146. Directional Preferences of Ether O-Atoms Towards Alkali and Alkaline Earth Cations

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Summary

An analysis of the environments of alkali and alkaline earth cations complexed to ethers has been made with the *Cambridge Structural Database.* The cations invariably lie close to the bisecting plane through the O-atoms. The larger cations show an apparent preference to approach the ether group along a tetrahedral lone pair direction, whereas Li^+ cations tend to be found along the C–O–C bisector, *i.e.* along the trigonal lone pair direction. These observations are discussed in relation to recent theoretical and experimental findings.

Knowledge about non-bonded or secondary interactions is likely to become of more importance in many developing areas of chemistry, biochemistry and pharmacology. One important store of information about non-bonded interactions is the solid state: information about the ways in which molecules or functional groups approach one another in crystals. This information is coded in the atomic coordinates of the thousands of crystal structures that have been determined by X-ray crystallography but it has hardly been touched so far¹), in spite of the availability since several years of the *Cambridge Structural Database* (CSD), which makes it possible to retrieve and collate the data from published organic crystal structures without too much trouble [8].

Among the factors responsible for the variation in binding energies of metal cations with neutral and anionic organic ligands, the preferred coordination numbers and geometries of the cations have received considerable attention [8]. The directional preferences of the coordination sites on the organic ligands should be equally important but have been comparatively neglected. In this paper we report

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¹) Exploratory probings up till now include studies of approach directions of nucleophiles towards carbonyl groups [1], of nucleophiles and electrophiles towards divalent S-atoms [2], of nucleophiles towards sulfonium S atoms [3], of iodo groups towards C,I-bonds [4], and of C^{2+} ions towards carboxylate anions [5]. Studies of the mutual approaches of CdS_3X tetrahedral species [6] and of SnR_3X and SnR_2X_2 ones [7] form part of structural studies of the S_N2 (and S_N3) pathways.

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results of a study about preferred approach directions of metal cations towards ether O-atoms[2]).

A search of the CSD (version of May, 1981 with 29052 entries in the bibliographic file) gave 135 crystal structures containing a group IA or IIA metal (M) cation coordinated to at least one ether O-atom[3]). These are listed in *Table 1* under their CSD acronyms. For each ether group the relative position of the coordinated cation was expressed in terms of spherical polar coordinates: the O · · · M distance *d*; the angle θ between the O · · · M direction and the normal to the C–O–C plane, the colatitude; the angle φ between the C–O–C angle bisector and the projection of the O · · · M direction on the C–O–C plane, the longitude, taking the angle bisector as reference angle zero.

The stereographic projection plot shown in *Figure 1* shows that all the group IA cations lie fairly close to the bisecting plane of the ether grouping. *Figure 2* shows the plot of O · · · M distance *vs.* colatitude for these cations. The distributions for $M = Li^+$, Na^+ and K^+ are non-random[4]) and appear to be different for

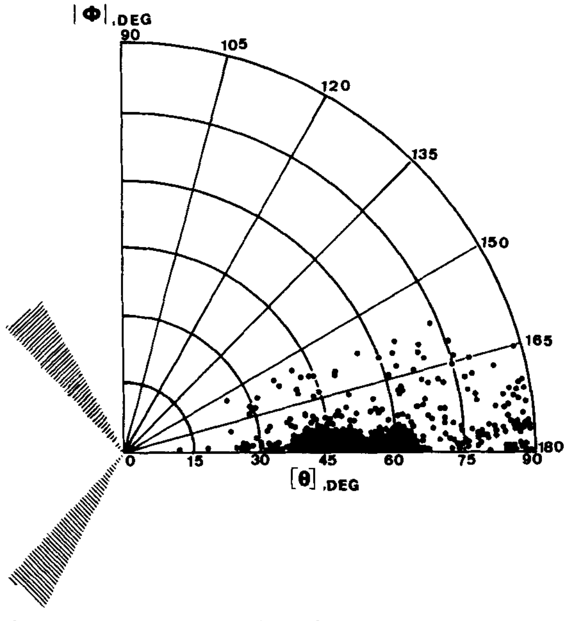

Fig. 1. *Distribution of colatitudes θ and longitudes φ for group IA cations coordinated to ether O-atoms* (The C–O–C angle bisector is at $\varphi = 0°$ (180°))

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[2]) One incentive for this study came from observations made during our recent X-ray crystallographic investigations of organo-lithium compounds [9]; we noticed that in tetrahydrofuran-solvated complexes the Li-atoms tend to lie close to the bisector of the C–O–C angle. This finding ran counter to earlier observations on divalent sulfur [2], which tends to be approached by electrophiles, including alkali cations, at a steep angle to the R–S–R plane.

[3]) As criterion for coordination we use the condition that the O · · · M distance be not greater than the sum of the *van der Waals* radii as listed by *Pauling* [10].

[4]) For a random distribution of sample-points, the number at a given colatitude θ would be proportional to sin θ.

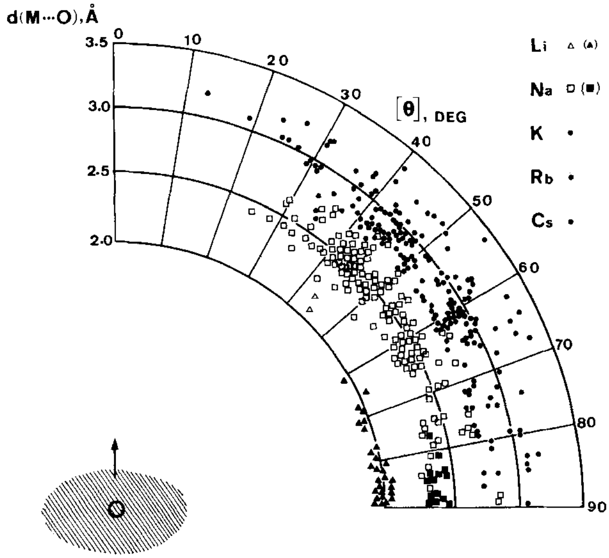

Fig. 2. *Distribution of colatitudes θ and M · · · O distances* d (in Å) *for group IA cations coordinated to ether O-atoms* (For Li^+ and Na^+ we distinguish between coordination to monodentate ligands (filled triangles and squares) and to polydentate ones (open triangles and squares). The other cations are invariably coordinated to polydentate ligands)

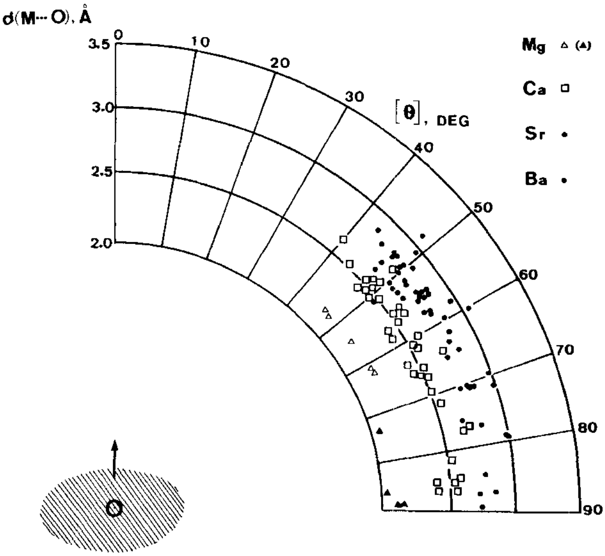

Fig. 3. *Distribution of colatitudes θ and M · · · O distances* d (in Å) *for group IIA cations coordinated to ether O-atoms* (For Mg^{2+} the four examples of coordination to monodentate ligands are indicated by filled triangles: the other cations are invariably coordinated to polydentate ligands)

Table 1. *CSD acronyms for crystal structures containing a group IA or IIA metal ion coordinated to at least one ether O-atom* (For each entry the actual number of coordinated, crystallographically independent ether O-atoms is given in parentheses)

Li	BYFELI(1), CMDWLT01(1), CODCOL(2), COLCUR11(4), COSALL(2), CROBLI(1), DOLICL(2), DTLICR(3), LCRYPT(2), LIBCRA(1), LIOMRE(1), LIPRAL(1), MSIYBL(2), OMDWLI(1), OMEDMO(1), PAUELI10(1), THCHCR(2), TMCRLI(1)
Na	ABXBPC(1), ACDPRS(1), ACFENA(2), ANTBRN(4), ANTINA(4), XZCNAP(3), BZCNOP(4), BZCSUR(5), CPNASN(5), CRNAPB10(4), CRSHSB10(6), CRYPNA10(1), DIOXSP(1), DOLNAT(4), ESCTSB(2), HDHBNA(6), MONSBR(4), MXPENA(6), NAHOXY(1), NAICRP10(5), NALASC(2), NAMXAC(1), NAPHBZ(2), NATHOD(6), NCRYFE(6), NEMNAL(2), NIGERI(4), NONACS(2), OHBZPA(5), OHBZPB(4), OHBZPC(5), PCFENA(6), PEANNA(3), PKOJSI(1), POZTNA(5), SALCNA(1), SANMAL(2), SBHOCD(6), SMCPCO(6), SPHENC(2), TOXDOD(8), TXCDNA(4), TXEANA(3)
K	BPTGLK(5), CATDAC10(2), CHAMPA(1), CMXPIC10(5), CRKEAC10(6), CRPKTE(6), DOLKTC(8), HBXCTK(5), HOXOKM(6), HOXOMK(6), KAOXYA(1), KAOXYA10(1), KBICRP(6), KCRYPT10(3), KDMTNB10(2), KECOCE10(2), KMOXAL(1), KMXCHY(1), KOXDZO(2), KTHOXD(3), MXNBZK(1), NPXPKT10(5), NPXUNK(5), OAZKCN(3), OCXCPK(8), TNPTKE(2), ZZZAVY10(10), APHOUB(4)
Rb	BDORBT(10), BQXERB(2), BZHORB(6), HNFCRB(1), MQOERB(5), MQUEAB(3), NBHORB(6), QUOXRB10(8), RBBIPH(5), RBCRYP10(3), RBFURC10(1), RBHOXY(1), RBORMY(3)
Cs	CSCRYP10(3), GMBZCS(3), MBZCST(6), NBOCCS(6), NONACU(2)
Mg	BZMGIC(5), CPHMOM10(2), THFMGB(2)
Ca	ALARCA(1), ALTRCA(1), BCRCIH10(5), BCRNBZ(3), BZCAIM10(5), CACRPB(6), CAGLUC10(1), CAKGLT10(1), CAOADH(1), CAOGUC(1), EDXOCA(2), GGHPCA(1), IONCAH(1), TOXCDO(2), TPODCA(1), TZOPCA(3)
Sr	HODCSR(6), TZOPSR(3), ZTXESR(4)
Ba	AHEDZT10(6), BAANTX10(2), BZCBAP(8), DHEDZT10(7), HODCBA(6), PXCDBA(10)

the individual cations. The Li^+ ions tend to lie close to the plane of the ether grouping, *i.e.* along the direction of the trigonal (sp^2) lone pair on the O-atom. This tendency does not seem to be shared by the larger group IA cations, which cover a wider range of colatitude with some clustering at colatitudes of about 45° and possibly about 60°, *i.e.* approximately in the direction of a tetrahedral lone pair on the O-atom. The distribution for Na^+ covers both regions.

The tendency of the small group IIA cations Mg^{2+} and Ca^{2+} to lie in the C–O–C plane does not seem to be as pronounced as for Li^+, judging from the colatitude distribution shown in *Figure 3.* However, the relative sparseness of the data makes it difficult to draw a definite conclusion. On the other hand, there is no doubt about the tendency for the group IIA cations to lie close to the C–O–C bisecting plane *(Fig. 4)*, like the alkali cations.

Theoretical calculations of interaction energies of metal cations with ethers [11] indicate that most stable position of the cation is along the C–O–C bisector, not only for Li^+ but also for the others. The strength of binding decreases in the order $Li^+ > Na^+ > K^+$. Similar results have been obtained for $(H_2O \cdots M^+)$-systems [12]. A survey [13] of the environment of metal ions in crystalline hydrates, based on results of 40 neutron-diffraction studies has shown that metal ions in general tend to lie close to the bisecting plane of coordinated water molecules with a bimodal distribution of colatitudes, a main peak at $\theta \sim 90°$ and a minor one at $\theta \sim 45°$[5]).

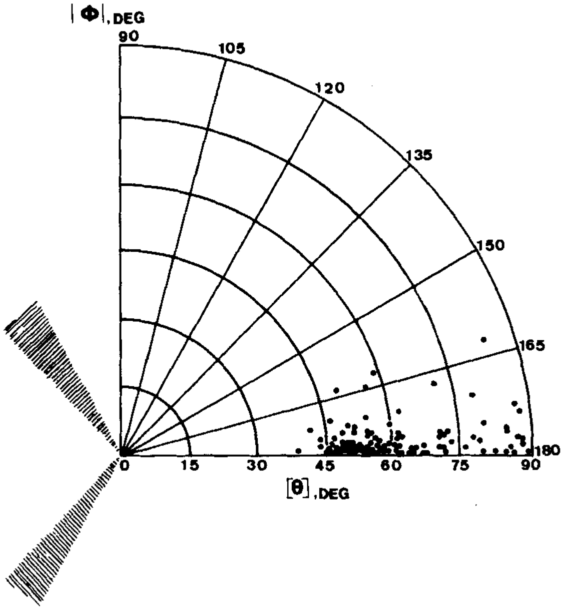

Fig. 4. *As* Figure 2 *but for group IIA cations*

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[5]) Note, however, that although the equilibrium structure of the hydronium ion (H_3O^+) is still controversial [14], a pyramidal structure is indicated both by neutron diffraction analysis [15] and by calculation [14].

Our new results are not necessarily in conflict with the theoretical conclusions [11]. The larger group IA cations with relatively small interaction energies are found only in large polyfunctional host molecules with convergent binding sites. The conformations available to such molecules are severely restricted. Points that are roughly equidistant from the binding sites will not in general lie close to the C–O–C bisectors, so an enclosed cation will have to fit as best it can into the cavity provided by the host. Thus the apparent inclination of these cations for the tetrahedral lone pair directions of the O-atoms need not represent an intrinsic preference of the ions but rather the result of a compromise among several factors.

On the other hand, the Li^+ cations in our survey are complexed mainly with mono-ethers[6]) and there seems no reason to doubt that the preference for coordination along the C–O–C bisector is intrinsic for this ion. This suggests that a polyfunctional ether with an appropriate geometry should complex very efficiently with Li^+ cations. For optimal complexation with Li^+, we expect that the ligand cavity should not only have a radius (M · · · O distance) of *ca.* 2 Å but should also have the C–O–C bisectors of the ether groups converging on a point. This has recently been substantiated by the synthesis of macrocyclic polyanisoles and related molecules (spherands) with remarkably large complexation constants for Li^+ (in some cases even greater than for Na^+) [17]. The recently described structure of the most stable of these Li^+ complexes [18] ($-\Delta G^\circ > 22$ kcal mol^{-1}) [19] shows that the cation sits at the centre of an octahedral cavity, nearly along the bisector of six equivalent C–O–C units ($\theta = 86°$, $\varphi = 174°$). The Li · · · O distance is 2.14 Å, which is slightly on the long side (compare *Fig. 1*); the lengthening is due to the change from four- to six-coordination.

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[6]) A recent monograph on the structures of natural and synthetic ionophores [16] mentions only two crystal structures of ionophores complexed with Li^+.

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