 4; Ca complex, a = 6.293 (4) Å, b = 6.944 (2) Å, c = 8.853 (5) Å, α = 110.15 (3)°, β = 105.60 (6)°, γ = 95.34 (5)°, Z = 1; Mg complex, a = 20.686 (11) Å, b = 10.962 (18) Å, c = 14.885 (9) Å, β = 91.45 (5)°, Z = 4. Lithium is tetrahedrally coordinated while the other three cations are octahedrally coordinated; the observed metal–oxygen distances are within the ranges generally found in oxygen donor complexes of these metals. The lithium and sodium complexes are polymeric, with the amide and the anion forming bridging groups between neighboring cations. The carbonyl distances become longer in the complexes accompanied by a proportionate decrease in the length of the central C–N bond of the amide; the N–C bond of the dimethylamino group also shows some changes in the complexes. The cations do not deviate significantly from the lone-pair direction of the amide carbonyl and remain in the amide plane. Infrared spectra of the complexes reflect the observed changes in the amide bond distances.

Introduction

Coordinating properties of the amide bond and transition-metal ion complexes of amides have been active areas of investigation in the last two decades.[1] Binding of alkali- and alkaline-earth-metal salts to amides is of special relevance to several biological phenomena including conformation transitions of polypeptides and proteins.[2] Coordination chemistry of these d° metal ions is also of considerable interest. Interaction of alkali- and alkaline-earth-metal ions with amides has been investigated by employing vibrational spectroscopy,[3] NMR spectroscopy,[4] and quantum-mechanical calculations.[2,5] A recent study[6] of alkali- and alkaline-earth-metal complexes of *N*-methylacetamide (NMA) by X-ray crystallography has provided valuable information on bonding in these complexes, but the results of this study are subject to the limitation that the geometry of the secondary amide could also be affected significantly by the anions that are strongly hydrogen bonded to the N–H bond of the amide. Furthermore, there was considerable disorder in many of the complexes, and this introduced some uncertainty with regard to the structural parameters. We have, therefore, carried out a systematic investigation of the structure and bonding in complexes of Li, Na, Mg, and Ca with the tertiary amide *N*,*N*-dimethylformamide (DMF). The present study has yielded interesting and useful results on the coordination chemistry of alkali- and alkaline-earth-metal ions and also on the effect of binding of these cations on peptide geometry. We have found that the carbonyl bond distance increases progressively with the decrease in the length of the central C–N bond; the N–C distances of the dimethylamino group also change with C–N bond distance. Bond distances in free tertiary amides[7,8] as well as in the standard peptide geometry[9] follow the trends exhibited by the complexes. Infrared spectra of the complexes are consistent with the changes observed in the bond distances.

Experimental Section

Complexes of alkali- and alkaline-earth-metal ions with DMF were prepared by the interaction of dried metal salts with the neat amide slightly above room temperature. This was done in a glovebox in a nitrogen atmosphere to minimize the moisture content. Amide salt solutions were placed in a vacuum desiccator in order to grow the crystals. Sufficiently good crystals could be obtained within 2 days. The crystals were very hygroscopic and were readily destroyed on exposure to air. Crystals were therefore mounted in sealed Lindemann capillaries for X-ray diffraction studies. Densities of fresh crystals were measured in benzene–CCl_4 mixtures, and the values of the density along with the molecular formulas of the complexes are listed in Table I.

X-ray diffraction data of the complexes were obtained by means of a CAD-4 diffractometer equipped with a graphite monochromator. Mo Kα radiation was used for the purpose. Unit cell parameters (Table I) were determined by a least-squares procedure based on 25 high-order reflections. X-ray reflections were measured by using an $\omega'/2\theta$ scan mode with a scan rate of 1° min^{-1} to the limit of θ given in Table I. Data were collected on several crystals of each complex, monitoring the intensities of two standard reflections after every 50 min of exposure. Corrections were made for Lorentz and polarization factors; absorption correction was found unnecessary. The intensity data and the normalized structure factors clearly showed the presence of centrosymmetry in all the complexes studied. Systematic absences enabled the determination of the space groups (Table I). All the computations were performed on a DEC-1090 system.

All the structures were solved through direct methods using MULTAN 80[10] and employing Karle's recycling procedure.[11] Details of the refinement are given in Table I. Initially, the refinement was carried out with non-hydrogen atoms on the basis of isotropic temperature factors until convergence in the R factor was obtained. The temperature factors were then made anisotropic, and refinement continued until convergence was achieved. A difference Fourier was then computed to locate many of the hydrogen atoms. Finally, we refined both non-hydrogen atoms (anisotropic) and hydrogen atoms (isotropic),

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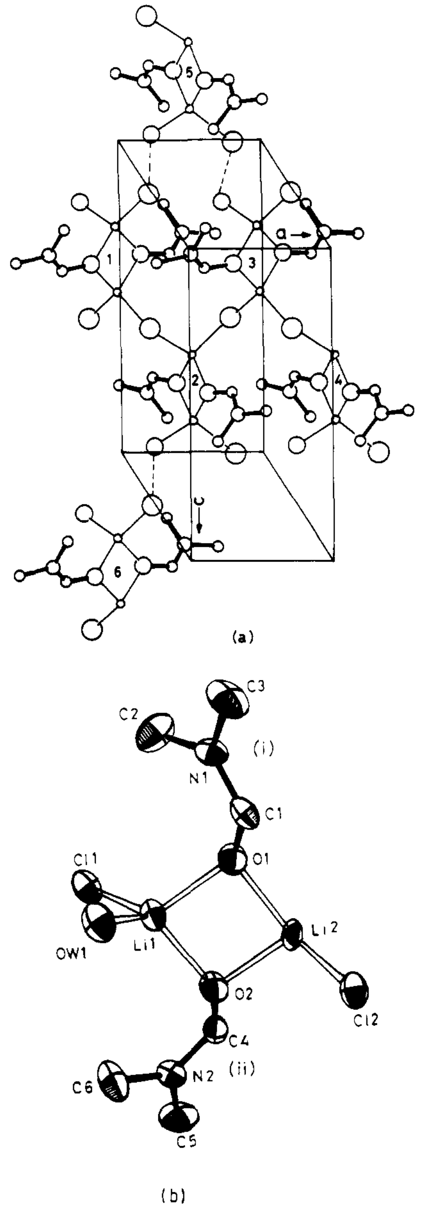

Figure 1. (a) Packing diagram of $\mathrm{LiCl\cdot DMF\cdot {}^1/_2H_2O}$. This as well as the remaining unit cells are viewed down *b* axis: (1) x, y, z; (2) $1 - x, {}^1/_2 + y, {}^3/_2 - z$; (3) $x, 1 + y, z$; (4) $1 - x, {}^3/_2 + y, {}^3/_2 - z$; (5) $-x, {}^1/_2 + y, {}^3/_2 - z$; (6) $1 + x, y, z$. (b) Coordination around two crystallographically nonequivalent lithium atoms (Li1, Li2).

and the positional parameters so obtained are listed in Table II. The numbering schemes for the atoms in the asymmetric units are shown in Figures 1–4.

Infrared spectra of the complexes were recorded with a Perkin-Elmer 580 spectrophotometer as Nujol and Fluorolube mulls.

Results and Discussion

Metal–ligand distances in the various complexes are listed in Table III along with the metal···O=C′ angles. The metal···O=C′ angles give an indication as to whether the alkali- or the alkaline-earth-metal ion is along the lone-pair direction of the amide carbonyl. Table III also provides information as to whether the metal ion is in the peptide plane. The ligand–metal–ligand angles in the complexes are listed in Table IV. The effect of complexation with the alkali- or the alkaline-earth-metal ions on the structural parameters of *N*,*N*-dimethylformamide can be seen from the results presented in Table V. Especially noteworthy are the C′=O, C′—N, and N—C distances of the amide in the complexes. Torsional angles and the deviation of the amide nitrogen from the OCNC least-squares planes are shown in Table VI.

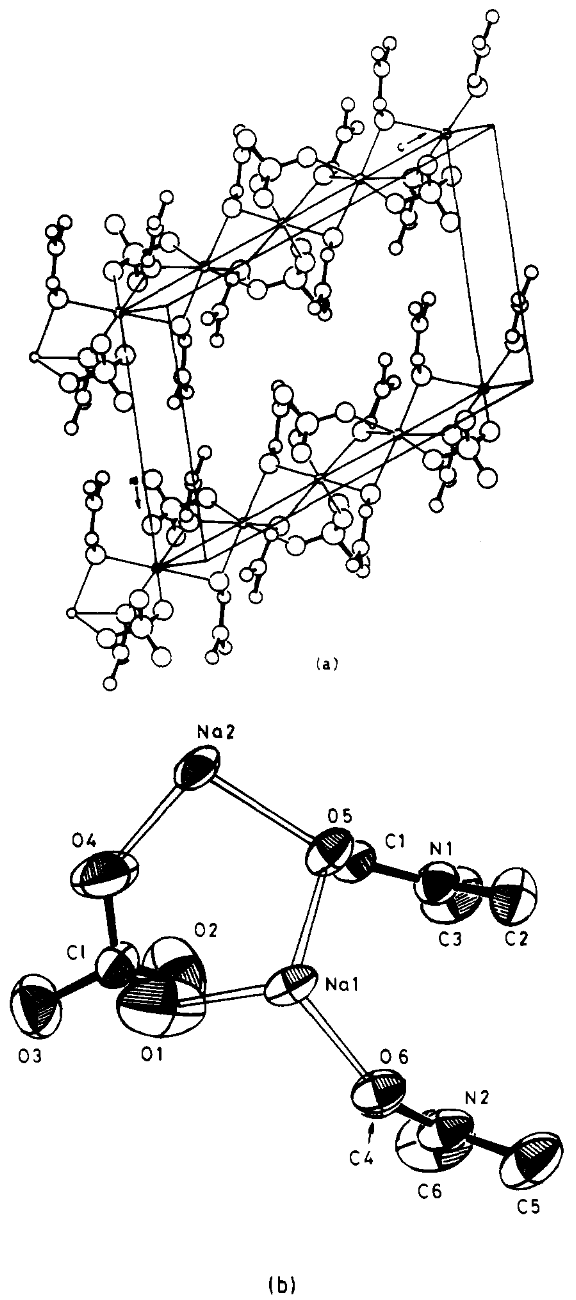

Figure 2. (a) Packing diagram of $\mathrm{NaClO_4\cdot 2DMF}$. (b) Asymmetric part of unit cell indicating Na1 and Na2 as nonequivalent.

Lithium and Sodium Complexes. The packing diagram of the lithium complex, $\mathrm{LiCl\cdot DMF\cdot {}^1/_2H_2O}$, is shown in Figure 1 along with the coordination around the two nonequivalent tetracoordinated lithium ions. One of the lithium ions is coordinated to two amide oxygens, a water molecule, and a chloride ion, while the other lithium ion is coordinated to two amide oxygens and two chloride ions. The bond angles in the first coordination sphere show essentially tetrahedral geometry (Table IV) just as the LiCl–NMA complex.[6] The average distance between $\mathrm{Li^+}$ and the amide oxygen is 1.965 Å, while the distance between $\mathrm{Li^+}$ and the water oxygen is 1.904 Å (Table III). These $\mathrm{Li^+}$···O distances are within the range expected for tetrahedral complexes of lithium with oxygen donors.[12] The amide units bridge the two lithium ions of the same asymmetric unit cell (Li···Li distance being 2.77 Å) with an Li···O···Li angle of 90°; the chloride ions bridge lithium ions of adjacent asymmetric unit cells.

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Table I. Crystal Data[a] and Detatils of Intensity Data Measurement and Refinement

	Li	Na	Ca	Mg
mol formula	$LiCl\cdot DMF\cdot {}^1/_2H_2O$	$NaClO_4\cdot 2DMF$	$CaCl_2\cdot 2DMF\cdot 2H_2O$	$Mg(ClO_4)_2\cdot 6DMF$
cryst shape	parallelepiped and cylindrical	platelike	cubic and plate type	plate type with hexagonal shape
rel mol mass	124.4	268.5	293.1	661.3
cryst syst	monoclinic	monoclinic	triclinic	monoclinic
a/Å	13.022 (7)	9.297 (4)	6.293 (4)	20.686 (11)
b/Å	5.978 (4)	10.203 (3)	6.944 (2)	10.962 (18)
c/Å	17.028 (10)	13.510 (6)	8.853 (5)	14.885 (9)
α/deg			110.15 (3)	
β/deg	105.48 (4)	110.08 (4)	105.60 (6)	91.45 (5)
γ/deg			95.34 (5)	
space group	$P2_1/c$	$P2/c$	$P\bar{1}$	$P2_1/a$
Z, molecules/unit cell	8	4	1	4
D_{obsd}/g cm^{-3}	1.281	1.464	1.382	1.273
D_{calcd}/g cm^{-3}	1.299	1.487	1.427	1.307
V/Å^3	1277.4	1203.6	342.3	3374.3
μ/cm^{-1}	4.65	3.21	7.76	2.30
$F(000)$	520	556	152	1392
cryst dimens	0.8 × 0.05 × 0.5	1 × 0.04 × 0.6	0.5 × 0.04 × 0.6	0.7 × 0.03 × 0.6
max angle θ/deg	24	24	28	24
no. of unique reflcns measd	1684	1724	1537	3372
no. of signif reflcns [$\lvert F_o\rvert > 3\sigma(F_o)$]	1581	1663[c]	1506[c]	2900
weighting, w	Hughes,[b] $F_{min} = 2.3$	Hughes, $F_{min} = 6.9$	Hughes, $F_{min} = 4.7$	Cruikshank $[4.24 + \lvert F_o\rvert + 0.0035\lvert F_o\rvert^2]^{-1}$
nonreliability factor, R	0.089	0.062	0.055	0.121

[a] Crystal data are measured with Mo Kα ($\lambda = 0.7107$ Å) radiation. [b] Hughes weighting scheme: $w = 0$ for $F_{obsd} = 0$; $w = 1/(4F_{min})^2$ for $F_{obsd} < 4F_{min}$; $w = 1/F^2$ for $F_{obsd} > 4F_{min}$. [c] $\lvert F_o\rvert > 2\sigma(F_o)$ as significant reflections.

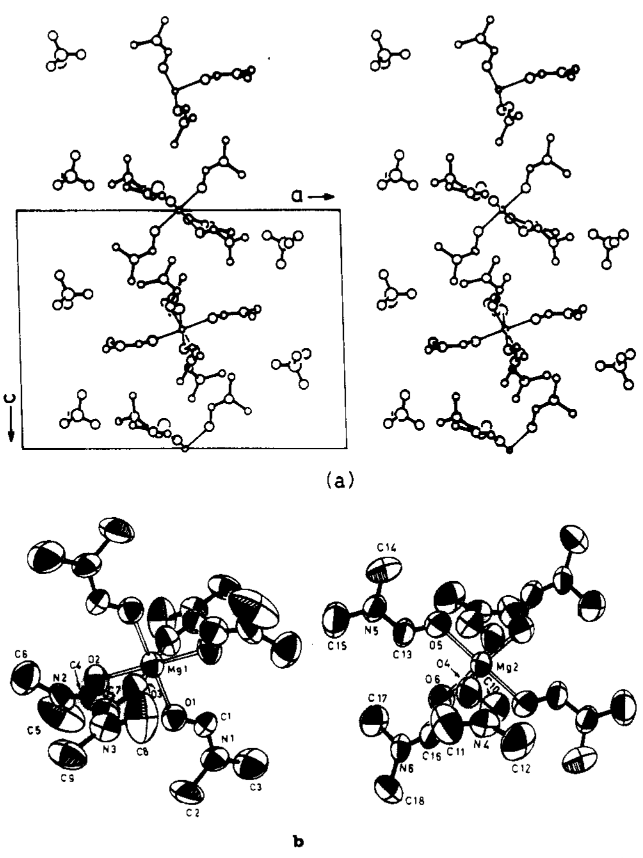

Figure 3. (a) Packing diagram of $Mg(ClO_4)_2\cdot 6DMF$. (b) Coordination around crystallographically nonequivalent magnesium atoms (Mg1, Mg2).

The approach of lithium ion does not deviate much from the direction of the lone-pair orbital of the amide carbonyl (Table III). Accordingly, the Li···O=C′ angle is between 125.0 and 138.0°. This deviation is considerably smaller than that found in the Li–antamanide complex[13] (132–156°) or the LiCl complex with NMA[6] (141–175°). One of the lithium ions shows deviation from the peptide plane to the extent of 1.1 Å, but the other ion shows only a deviation of ~0.45 Å. The carbonyl distance in the LiCl–DMF complex is ~1.26 Å compared to the value of ~1.22 Å in free tertiary amides.[7,8] The central C′–N bond distance in the complex is 1.286 Å compared to ~1.35 Å in tertiary amides. Such lengthening of the C′=O bond and shortening of C′—N bond are indeed what we would expect when lithium ion binds to the carbonyl oxygen. These variations in C′=O and C′—N distances predict an increase in the barrier to rotation about the C′–N bond in DMF due to interaction with Li^+, as indeed was found experimentally from NMR studies.[14] It is interesting that the N–C bonds of the dimethylamino group of DMF also vary with the C′–N distance.

The lithium complex shows some interesting structural features (Figure 1). Both the amide and the chloride ions act as bridging groups between neighboring lithium ions, giving rise to a polymeric structure. Furthermore, there is hydrogen bonding of the O–H···Cl^- type between H_2O and Cl^- present in adjacent polymeric units. Hydrogen bonding between water and chloride ions within the same polymeric units is not favored.

In Figure 2, we have shown the asymmetric part of the unit cell of the sodium complex, $NaClO_4\cdot 2DMF$, along with the packing diagram. Sodium ions exhibit octahedral coordination in this complex; Na^+ is pentacoordinated in the NMA complex[6] as well as in the antamanide complex.[15] In the DMF complex, sodium ions are coordinated by four amides and two perchlorate oxygens, and the Na···O distances are between 2.35 and 2.58 Å (Table III) within the range of Na···O found in octahedral oxygen donor complexes of sodium.[12] Na^+ ions do not deviate much from the peptide plane and are essentially along the lone-pair direction of the amide carbonyls. Sodium ion, unlike lithium ion, has a marginal effect on the amide distances (Table V). Thus, the longest carbonyl distance in the Na complex is ~1.23 Å while the shortest C′–N distance

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Table II. Final Positional Parameters for Non-Hydrogen Atoms (Esd's in Parentheses)

atom	10^4x	10^4y	10^4z	atom	10^4x	10^4y	10^4z
Lithium Complex							
Li1	2030 (13)	−1399 (26)	7933 (11)	C2	2801 (11)	−4098 (21)	9835 (8)
Li2	4037 (12)	−1334 (28)	7661 (10)	C3	3852 (10)	−7519 (21)	9815 (8)
Cl1	1185 (2)	1358 (4)	8534 (2)	O2	2653 (5)	99 (12)	7151 (5)
Cl2	4580 (2)	−3825 (4)	6784 (2)	C4	2539 (8)	1919 (18)	6764 (6)
OW1	1141 (6)	−3957 (13)	7636 (5)	N2	1656 (7)	2572 (14)	6268 (5)
O1	3429 (6)	−2784 (13)	8458 (4)	C5	1600 (11)	4736 (23)	5852 (8)
C1	3733 (7)	−4607 (17)	8818 (6)	C6	695 (10)	1253 (22)	6097 (9)
N1	3491 (7)	−5308 (13)	9456 (5)				
Sodium Complex							
Na1^a	10000	0000	0000	N1	13453 (7)	2356 (7)	1191 (5)
Na2^a	10000	782	2500	C2	14256 (10)	1246 (10)	994 (8)
Cl	7968 (2)	2833 (2)	272 (2)	C3	13995 (13)	3647 (11)	1073 (9)
O1	8219 (14)	1703 (10)	−231 (7)	O6	10955 (7)	972 (5)	−1235 (4)
O2	8962 (11)	3770 (10)	112 (9)	C4	11178 (10)	2124 (8)	−1338 (6)
O3	6465 (8)	3284 (8)	−216 (7)	N2	12165 (9)	2598 (7)	−1755 (5)
O4	8269 (10)	2579 (9)	1352 (6)	C5	13116 (13)	1738 (12)	−2092 (9)
O5	11634 (6)	1144 (5)	1529 (4)	C6	12276 (17)	3982 (11)	−1929 (10)
C1	12221 (9)	2198 (8)	1451 (6)				
Calcium Complex							
Ca^a	5000	5000	10000	N1	−795 (7)	2616 (6)	5097 (5)
Cl	7405 (2)	1948 (2)	9266 (1)	C2	182 (13)	1828 (9)	3753 (6)
O1	2549 (6)	3680 (6)	7198 (4)	C3	−3235 (10)	2397 (13)	4626 (10)
C1	467 (8)	3466 (7)	6701 (6)	OW1	2658 (5)	2711 (5)	10620 (5)
Magnesium Complex							
Mg1^a	5000	0000	5000	C6	5049 (15)	3174 (27)	7179 (18)
Mg2^a	5000	0000	10000	O3	4069 (7)	280 (14)	4535 (11)
Cl1	8485 (3)	657 (7)	3526 (5)	C7	3684 (11)	−580 (21)	4382 (17)
O11	7858 (13)	1094 (36)	3498 (25)	N3	3065 (8)	−471 (19)	4307 (13)
O12	8835 (20)	1384 (35)	3950 (26)	C8	2764 (15)	700 (27)	4417 (21)
O13	8735 (21)	618 (35)	2696 (20)	C9	2645 (16)	1477 (45)	4152 (23)
O14	8519 (18)	−470 (23)	3860 (34)	O4	5628 (7)	−651 (6)	9049 (11)
Cl2	8276 (4)	808 (6)	8602 (5)	C10	6055 (11)	−1375 (23)	9191 (16)
O21	8126 (27)	922 (61)	7771 (22)	N4	6542 (8)	−1602 (20)	8645 (13)
O22	8720 (19)	1497 (39)	8960 (26)	C11	6570 (15)	−928 (28)	7836 (19)
O23	7737 (15)	946 (39)	8988 (36)	C12	7035 (16)	−2383 (34)	8868 (24)
O24	8401 (19)	−302 (28)	8587 (35)	O5	4240 (7)	15 (15)	9098 (11)
O1	5370 (7)	1164 (15)	4062 (10)	C13	4152 (11)	415 (25)	8328 (16)
C1	5181 (10)	1741 (20)	3383 (15)	N5	3577 (7)	474 (16)	7941 (12)
N1	5548 (8)	2358 (15)	2886 (12)	C14	3487 (16)	960 (30)	7036 (20)
C2	5284 (15)	2965 (23)	2102 (16)	C15	3016 (12)	309 (30)	8468 (19)
C3	6238 (13)	2459 (31)	3097 (29)	O6	5247 (7)	1687 (18)	9647 (12)
O2	4933 (7)	1437 (13)	5854 (10)	C16	5801 (13)	2024 (23)	9409 (19)
C4	4711 (10)	2444 (19)	5727 (14)	N6	5949 (9)	3177 (16)	9293 (12)
N2	4736 (10)	3348 (16)	6297 (12)	C17	5548 (17)	4117 (29)	9382 (21)
C5	4480 (18)	4504 (28)	6094 (22)	C18	6611 (14)	3453 (36)	9036 (23)

[a] Indicates the atoms with 0.5 occupancy.

is ~1.32 Å. Both the amide and the perchlorate ions act as bridging groups between neighboring sodium ions and give rise to a polymeric structure similar to that in the lithium complex. It is noteworthy that while Li and Na complexes possess such bridging amides and anions resulting in the polymeric structure, magnesium and calcium complexes do not exhibit such structures.

Magnesium and Calcium Complexes. The packing diagram of the magnesium complex, $Mg(ClO_4)_2 \cdot 6DMF$, is shown in Figure 3 along with the coordination spheres of the two crystallographically unique Mg^{2+} ions. Unlike in the lithium and sodium complexes, we have only DMF molecules as ligands in the octahedral magnesium complex, with a characteristic Mg⋯O distance of about 2.1 Å (Table II). The magnesium ion does not deviate much from the lone-pair direction of the amide carbonyl (Table III); the Mg⋯O=C′ angle is in the range 122–139°, and the Mg^{2+} ion is essentially in the plane of the peptide. The effect of binding of the magnesium ion on the geometry of DMF is significant just as in the case of the lithium complex (Table V). The carbonyl distance becomes as long as ~1.27 Å while the C′–N bond decreases down to 1.275 Å. The N–C bond of the dimethylamino group also shows some changes.

In the calcium complex, $CaCl_2 \cdot 2DMF \cdot 2H_2O$ (Figure 4), we have two amide molecules, two water molecules, and two chloride ions in the primary coordination sphere, with the calcium ion occupying the center of symmetry of the unit cell. This complex also consists of molecular units as in the case of magnesium, but not the polymeric structure found in the lithium or the sodium complex. The Ca⋯O distance is ~2.35 Å and falls within the range found in the octahedral complexes of Ca^{2+} with oxygen donors.[12] The Ca⋯Cl distance (2.71 Å) in the complex is, however, considerably shorter than that in α-$CaCl_2 \cdot H_2O$ (2.85–2.93 Å). The Ca^{2+} ion has a smaller effect on the amide distances than Mg^{2+} (Table V). The calcium ion is essentially in the lone-pair direction of the amide carbonyl and shows little deviation from the peptide plane (Table III).

Systematics in Structural Parameters. In all the complexes we studied, the metal–oxygen distances (Table III) are characteristic of the polyhedra and conform to the ranges of metal–oxygen distances in coordination compounds of alkali and alkaline-earth metals with oxygen donors.[12] In general, the metal–oxygen distance increases with an increase in the

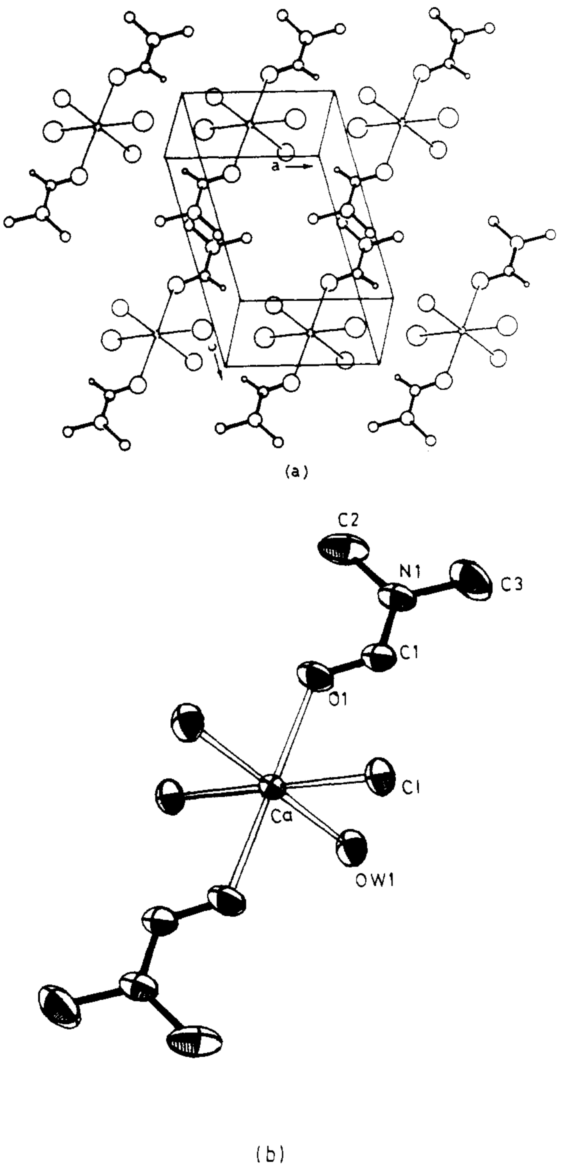

Figure 4. (a) Packing diagram of $CaCl_2{\cdot}2DMF{\cdot}2H_2O$. (b) Coordinated species of calcium.

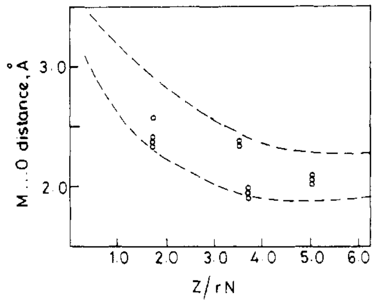

Figure 5. Variation of the metal-oxygen distances with the ionic potential per ligand (*Z*/*rN*): circles, values from the present study; broken curves, regions defined by the structural data on the various alkali- and alkaline-earth-metal complexes with oxygen donors.[6]

coordination number of the alkali- or the alkaline-earth-metal ion. It has been found convenient to rationalize metal-oxygen distances in alkali and alkaline-earth metal complexes in terms of the parameter *Z*/*rN*, where *Z* is the charge, *r* the radius of cation, and *N* the coordination number.[6] The dependence of the metal-oxygen distances in the complexes of alkali and alkaline-earth metals on *Z*/*rN* is indicated by the dotted curves in Figure 5. The metal-oxygen distances found in the present

Table III. Metal-Oxygen Distances, Positions of the Metal with Respect to the Oxygen Lone Pair, and Deviations from the DMF Plane

atoms	M···L dist/Å	M···O-C′ angle/deg	dev of M from amide plane/Å
	Lithium Complex		
Li1···O1	1.984 (19)	135.3	1.19
Li1···O2	1.952 (19)	137.8	−1.12
Li1···OW1	1.904 (18)		
Li2···O1	1.949 (18)	126.1	−0.43
Li2···O2	1.975 (18)	124.8	0.50
Li1···Cl1	2.361 (17)		
Li2···Cl2	2.347 (17)		
Li2(I)···Cl2(II)	2.341 (17)		
	Sodium Complex		
Na1···O5	2.352 (6)	125.5	−0.70
Na2···O5	2.404 (5)	121.3	2.02
Na2···O6[a]	2.361 (6)	127.6	−0.79
Na1···O4[a]	2.578 (9)		
Na2···O1	2.346 (11)		
	Calcium Complex		
Ca···O1	2.341 (3)	128.1	−0.11
Ca···OW1	2.365 (4)		
Ca···Cl	2.713 (1)		
	Magnesium Complex		
Mg1···O1	2.064 (16)	139.0	0.11
Mg1···O2	2.044 (14)	130.1	0.16
Mg1···O3	2.053 (14)	122.2	−0.54
Mg2···O4	2.080 (16)	125.2	−0.44
Mg2···O5	2.044 (15)	134.9	−0.28
Mg2···O6	2.006 (19)	125.9	−0.24

[a] Perchlorate oxygens: (1) *x*, *y*, *z*; (II) −*x*, $^1/_2$ + *y*, $^3/_2$ − *z*.

Table IV. Ligand-Metal-Ligand Angles (deg) in Various Coordination Spheres

	Lithium Complex		
Cl1-Li1-O1	125.0	Cl2-Li2(I,II)-O2	112.9
Cl1-Li1-O2	107.6	O1-Li2(I,II)-O2	90.4
Cl1-Li1-OW1	110.8	Li1-O1-Li2	89.7
O1-Li1-O2	90.0	Li1-O2-Li2	89.9
O1-Li1-OW1	101.8	O1(I)-Li2(I)-Cl2(II)	113.0
O2-Li1-OW1	121.5	O2(I)-Li2(I)-Cl2(II)	114.4
Cl2-Li2(I,II)-O1	114.1	Cl2(I)-Li2(I)-Cl2(II)	109.5
	Sodium Complex		
O5-Na1-O6	97.1	O6-Na1-O1[a]	90.8
O5-Na1-O6(III)	82.9	O6-Na1-O1(III)[a]	89.2
O6-Na1-O5(III)	82.9	O5-Na2-O6(III)	82.7
O5-Na1-O1[a]	87.9	O5-Na2-O4[a]	86.7
O5-Na1-O1(III)[a]	92.1	O6(III)-Na2-O4[a]	95.7
	Calcium Complex		
O1-Ca-Cl	92.1	Cl-Ca-OW1	87.5
O1-Ca-OW1	89.2		
	Magnesium Complex		
O1-Mg1-O2	88.5	O4-Mg2-O5	92.0
O1-Mg1-O3	92.1	O4-Mg2-O6	88.4
O2-Mg1-O3	90.9	O5-Mg2-O6	90.9

[a] Oxygen atoms from perchlorate group: (I) *x*, *y*, *z*; (II) *x*, $^1/_2$ + *y*, $^3/_2$ − *z*; (III) 2 − *x*, −*y*, −*z*.

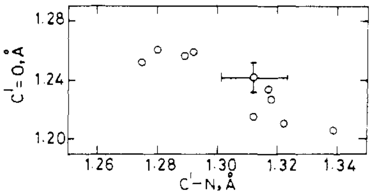

Figure 6. Plot of the C′═O bond length against the C′—N bond length (data from Table V).

Table V. Bond Lengths (Å) and Bond Angles (deg) for DMF Molecules in Various Metal Complexes[a]

C′–N	C′=O	N–C1	N–C2	O–C′–N	C′–N–C1	C′–N–C2	C1–N–C2
			Lithium Complex				
1.280 (13)	1.261 (13)	1.434 (16)	1.479 (15)	125.4 (10)	122.9 (9)	121.3 (9)	115.6 (9)
1.292 (13)	1.259 (13)	1.442 (16)	1.467 (16)	124.3 (10)	122.7 (9)	120.3 (9)	117.1 (10)
			Sodium Complex				
1.318 (11)	1.227 (10)	1.430 (12)	1.439 (13)	125.7 (8)	120.6 (7)	120.8 (8)	118.6 (8)
1.322 (12)	1.210 (10)	1.427 (15)	1.442 (13)	125.1 (8)	120.5 (8)	121.8 (8)	117.7 (9)
			Calcium Complex				
1.317 (6)	1.234 (6)	1.452 (8)	1.454 (8)	124.2 (4)	121.0 (4)	120.7 (5)	118.3 (5)
			Magnesium Complex				
1.275 (28)	1.252 (27)	1.459 (33)	1.444 (30)	124.6 (20)	120.6 (21)	120.2 (19)	119.1 (21)
1.312 (28)	1.215 (26)	1.466 (33)	1.411 (36)	125.9 (20)	119.5 (20)	122.6 (21)	117.8 (22)
1.289 (29)	1.256 (27)	1.445 (36)	1.425 (49)	124.8 (22)	120.2 (21)	122.9 (24)	116.9 (24)
1.338 (29)	1.206 (29)	1.422 (35)	1.371 (40)	125.2 (22)	118.0 (21)	122.5 (23)	119.3 (24)
1.312 (28)	1.242 (29)	1.431 (31)	1.462 (35)	122.4 (22)	119.3 (20)	121.2 (21)	118.1 (21)
1.321 (31)	1.265 (31)	1.338 (37)	1.465 (36)	122.4 (24)	126.0 (23)	117.2 (22)	116.9 (23)

[a] C1 and C2 refer to the two methyl group carbons linked to the N atom.

Table VI. Selected Torsional Angles (deg) and Deviation (Å) of Nitrogen from the Amide Plane

OC′NC1 (ω_1)	OC′NC2 (ω_2)	deviation	
		OC′NC1	OC′NC2
	Lithium Complex		
1.8 (17)	177.5 (10)	−0.006	−0.010
179.4 (10)	−0.5 (17)	0.003	−0.002
	Sodium Complex		
−1.5 (13)	176.9 (9)	0.005	−0.012
−2.5 (14)	174.8 (9)	0.009	−0.020
	Calcium Complex		
0.7 (8)	179.3 (5)	0.002	0.004
	Magnesium Complex		
178.3 (21)	−1.5 (35)	−0.007	0.005
178.4 (24)	−0.5 (34)	−0.006	0.002
−1.2 (3.7)	−178.6 (27)	0.004	0.006
1.1 (3.7)	−175.9 (27)	0.004	0.016
179.5 (23)	13.0 (35)	0.002	0.049
−1.9 (23)	178.6 (27)	−0.007	0.006

study (Table III) conform to the ranges as can be seen from this figure.

The bond lengths of DMF in the complexes (Table V) show interesting trends. Accordingly, the carbonyl distance of the amide increases progressively as the central C′–N bond of the amide decreases (Figure 6). It is interesting that the C′═O and the C′—N distances in the standard peptide geometry[9] as well as in free tertiary amides[8] fall in line with the data plotted in Figure 6. Least-squares fit of the data in Figure 6 gives a correlation coefficient of 0.70, a slope of −0.76, an intercept of 2.235, and standard deviation of 0.015. The N–C distances of the dimethylamino group seem to generally show an increasing trend with the decreasing C′–N distance, but least-squares fit of the data show correlation coefficients of around 0.5 or less.

As mentioned earlier, in all the complexes we studied, the deviation of the metal ion from the amide carbonyl lone-pair direction is generally small, the maximum deviation being in the lithium and magnesium complexes (see Table III). The peptide group is essentially planar, the nitrogen atom showing negligible pyramidal character. This can be seen from the torsional angles as well as the deviation of the nitrogen atom from the least-square planes defined by OC′NC1 and OC′NC2 (Table VI).

From the bond lengths listed in Table V, we see that the perturbation of bond lengths is maximum in lithium and magnesium complexes; the distances are not much affected in sodium and calcium complexes. This is in conformity with the interaction strengths of amides with alkali- and alkaline-earth-metal cations predicted by quantum-mechanical calculations.[2,5] The observed changes in distances are also similar to the trends found in the barrier to rotation around the C′–N bond, which varies as $\mathrm{Li}^+ \gtrsim \mathrm{Mg}^{2+} > \mathrm{Na}^+ \gtrsim \mathrm{Ca}^{2+}$.

Infrared Spectra. We have studied the infrared spectra of several alkali- and alkaline-earth-metal complexes of DMF. All the complexes show lower carbonyl stretching frequencies (by about 10–17 cm^{-1}) than the free amide (1675 cm^{-1}). There is generally an increase in the frequency of the 1388-cm^{-1} band up to 5 cm^{-1}; this band has a significant contribution from the C′–N stretching mode. These changes in intramolecular vibration frequencies of DMF in the complexes are in conformity with the changes in bond distances caused by complexation. The asymmetric C–N stretching frequency (1258 cm^{-1}) of the dimethylamino group is lower in the complexes (3–5 cm^{-1}). The torsional frequency (354 cm^{-1}) of the amide is considerably increased in the complexes as we would expect from the increase in the C′–N bond order.

The lithium complex gives a band ~354 cm^{-1} due to the asymmetric $\mathrm{Li}^+\cdots\mathrm{O}$ stretching vibration of the $\mathrm{LiO}_n\mathrm{Cl}_{4-n}$ tetrahedron while the Mg^{2+} complex shows the corresponding band around 406 cm^{-1} characteristic of the MgO_6 octahedron. The calcium complex shows the metal–oxygen stretching band around 240 cm^{-1}; the Na^+–O stretching frequency is too low to observe with the spectrometer available. These metal–oxygen stretching frequencies are characteristic of the oxygen coordination around the alkali- and alkaline-earth-metal cations, and the positions observed here are similar to those found in solutions of alkali- or alkaline-earth-metal salts in oxygen donor solvents and in oxide glasses of these metals.[3,16] Interestingly, these vibrations are Raman inactive, suggesting thereby that bonding between the alkali or the alkaline-earth metal and the amide is predominantly electrostatic.

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Registry No. $\mathrm{LiCl{\cdot}DMF{\cdot}{}^1/_2H_2O}$, 90065-20-6; $\mathrm{NaClO_4{\cdot}2DMF}$, 90065-21-7; $\mathrm{CaCl_2{\cdot}2DMF{\cdot}2H_2O}$, 90065-22-8; $\mathrm{Mg(ClO_4)_2{\cdot}6DMF}$, 90065-23-9.

Supplementary Material Available: Tables of isotropic temperature factors, fractional coordinates, and structure factors (56 pages). Ordering information is given on any current masthead page.

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