line complexes, since most of the water molecules in these crystal structures are bound to two or more species in addition to the Ca ion. The apparent relationship between θ and Ca--O distance (Fig. 9) indicates that the shorter (*i.e.* stronger) calcium–water interactions are those with configurations where the Ca ion is more nearly colinear with the water dipole. The segregation of Class 1 and Class 2 examples in Fig. 9 lends support to this interpretation: Class 1 examples, which have water molecules that are subject to fewer competing interactions than those from Class 2 examples, show shorter Ca--O distances and lower θ values. This trend, when extrapolated to the isolated system, suggests a preferred configuration which is consistent with that predicted by simple electrostatic considerations.

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* See also Table 1.

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On the Geometry of Urea–Cation Bonding in Crystalline Urea Adducts

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Abstract

A survey of 26 crystal structures of urea adducts has revealed that there are systematic features in urea–cation bonding. It has been found that in complexes with monovalent cations urea coordinates to two cations. In complexes with divalent cations urea shows a preference to bond to only one cation, in the plane of the molecule, with an M^{2+}—C=O angle of about 130–140°, rather than along the dipole-moment direction. The preferred geometry is the same for transition- and non-transition-metal cations.

Introduction

A systematic survey of crystalline urea adducts formed with a large variety of inorganic salts was undertaken as a part of a study of cation bonding to the amide group. The rationale behind this kind of study is that much information of chemical interest is imbedded in crystal structures, which represent minimum-energy arrangements. Little information about intermolecular interactions can be extracted from a single structure alone; however, certain trends are apparent if sufficient structural data are taken into account. Although a great deal is known about how cations bond to ligands, relatively little work has been carried out to determine how a ligand bonds to cations.

The aim of this work was to establish the preferred geometry of urea–cation bonding. The structural relationships in cation–urea complexes can be of some relevance in a discussion of interactions between cations and amides or peptide groups, especially in the *cis*-planar conformation which is often found in oligopeptides, which act as ion carriers (Karle, 1975).

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Table 1. *Geometry of urea–cation bonding*

All data are given in the same format but do not always refer to the actual accuracy.

M–urea oxygen	φ (°)	θ (°)	∠M–O=C (°)	M–O (Å)	M–urea plane (Å)	Other ligands to O atom	Compound, discrepancy factor	Reference
Li–O	14·4	152·7	149·4	1·882	0·467	Li′	LiI.urea, $R = 0·139$	Verbist, Meulemans, Piret & Van Meerssche (1970)
Li′–O	45·5	135·9	120·2	1·946	−1·388	Li		
Na–O	51·0	146·4	121·6	2·465	1·915	Na′	$\mathrm{NaCl.H_2O.urea}$, $R = 0·140$	Palm & MacGillavry (1963)
Na′–O	3·4	124·4	124·3	2·496	−0·149	Na		
Mg–O(1)	1·8	135·8	135·8	2·054	0·061	–	$\mathrm{[Mg(urea)_6]Br_2.4urea}$, $R = 0·049$	Lebioda, Stadnicka & Sliwinski (1979)
–O(2)	18·0	136·6	133·7	2·066	0·632	–		
–O(3)	0·8	133·2	133·2	2·084	0·031	One H		
Mg–O(1)	8·4	139·6	138·9	2·050	0·301	One H	$\mathrm{[Mg(urea)_4(H_2O)_2]Br_2}$ $R = 0·029$	Lebioda & Lewinski (1979)
–O(2)	5·3	139·2	138·9	2·078	0·191	One H		
Ca–O(7)	17·1	143·2	139·9	2·351	0·692	–	$\mathrm{Ca(NO_3)_2.3H_2O.urea}$, $R = 0·128$	Lebioda (1972)
Ca–O(4)	3·3	144·6	143·5	2·307	0·133	One H	$\mathrm{Ca(NO_3)_2.4urea}$, $R = 0·057$	Lebioda (1977)
–O(5)	5·8	151·3	150·8	2·299	0·233	One H		
Ca–O(1)	1·1	137·0	137·0	2·316	0·046	–	$\mathrm{[Ca(urea)_6]Br_2}$, $R = 0·043$	Lebioda & Stadnicka (1977)
–O(2)	1·9	142·2	142·2	2·327	0·079	One H		
–O(3)	48·5	157·7	127·8	2·331	1·745	One H		
Ca–O(3)	10·8	137·5	136·4	2·379	0·447	One H	$\mathrm{CaSO_4.4urea}$, $R = 0·059$	de Villiers & Boeyens (1975)
–O(4)	38·3	147·8	131·6	2·365	1·466	One H		
–O(5)	4·1	139·3	139·1	2·349	0·169	One H		
–O(6)	1·7	135·2	135·2	2·365	0·070	One H		
Cu–O(9)	0·3	132·8	132·8	2·155	0·011	One H	$\mathrm{Cu_2(C_6H_5CH_2COO)_4}$.-2urea, $R = 0·035$	Ivanov & Simonov (1976)
–O(10)	6·0	134·0	133·7	2·186	0·221	One H		
Cu–O(M)	7·2	136·8	136·3	2·102	0·241	One H	$\mathrm{Cu_2(CH_2ClCOO)_4}$.-2urea, $R = 0·040$	Ivanov & Simonov (1976)
Cu–O(9)	3·5	130·5	130·4	2·118	0·132	One H	$\mathrm{Cu_2(CH_2ClCOO)_{1·75}}$-$\mathrm{(CH_3COO)_{2·25}}$.2urea, $R = 0·083$	Ivanov & Simonov (1976)
–O(10)	43·0	148·5	128·6	2·116	1·451	–		
Cu–O(5)	0·6	132·4	132·4	2·114	0·021	One H	$\mathrm{Cu(HCOO)_2.urea}$, $R = 0·089$	Yawney & Doedens (1970)
Cu–O(3)	15·2	136·7	134·6	1·936	0·527	One H	$\mathrm{CuSO_4.3urea}$ $R = 0·032$	Kuskov, Kurkutova, Treushnikov, Ionov, Ilyukin & Belov (1977)
–O(4)	24·2	125·3	121·8	2·608	1·172	Cu		
Co–O(3)	5·9	134·6	134·3	2·090	0·215	One H	$\mathrm{[Co(urea)_4(H_2O)_2](NO_3)_2}$, $R = 0·192$	Rau & Kurkutova (1971)
–O(2)	4·4	136·9	136·7	2·093	0·159	–		
Co–O(1)	4·7	132·2	132·0	2·082	0·172	One H	$\mathrm{[Co(urea)_6](NO_3)_2.4urea}$, $R = 0·168$	Kurkutova & Rau (1972)
–O(2)	0·2	132·1	132·1	2·067	0·007	One H		
–O(3)	24·5	131·4	127·0	2·062	0·855	One H		
Co–O(1)	46·2	154·6	128·7	2·055	1·484	–	$\mathrm{[Co(urea)_4](NO_3)_2}$, $R = 0·075$	Gentile *et al.* (1974)
–O(2)	2·4	133·6	133·6	2·100	0·089	–		
Co–O(1)	3·3	129·2	129·1	2·108	0·121	–	$\mathrm{[Co(urea)_6]SO_4.H_2O}$ $R = 0·083$	Ponomarenko, Kurkutova, Porai-Koshits & Soulaimankulov (1977)
–O(2)	12·0	135·9	134·6	2·088	0·435	–		
–O(3)	9·0	133·7	133·0	2·101	0·330	–		
–O(4)	14·2	135·9	134·1	2·100	0·514	–		
–O(5)	17·5	131·2	128·9	2·129	0·641	–		
–O(6)	0·3	126·6	126·6	2·146	0·012	–		
Mn–O(1)	14·1	137·0	135·2	2·076	0·506	–	$\mathrm{Mn(CNS)_2.4urea}$, $R = 0·177$	Tsintsadze, Tsintsadze & Oberladze (1974)
–O(2)	10·4	134·5	133·6	2·001	0·362	–		
Zn–O(1)	18·2	135·0	132·2	2·147	0·672	Two H	$\mathrm{[Zn(urea)_6](NO_3)_2}$, $R = 0·45$	van de Giesen & Stam (1972)
–O(2)	1·3	132·8	132·8	2·073	0·046	One H		
–O(3)	31·4	138·4	129·7	2·091	1·089	One H		
U–O(1)	17·9	140·9	137·6	2·462	0·759	–	$\mathrm{[UO_2OH(urea)_3]_2I_4}$, $R = 0·108$	Mikhailov, Kuznietzov & Kovaleva (1968)
–O(5)	1·4	144·8	144·8	2·336	0·058	–		
–O(6)	0·1	135·5	135·5	2·335	0·005	–		
U–O(1)	10·1	146·1	144·8	2·354	0·416	–	$\mathrm{[UO_2F_2(urea)_2]_2}$, $R = 0·103$	Mikhailov, Ivanov, Orlova, Podniebiesnikova & Kuznietzov (1976)
–O(2)	6·9	139·5	139·0	2·359	0·286	–		

Table 1 (*cont.*)

U–O(1)	24·0	145·2	138·6	2·378	0·968	One H	$[UO_2(urea)_4(H_2O)](NO_3)_2$, $R = 0{\cdot}047$	Dalley, Mueller & Simonsen (1972)
–O(2)	4·1	135·6	135·6	2·385	0·170	One H		
–O(3)	28·7	142·1	133·8	2·341	1·126	–		
–O(4)	10·3	140·7	139·6	2·337	0·417	–		
Al–O	15·2	137·8	135·6	1·895	0·497	One H	$[Al(urea)_6](ClO_4)_3$, $R = 0{\cdot}082$	Mooy *et al.* (1976)
Ce–O(1)	0·5	176·2	176·2	2·317	0·019	–	$Ce_2(SO_4)_3.2urea.5H_2O$ $R = 0{\cdot}078$	Ponomarenko *et al.* (1976)
Ce–O(2)	5·1	154·1	153·6	2·322	0·208	–		
Sc–O(1)	9·8	148·6	147·2	2·077	0·352	–	$[Sc(urea)_4(NO_3)_2]NO_3$ $R = 0{\cdot}028$	Kuskov *et al.* (1978*a*)
–O(2)	1·3	138·3	138·3	2·125	0·050	–		
–O(3)	15·3	145·8	142·9	2·094	0·552	–		
–O(4)	5·0	137·0	136·8	2·134	0·134	–		
La–O(1)	14·7	169·5	162·0	2·461	0·625	–	$[La(CH_3COO)_3(urea)].urea$, $R = 0{\cdot}048$	Kuskov *et al.* (1978*b*)

The urea molecule is small and planar (Pryor & Sanger, 1970) with a dipole moment of $1{\cdot}54 \times 10^{-29}$ C m (McClellan, 1963). On the difference electron density maps there are clear maxima corresponding to the lone pairs of electrons on the sp^2-hybridized O atom (Scheringer, Mullen, Hellner, Hase, Schulte & Schweig, 1978). The direction of the dipole moment is along the bisectrix of the lone pairs.

70 symmetry-independent urea molecules in 26 crystal structures cited in Vols. 1–9 of *Molecular Structures and Dimensions* (1970–1978) or in *Chem. Abstr.* Vols. 88–89 are reviewed here. NH_4^+ complexes were omitted and isomorphic structures are treated as a single observation.

Cation–urea bonding

All urea molecules forming complexes in the analysed structures have the cation bonded to the O atom of the carbonyl group. An unusual situation is encountered in the structure of $[Co(urea)_4](NO_3)_2$, where one of the molecules acts as a bidentate ligand and is coordinated to two cations through the O atom and one of the N atoms (Gentile, White & Haddad, 1974). This arrangement, however, is not very stable as the crystals are hygroscopic and in the presence of H_2O change to $[Co(urea)_4(H_2O)_2](NO_3)_2$, where all the urea molecules are monodentate (Rau & Kurkutova, 1971).

In adducts with monovalent cations (Na^+, Li^+, NH_4^+), whose structures are known, urea molecules coordinate two cations. The same situation is found in the structure of $CuSO_4.3urea$ where an axial urea ligand with a very long O—Cu^{2+} distance of 2·612 Å is shared by two Cu^{2+} cations. No further generalization can be made because of the limited number of observations, especially as NH_4^+ complexes should be treated separately.

Most of the structures surveyed are urea complexes with divalent cations. Their bonding geometries were analysed in terms of the angles φ and θ used in the studies of cation–amide interactions (Fig. 1). φ is the angle between the M^{2+}—O bond and the plane of the urea molecule, θ is the angle between the C=O bond and the projection of the M^{2+}—O bond on the urea plane. The C_{2v} symmetry of the urea molecule restricts the angles to ranges $0 < \varphi < 90°$ and $0 < \theta < 180°$. The bond lengths and angles are summarized in Table 1.

Fig. 2 presents histograms of the distributions of the angles φ and θ. The joint distribution is shown in Fig. 3 in the form of a stereographic projection of M^{2+}—O bonds on the plane of the urea molecule. From the histogram of the φ angles it is apparent that the cation tends to lie in the plane of the urea molecule. LCAO-SCF calculations on cation—amide bonding in (Na^+,K^+)-*N*-methylacetamide (Pullman, 1974) also show an energy minimum for the coplanar arrangement. The distribution of θ angles shown in Fig. 2(*b*)

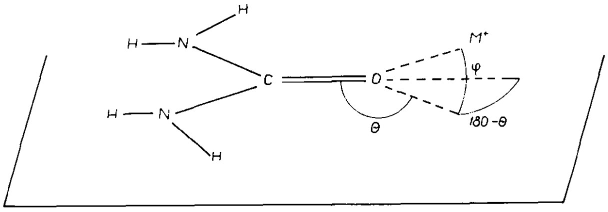

Fig. 1. Urea molecule showing angles φ and θ.

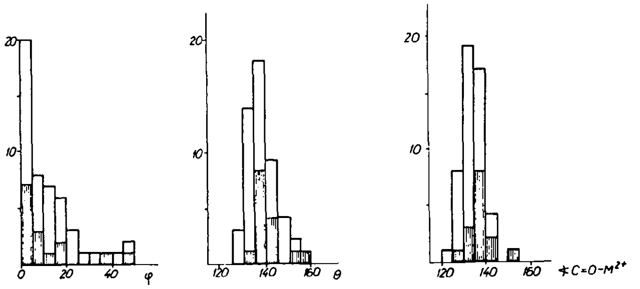

Fig. 2. Histograms of angles (*a*) $\varphi(\sigma = 17°)$, (*b*) θ, mean 138 (7)°, (*c*) C=O—M^{2+}, mean 135 (5)° for M^{2+}—urea complexes. Hatched areas correspond to alkali-earth cations.

has a clear maximum at 135–140°. This is different from that expected from the above-quoted calculations which showed only a very shallow minimum, and is also different from the approximate *ab initio* calculations on the formamide adduct $Li(HCONH_2)_2$ (Rode, 1976) which gave a minimum along the C=O bond. The results for these amide and urea complexes are comparable because the electron distribution at the O atom and the direction of the dipole moment ($1{\cdot}34\times10^{-29}$ C m) (Coppens, Row, Hansen, Leung & Stevens, 1978) are similar. It seems more probable that the discrepancy between the observed tendency and the theoretical results is due to the approximation of the calculations rather than to differences between the formamide and urea molecules (Gołebiewski, 1978).

The molecular electrostatic potential of the urea (Panteleiev & Lipovskij, 1976), though indicating correctly the geometry of a protonated molecule, does not show a minimum at a distance greater than 1·5 Å from the O atom.

There is only a small dependence of the $C{=}O{-}M^{2+}$ angle on the $O{-}M^{2+}$ distance, as shown in Fig. 4. This makes it possible to state the results of the survey in terms of the φ and θ angles only.

It can be concluded that the urea molecule shows a strong preference to bond to divalent cations along the directions of the lone-pair electrons of the sp^2-hybridized O atom rather than along the direction of the dipole moment. In fact, the latter bonding situation, while the most frequent in hydrates (Ferraris & Franchini-Angela, 1972), has not been found in divalent cation–urea complexes. There is no difference between the geometries of bonding for transition-metal and alkaline-earth cations.

The structures of urea adducts with trivalent cations determined for isomorphic compounds of the type $[M^{3+}(\text{urea})_6]X_3^-$ (Durski, 1978) are treated as a single observation based on the accurate data obtained for $[Al(\text{urea})_6](ClO_4)_3$ (Mooy, Krieger, Hejednjk & Stam, 1976). The geometry of the urea–cation bonding in these compounds and in $[Sc(NO_3)_2(\text{urea})_4]NO_3$ (Kuskov, Treushnikov, Soboleva, Ilyukin & Belov, 1978*a*) is similar to that in divalent-metal complexes. However, the geometry of the urea bonding in the Ce^{3+} adduct (Ponomarenko, Kurkutova, Porai-Koshits, Aslanov & Sulaimankulov, 1976) where the θ angles are 176 and 151°, and that of the La^{3+} adduct (Kuskov, Treushnikov, Soboleva, Ilyukin & Belov, 1978*b*) where θ is 170°, indicates that for trivalent cations bonding along the dipole-moment direction can occur.

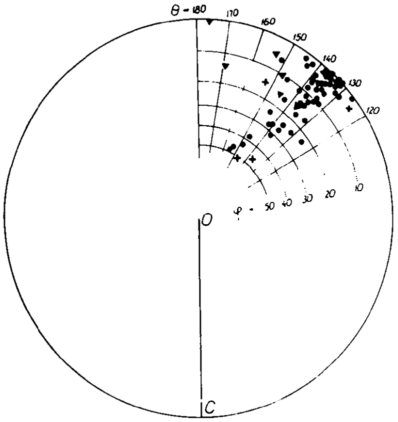

Fig. 3. Distribution of cations coordinated by urea molecules shown as a stereographic projection on the urea plane. Symbols: crosses M^+, circles M^{2+}, and triangles M^{3+} cations.

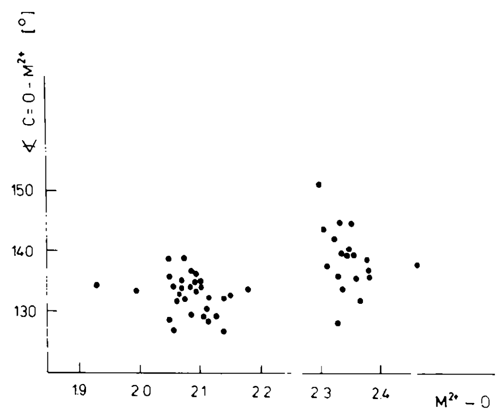

Fig. 4. Angle $C{=}O{-}M^{2+}$ as a function of the $O{-}M^{2+}$ distance.

In all the structures discussed distortion of the urea molecule is small with the exception of the bidentate molecule in $[Co(\text{urea})_4](NO_3)_2$. In the structures with e.s.d.'s in the bond lengths less than 0·01 Å it was found that average ⟨C=O⟩ and ⟨C–N⟩ lengths are 1·250 (2) and 1·339 (5) Å for Mg^{2+} complexes, 1·251 (2) and 1·335 (2) Å for Ca^{2+} complexes, 1·258 (3) and 1·336 (4) Å for Zn^{2+} complexes, and 1·264 (4) and 1·333 (4) Å for Sc^{3+} complexes, where the averages are based on five, nine, three and four observations respectively. The differences are insignificant apart from the expected influence of the cation charge on the C=O bond length.

A systematic deformation observed in these structures is that the O=C–N angles are slightly greater on the cation side than on the side opposite the cation; the average values are 121·8 (1) and 120·6 (2)° for M^{2+} cations, and 121·8 (3) and 119·0 (1)° for Sc^{3+}, respectively. The bonding electron density measured in $CuSO_4.3\text{urea}$ (Treushnikov, Kuskov & Belov, 1977) shows the expected shift in the lone-pair region towards the cation. These results are only qualitative, but, in agreement with the results of the survey, they underline the role of the polarization of the urea molecule upon the interaction with cations.

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The Structures of High-Spin (298, 150 K) and Low-Spin (90 K) States and the Spin Phase-Transition Mechanism of a Spin Crossover Complex; Tris(α-picolylamine)iron(II) Chloride–Ethanol

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Abstract

The crystal structures of $[Fe(\alpha\text{-pic})_3]Cl_2.EtOH$, $[Fe(C_6H_8N_2)_3]Cl_2.C_2H_6O$, $[C_{18}H_{24}FeN_6]^{2+}.2Cl^-.C_2H_6O$, in its high-spin state (298, 150 K) and low-spin state (90 K) were determined by X-ray diffraction. The space group is $P2_1/c$, $Z = 4$, over the entire temperature range. At room temperature, $a = 11{\cdot}831$ (3), $b = 22{\cdot}021$ (4), $c = 11{\cdot}551$ (3) Å, $\beta = 124{\cdot}28$ (2)°, $U = 2485{\cdot}2$ (11) Å^3, $D_m = 1{\cdot}33$, $D_c = 1{\cdot}329$ Mg m^{-3} and at

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