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Acute-Angled Attachment of Cations in Main Group Ion−Molecule Adducts

Eric Magnusson

*School of Chemistry, University College (ADFA), University of New South Wales,
Canberra ACT 2600, Australia*

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Adducts of main group cations with neutral and anionic second row species (H_2S, SH^-, and $PH_2{}^-$) are calculated to be severely bent, the inclination angle often being less than 90°. The corresponding adducts of H_2O, OH^-, and $NH_2{}^-$ favor the aligned conformation (inclination angle 180°). Analysis of the wave functions of Li^+, Na^+, K^+, Be^{2+}, Mg^{2+}, and Ca^{2+} adducts shows that a preference for off-axis binding arises when the combined effects of covalency and the electrostatic ion−quadrupole term outweigh the usually dominant ion−dipole binding. Adducts of the radical cations Be^+, Mg^+, and Ca^+ display the same conformational preferences as do the compounds of closed shell cations.

Gas-phase ion−molecule adducts are being vigorously studied in many laboratories, some fairly recently by mass spectrometric methods,[1] others over a longer period by spectroscopic methods[2−4] prompting computational studies to explain the experimental results. This report is an analysis of single ligand adducts formed by Li^+, Na^+, K^+, Be^{2+}, Mg^{2+}, and Ca^{2+} cations together with the radical adducts formed by Be^+, Mg^+, and Ca^+. These compounds possess parallels with ligand conformations in main group and transition metal complex ions[5,6] in crystals and in solution.[7,8] The surprising observation is the severely bent structures of many adducts. For third row ligands such as H_2S and SH^- the cation−ligand bond is often inclined by more than 90° from the dipole axis of the ligand, in contrast to the "in-line" conformations preferred by H_2O and OH^-. This paper attempts a rationalization of these results, at a moderate computational level (MP2/6-311+G(d,p)) and by the use of readily accessible tools. The results are expected to be adequate for characterizing the molecules and rationalizing the unusual acute-angled structures but are, of course, less suitable for predicting spectroscopic parameters.

Off-axis binding is not the result expected if the attachment of cations to small ligands is dominated by charge−dipole attraction. For this reason quadrupole effects were investigated as a possible explanation for the highly "inclined" geometries found for H-bonded dimers formed by H_2S and other third row acceptors.[9] Using their "multipole expansion" method, Buckingham and Fowler and others[10,11] have been able to accurately predict the geometries of van der Waals dimers, including cases with strongly inclined conformations. However, purely electrostatic methods are not applicable if the bonding is partly covalent and it then becomes necessary to inspect the full electronic wave function of the adduct.

Computational Method

Hartree−Fock and MP2 level calculations (frozen core approximation) were made to obtain binding energies and geometries of the adducts using the Gaussian 98 package.[12] Most results are new, but those of H_2O and H_2S adducts of the closed shell cations were reported previously.[13] The 6-311+G(d,p) basis set was used for the ligands and for Li, Mg, and Na; for K and Ca an 8s 6p contraction of the Wachters 14s 11p basis set was used in each case[14] with the addition of a single d function ($z_d = 0.039$ and 0.050 for K and Ca, respectively). Check calculations of the counterpoise correction for basis set superposition error showed that the conclusions drawn here would not be affected if it were neglected. As a test of the reliability of the computed geometries, inclination angles were recalculated on a group of compounds with rather shallow bending potentials, the six adducts of the SH^- ion formed by the closed shell cations. At the lower level used in G2 theory [MP2/6-31G(d)], the six inclination angles differ from the results in the present work by an average of only 2.5°. These differences would probably converge to much smaller values at successively higher computational levels.

As is well-known, calculations of polarization moments of molecules at all but the very highest computational levels usually conflict with experiment, raising the question of whether complexes dependent for their existence on ion−multipole interactions will show similar discrepancies in other properties. As shown earlier, the anticipated errors do not eventuate and "changes in the wave function sufficient to alter the dipole moment mostly seem to occur in parts of the molecule which do not affect attachment of the cation".[15] Experimental values of the dipole moments of the neutral ligands are included in Table 7.

Covalent contributions to cation−ligand bond energies were estimated by a method introduced by Horn and Ahlrichs[16] and modified by the author.[13] Energies were obtained at the MP2-optimized geometries with an effective core potential (ECP) basis for the metal (the Lanl2DZ basis[17−19] or the CEP-31G basis[20]) plus a conventional basis for the metal valence electrons. The 6-311+G(d,p) basis was retained for the ligand atoms. The results follow the original MP2//6-311+G(d,p) binding energies quite closely, the average deviations for the Li^+ adducts listed in Table 6 being 0.007 hartree (neutral ligands) and 0.013 hartree (anionic ligands). "Truncated basis set" calculations were then performed at the same geometry, removing the functions required for any covalent binding (the metal valence shell s and p functions). The cation is thus represented solely by the ECP potential function and is capable of closed shell interactions

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TABLE 1: MP2(FC) Energies and Optimized Geometries of Adducts of Li^+, Na^+, K^+, Mg^{2+}, and Ca^{2+} Cations with Anions[a,b]

compound	energy (hartrees)	r(M−L) (pm)	r(L−H) (pm)	A(MLX) (deg)
$LiNH_2$	−63.284 48	175.9	101.7	180.0
$LiOH$	−83.175 90	160.7	95.2	180.0
$LiPH_2$	−349.489 63	232.2	142.1	86.4
$LiSH$	−405.757 88	214.5	134.0	91.4
$NaNH_2$	−217.664 29	212.5	101.8	179.4
$NaOH$	−237.551 70	198.0	95.4	177.8
$NaPH_2$	−503.885 66	264.8	142.1	86.5
$NaSH$	−560.148 38	249.2	133.9	92.2
KNH_2	−654.990 88	253.7	102.2	180.0
KOH	−674.882 71	235.1	95.6	179.2
KPH_2	−941.318 46	303.7	140.7	98.5
KSH	−997.577 43	299.7	133.7	103.2
$MgNH_2^+$	−255.190 85	188.9	101.8	143.9
$MgOH^+$	−274.061 62	174.1	95.4	160.6
$MgPH_2^+$	−541.408 98	242.5	141.9	84.2
$MgSH^+$	−1074.809 41	271.5	133.9	96.5
$CaNH_2^+$	−732.355 06	224.6	101.5	179.1
$CaOH^+$	−752.192 28	209.9	96.5	179.9
$CaPH_2^+$	−1018.560 65	292.4	141.7	90.3
$CaSH^+$	−1074.764 28	271.3	134.6	99.7

[a] Energies are at UMP2(FC)//6-311+G** level, geometry-optimized and exclusive of the zero-point contribution. [b] A(MLX) is the attachment angle, LX being the dipole axis of the ligand.

TABLE 2: Energies and Geometries of Ground and Excited State Radical Adducts of the Be^+, Mg^+, and Ca^+ Cations[a,b]

compound	out shell	energy (hartrees)	r(M−L) (pm)	r(L−H) (pm)	A(MLX) (deg)
$BeNH_2$	$2s^1$	−70.474 51	151.0	101.1	165.2
BeH_2O^+	$2s^1$	−90.648 67	158.7	97.3	180.0
$BeOH$	$2s^1$	−90.357 41	141.9	95.4	133.8
$BePH_2^+$	$2s^1$	−356.646 89	206.2	141.7	87.9
BeH_2S^+	$2s^1$	−413.181 91	211.0	134.6	89.6
$BeSH$	$2s^1$	−412.914 54	190.5	134.2	88.7
$MgNH_2$	$3s^1$	−255.447 28	193.1	101.4	180.0
MgH_2O^+	$3s^1$	−275.689 89	209.2	96.7	180.0
$MgOH$	$3s^1$	−275.330 97	180.6	95.0	180.0
$MgPH_2$	$3s^1$	−541.649 30	248.9	141.9	85.5
MgH_2S^+	$3s^1$	−598.245 78	265.8	133.9	106.4
$MgSH$	$3s^1$	−597.911 40	232.8	134.0	90.4
$CaNH_2$	$4s^1$	732.568 63	232.0	101.8	180.0
	$4p^1$	732.484 05	229.9	101.5	180.0
CaH_2O^+	$4s^1$	752.844 82	303.9	97.8	180.0
	$4p^1$	752.752 46	275.3	97.7	180.0
$CaOH$	$4s^1$	752.458 47	219.4	95.3	180.0
	$4p^1$	752.253 80	288.5	97.1	133.5
$CaPH_2$	$4s^1$	1018.769 781	299.5	141.8	95.1
CaH_2S^+	$4s^1$	1075.407 09	331.0	133.6	116.7
	$4p^1$	1075.315 83	310.0	133.7	108.3
$CaSH$	$4s^1$	1075.033 10	280.5	133.8	97.7
	$4p^1$	1074.954 43	277.1	133.7	96.7

[a ,b] See Table 1.

TABLE 3: Calculated Metal−Ligand Inclination Angles and Estimates of Covalence in Adducts of Main Group Cations with One Neutral Ligand[a−c]

		ligand	
cation		H_2O	H_2S
H^+	full basis	132.4°	120.4°
Li^+	full basis	180.0°	109.3°
	truncated basis	180.0°	120.6°
	covalence (NRT bond order)	18% (0.000)	31% (0.001)
	AIM bond order	0.086	
Be^+	full basis	180.0°	89.6°
	(bond order)	(0.001)	(0.341)
Be^{2+}	full basis	0.180°	98.8°
	truncated basis	180.0°	104.6°
	covalence (NRT bond order)	38% (0.001)	58% (0.316)
	AIM bond order	0.220	
Na^+	full basis	180.0°	138.5°
	truncated basis	180.0°	180.0°
	covalence (NRT bond order)	6% (0.000)	21% (0.000)
	AIM bond order	0.087	0.113
K^+	full basis	180.0°	137.4°
	truncated basis	180.0°	180.0°
	covalence (NRT bond order)	2% (0.000)	4% (0.004)
Mg^+	full basis	180.0°	106.4°
	(bond order)	(0.001)	(0.005)
Mg^{2+}	full basis	180.0°	104.1°
	truncated basis	180.0°	120.3°
	covalence (NRT bond order)	15% (0.000)	49% (0.194)
	AIM bond order	0.171	
Ca^+	full basis	180.0°	166.7°
	(NRT bond order)	(0.000)	(0.001)
Ca^{2+}	full basis	180.0°	87.9°
	truncated basis	180.0°	122.8°
	covalence (NRT bond order)	10% (0.000)	11% (0.003)

[a] The "inclination angle" is the angle between the metal−ligand bond and the dipole axis of the ligand. [b] "Covalence" was estimated from truncated basis calculations (see text); for natural resonance theory (NRT) bond order and atoms-in-molecules (AIM) bond order see text. [c] Full geometries of adducts of neutrals are given in ref 13.

only. The binding energy so obtained is purely electrostatic, and to a first approximation, the difference between it and the regular ECP basis binding energy is the covalent contribution to binding.

Methods for obtaining quantitative estimates of covalent/electrostatic contributions to bonding are hard to find and often controversial. For the truncated basis method, the most probable source of error is relaxation of the ligand electrons in the potential field of the cation to slightly compensate for the loss of ligand-to-metal donation and an overestimation of the electrostatic part of the binding energy. The original method[16] was vulnerable also to incomplete core−valence separation in the metal basis set, but this separation is, of course, unequivocal when an ECP basis is used for the metal. In view of this, and the fact that covalence is likely to be underestimated by the method, the cautious use of the method to estimate covalent contributions to binding energies seems justified, especially when the perturbation (basis set truncation) is small.

Electron density contributions to covalence are available from "natural resonance theory"[21] and, where calculable, from AIM theory.[22] Although both are called "bond orders", the two measures are derived differently and do not necessarily follow the same trends.

Computational experiments can be carried out with the "truncated basis" to observe what happens when covalence is eliminated from cation−ligand interactions. The effects on metal−ligand bond length and bond inclination (see the entries in Tables 3, 4, and 6) are often quite large, especially for the adducts of sulfur and phosphorus ligands, the compounds displaying the larger covalent contributions to energy.

Results

The inclination angles in Tables 3 and 4 (cations at optimum geometries) and in Table 5 (long-range interactions) reveal that "off-axis binding" is a very common result. Adducts formed by the second row ligands usually have almost "perpendicular" conformations (inclination angle $\phi = 90°$) and some are

TABLE 4: Calculated Metal−Ligand Inclination Angles and Estimates of Covalence in Single Ligand Adducts of Main Group Cations with Anions[a]

		ligand			
cation		NH_2^-	OH^-	PH_2^-	SH^-
H^+	full basis	107.4°	103.5°	96.3°	92.1°
	truncated basis	90.2°	102.0°	86.4°	92.3°
Li^+	full basis	180.0°	180.0°	86.4°	91.4°
	truncated basis	180.0°	180.0°	101.9°	144.5°
	covalence (NRT bond order)	16% (−)	12% (−)	21% (0.189)	18% (0.076)
	AIM bond order		0.199		
Be^+	full basis	165.2°	133.8°	87.9°	88.7°
	(NRT bond order)	(0.057)	(0.042)		(0.135)
Be^{2+}	full basis	180°	180°	81.3°	87.9°
	truncated basis	180°	146.1°	94.0°	102.4°
	covalence (NRT bond order)	22% (0.099)	21% (0.042)	28% (0.709)	30% (0.348)
	AIM bond order	0.403	0.393		0.4814
Na^+	full basis	177.8°	179.4°	86.5°	92.2°
	truncated basis	180.0°	180.0°	180.0°	180.0°
	covalence (NRT bond order)	8% (0.021)	4% (0.000)	19% (0.241)	13% (0.093)
	AIM bond order	0.150	0.262	0.384	0.298
K^+	full basis	180.0°	179.2°	98.5°	103.2°
	truncated basis	180.0°	180.0°	180.0°	180.0°
	covalence (NRT bond order)	<1% (−)	<1% (0.003)	3% (−)	4% (−)
Mg^+	full basis	180.0°	177.2°	85.5°	90.4°
	(NRT bond order)	(0.061)	(0.024)	(0.262)	(0.135)
Mg^{2+}	full basis	143.9°	160.6°	84.2°	90.0°
	truncated basis	180°	180.0°	126.3°	128.3°
	covalence (NRT bond order)	15% (0.139)	9% (0.024)	26% (0.293)	21% (0.386)
	AIM bond order	0.441	0.330		
Ca^+	full basis	180.0°	180.0°	95.1°	97.7°
	(NRT bond order)	(0.023)	(0.011)	(0.178)	(0.062)
Ca^{2+}	full basis	179.1°	180.0°	90.3°	96.5°
	truncated basis	180°	180.0°	148.6°	150.1°
	covalence (NRT bond order)	1% (0.051)	4% (0.006)	9% (0.531)	15% (0.224)

[a] See footnotes to Table 3.

TABLE 5: Calculated Metal−Ligand Inclination Angles in Single Ligand Adducts at Optimum and Extended Cation−Ligand Separations (r_{ML})[a]

	r_{ML} (r_{opt})			
		200 pm	300 pm	400 pm
H_2O				
$H^+\cdots OH_2$	132.4° (97.8 pm)	109.6°	115.8°	
$Li^+\cdots OH_2$	180° at all separations			
$Mg^{2+}\cdots OH_2$	180° at all separations			
OH^-				
$H^+\cdots OH^-$	103.5° (95.9 pm)	88.1°	77.3°	
$Li^+\cdots OH^-$	180.0° (160.64 pm)	123.1°	102.1°	
$Mg^{2+}\cdots OH^-$	160.6° (174.1 pm)	115.7°		
NH_2^-				
$H^+\cdots NH_2^-$	120.3° (101.3 pm)	90.8°	88.6°	
$Li^+\cdots NH_2^-$	180.0° (175.9 pm)	177.8°	105.6°	
$Mg^{2+}\cdots NH_2^-$	143.9° (188.9 pm)	130.7°		
H_2S				
$H^+\cdots SH_2$	97.4° (134.7 pm)	93.7°	88.3°	79.6°
$Li^+\cdots SH_2$	109.3° (240.1 pm)		110.9°	119.4°
$Mg^{2+}\cdots SH_2$	104.1° (246.1 pm)		102.7°	
SH^-				
$H^+\cdots SH^-$	92.1° (133.4 pm)	88.9°	81.3°	147.7°
$Li^+\cdots SH^-$	91.4° (214.5 pm)		91.0°	91.0°
$Mg^{2+}\cdots SH^-$	90.0° (224.3 pm)		89.6°	
PH_2^-				
$H^+\cdots PH_2^-$	96.3° (140.9 pm)	91.7°	84.6°	37.6°
$Li^+\cdots PH_2^-$	86.4° (232.2 pm)		90.8°	87.9°
$Mg^{2+}\cdots PH_2^-$	84.2° (242.5 pm)		87.5°	

[a] The “inclination angle” is the angle between the metal−ligand bond and the major axis of the ligand; the optimum metal−ligand bond length is given in parentheses.

acute-angled ($\phi < 90°$). “Aligned” means that $\phi \approx 180°$. When $\phi < 180°$ for the most stable conformation, it is called “inclined”.

Experimental structural data for adducts of these cations are scarce except for the alkali metal hydroxides[23,24] and the alkaline earth metal hydroxide and sulfhydride radicals (MgOH, CaOH, ScOH, BaOH, and CaSH)[2−4,25] which have attracted major spectroscopic attention. The spectroscopic data, with which computationally determined geometries are consistent[26,27] show the radical hydroxide ground states to be linear (bent excited states may exist) and CaSH to be bent.

Overall, neutral ligands appear to favor cations in aligned conformations and anions to prefer inclined conformations. Adducts formed by ligands of the harder, first row elements tend to be aligned or, at least, less inclined than the adducts of sulfur and phosphorus ligands. Although the approach direction seems to be mainly determined by the ligand, doubly charged cations generally rotate further out of alignment than do singly charged cations.

The strength of conformational preference varies, not always in parallel with the strength of binding. Thus, it costs 113 kJ mol^{-1} to bend the aligned $Mg^{2+}(H_2O)$ adduct into the perpendicular form but only 38 kJ mol^{-1} to force the same operation on $Mg^{2+}OH^-$ even though the OH^- anion is 5 times more strongly bound than neutral H_2O. (See Table 6 for results calculated for the Li^+ adducts.)

The results of “electrostatic-only” calculations are very instructive. Most adducts which are “aligned” under this constraint are still aligned when covalence is permitted, but for some the introduction of covalence is enough to change the adduct to the “inclined” state (e.g., Na^+SH^- and K^+SH^-). Adducts which are “inclined” in the “electrostatic-only” condition respond to covalence by bending away from the dipole axis even further.

TABLE 6: Calculated Li^+ Adduct Binding Energies (BE) and Electrostatic Potentials (ESP) in "Aligned" and "Perpendicular" Conformations[a]

ligand	$r(Li^+-L)$ (pm) 6-311+G**	BE (hartree) 6-311+G**	BE (hartree) ECP (s,p)	BE (hartree) ECP (truncated)	ESP (hartree) 6-311+G**
H_2O (aligned)	186.6	0.0566	0.0532	0.0420	0.0585
H_2O (perp)	200.4	0.0325	0.0241	0.0081	0.0288
OH^- (aligned)	160.7	0.3001	0.2903	0.2633	0.3093
OH^- (perp)	170.9	0.2848	0.2722	0.2266	0.2957
NH_2^- (aligned)	175.9	0.2933	0.2851	0.2359	0.3219
NH_2^- (perp)	185.5	0.2749	0.2651	0.2110	0.2999
H_2S (aligned)	236.7	0.0313	0.0245	0.0131	0.0182
H_2S (perp)	240.2	0.0376	0.0295	0.0102	0.0246
SH^- (aligned)	214.0	0.2459	0.2194	0.1917	0.2030
SH^- (perp)	214.5	0.2487	0.2334	0.1853	0.2436
PH_2^- (aligned)	220.6	0.2334	0.2217	0.1822	0.2243
PH_2^- (perp)	232.5	0.2426	0.2317	0.1796	0.2399

[a] MP2 binding energies calculated with various basis sets at the optimum MP2//6-311+G** geometries. The ECP basis was used with the valence (s,p) basis intact and truncated (see text). Electrostatic potentials were calculated from MP2 densities at the Li^+ position.

TABLE 7: Calculated Moments (atomic units) of Dipole (μ) and Quadrupole (Θ) Polarization of Neutral and Anionic Ligands[a,b]

		components X (XX)	components Y (YY)	components Z (ZZ)	exptl
H_2O	$\mu_{X,Y,Z}$	0.00	0.00	−0.653	0.728
	$\Theta_{XX,YY,ZZ}$	−4.539	−3.322	−4.025	
NH_3	$\mu_{X,Y,Z}$	0.00	0.00	−0.687	0.578
	$\Theta_{XX,YY,ZZ}$	−4.722	−4.722	−7.251	
H_2S	$\mu_{X,Y,Z}$	0.00	0.00	−0.521	0.38
	$\Theta_{XX,YY,ZZ}$	−12.578	−9.247	−10.238	
PH_3	$\mu_{X,Y,Z}$	0.00	0.00	−0.314	0.23
	$\Theta_{XX,YY,ZZ}$	−11.073	−11.073	−12.999	
OH^-	$\mu_{X,Y,Z}$	0.00	0.00	−0.706	
	$\Theta_{XX,YY,ZZ}$	−7.865	−7.865	−6.062	
NH_2^-	$\mu_{X,Y,Z}$	0.00	0.00	−0.930	
	$\Theta_{XX,YY,ZZ}$	−11.130	−7.366	−9.341	
SH^-	$\mu_{X,Y,Z}$	0.00	0.00	−0.381	
	$\Theta_{XX,YY,ZZ}$	−16.316	−16.316	−12.942	
PH_2^-	$\mu_{X,Y,Z}$	0.00	0.00	−0.345	
	$\Theta_{XX,YY,ZZ}$	−20.703	−15.095	−16.666	

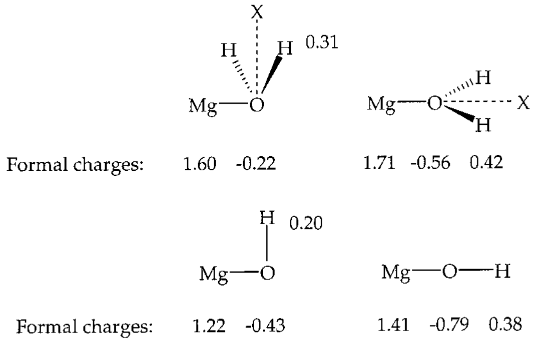
[a] Calculated from MP2 densities at MP2/6-311+G** optimum geometries. For the dipole moment (μ) the atomic unit is the bohr•electron (1 au = 2.5418 D), and for the quadrupole moment (Θ) it is the bohr^2•electron (1 au = 1.3451 D•Å). [b] The principal axis of the molecule is taken to be the *z*-axis, planar molecules to lie in the *yz* plane. The *xz*, *yz*, and *xy* components of the quadrupole moment vanish.

A surprising feature of the calculations is the preferred orientation of a cation forcibly withdrawn beyond its optimum binding distance. The approach paths for Li^+ and Mg^{2+} to OH^- or NH_2^- are oblique (Table 5) until they are quite close to the optimum binding distance. The cation then becomes aligned or near-aligned with the dipole axis.

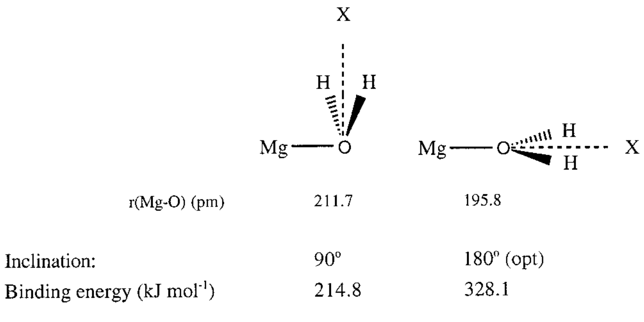
Discussion

Filled-Shell Adducts. Electrostatic and covalent contributions to binding are both able to affect the orientations of single ligand adducts. The dispersion interaction is considered to be small and insensitive to orientation.[28] Electrostatic binding comprises ion−dipole, ion−quadrupole, and higher terms, all of which contain "static" and "induced" components. Of these, polarization of the cation induced by the ligand can probably be ignored but not the reverse.

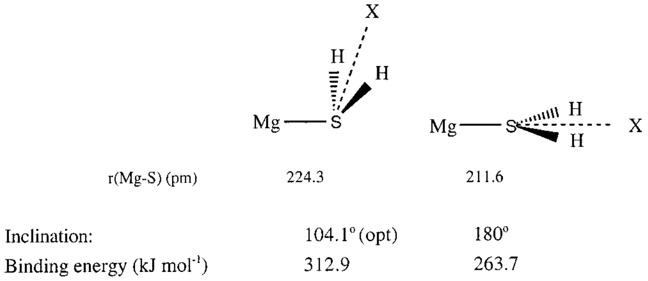
The first factor to be considered is the ion−dipole energy and, particularly, its angle dependence. In the absence of induced effects, this contribution to binding would drop catastrophically if the conformation were changed from "aligned" to "perpendicular". However, the calculated formal charges show that induction greatly reduces the penalty for bending the molecule. The polarity of the ligand declines at the close approach of the cation to the hydrogen atoms. So, for Mg^{2+} (H_2O) and Mg^{2+}-(OH^-):



Redistribution of electron density is not the only result of bending the bond: M−L bonds are up to 16 pm longer in the perpendicular conformation than when aligned (see Table 6 for results for the Li^+ adducts). Surprisingly, this is no impediment to their being stronger. In the cases in Tables 3 and 4 in which the inclined structure is the more stable, the M−L bond is also longer. Metal−ligand bond lengths for two Mg^{2+} adducts follow (the aqua adduct prefers the aligned conformation, the H_2S adduct prefers the inclined conformation):



For $Mg^{2+}(H_2S)$ the situation is reversed.



Without any easy way to assess the induced term, ion−quadrupole interactions can only be assessed from the quadrupole moments calculated for the free ligands (see Table 7). At the optimum Li−O distance for $Li^+(H_2O)$, the relative sizes of the dipole and quadrupole moments for water ensure that their combined energy contribution is greater in the aligned conformation (0.178 au) than in the perpendicular conformation (0.128 au). However, the much larger quadupole moment for H_2S produces almost equal ion−multipole energies for $Li^+(H_2S)$ in these two conformations (0.136 and 0.135 au, respectively). The computed values for the other ligands make it probable that the static ion−multipole energies will favor the "aligned" conformation for H_2O, OH^-, and NH_2^- adducts and slightly favor the "inclined" conformations for H_2S, SH^-,and PH_2^-.

The third factor considered is covalence. The perpendicular vs aligned energy comparisons in Table 3 show that the effect of covalence on energies is never very large and, consequently, hard to separate from the quadrupole field effect. The effect is small because the bonds are donor−acceptor bonds and are mainly electrostatic (see the measures of covalence in Tables 3 and 4). The inclination angles calculated for cations with and without valence shell s and p basis functions suggest that covalence is accompanied by forces which bend the M−L bond. Although this movement drives the ligand away from the cation, the covalence partly compensates for the loss of bond strength. Thus, with covalence, the metal−ligand distances in $Mg^{2+}(H_2O)$ and $Mg^{2+}(H_2S)$are calculated to be $r(MgO) = 195.8$ pm and $r(MgS) = 238.4$ pm, much shorter than the bond distances calculated for the "electrostatic-only" condition (203.7 and 264.4 pm, respectively).

The inclinations to the ligand axis calculated for Li^+ and Mg^{2+} deserve separate comment. They are just as large at long range as they are when close to the optimum bonding distances (see the inclination angles in Table 5 for separations in the range 200−400 pm), suggesting that covalence is not responsible for the inclined conformations at either distance. In fact, for these very electropositive elements, electron donation to the metal s and p orbitals falls away with distance only very slowly and at $r(LiO) = 400$ pm still exerts a significant effect on conformation. For separations beyond 200 pm it is only under the contrived "electrostatic-only" condition that the aligned conformation is favored.

Table 6, for Li^+ species, which shows calculated data for the six ligands in aligned and perpendicular conformations, allows a comparison of several different predictors of conformation, and corroborates some of the conclusions just drawn. A critical issue is raised by the electrostatic potential (ESP) data in the final column. Derived from the electron distributions of the ligands only, electrostatic potentials make no allowance for possible covalence, yet they still correctly predict whether the adduct geometries are aligned or inclined. The reason for this appears to be that the ESP data take full account of both dipole and quadrupole effects, predicting inclined conformations when the latter are large. However, covalence only overcomes the dominance of the dipole moment of the ligand under that same circumstance and the predictions are spurious. Since electrostatic potentials are based on a point charge, static, electrostatic model, the effect of correcting it for these errors might be expected to be beneficial. In fact, correcting for the point charge approximation (the truncated basis approach) worsens the performance, the prediction failing for half the cases. Only after allowing covalency to enter the cation−ligand bond is full reliability obtained.

Overall, the inclinations of the metal−ligand bond to the dipole axes of the ligands may be rationalized thus:

(a) The large dipole moment of H_2O makes the aligned conformation inevitable for all cations, the effects of covalence and the ion−quadrupole term being too small to compensate for the loss of ion−dipole energy when the cation moves out of alignment with the dipole axis of the ligand.

(b) OH^- and NH_2^- adducts of Mg^{2+} are slightly bent as a compromise between covalent and electrostatic contributions. With the other cations the aligned conformation is retained, the balance tipping slightly in favor of the ion−dipole electrostatic term.

(c) Compared with the water molecule, H_2S has a large quadrupole moment and a small dipole moment; its adducts favor "near-perpendicular" conformations. Li^+, Be^{2+}, Mg^{2+}, and Ca^{2+} bind to H_2S in the inclined conformation even when covalence is constrained to be absent, but for Na^+ and K^+ the electrostatic quadrupole term is not enough. The preferences are weak, due to the fact that the ion−quadrupole term has about the same order of magnitude as the ion−dipole term and the effect of covalency is not large.

(d) Almost every adduct of SH^- and PH_2^- is acute-angled. The S−H and P−H bonds are almost homopolar, so $M^{n+}\cdots H^{q+}$ repulsion is very small in these adducts with little energy penalty for bending into the conformation favored by the ion−quadrupole energy term. Soft cations such as Na^+ and K^+ attain the inclined arrangement only when electrostatic binding is augmented by covalency.

Radical Adducts. Spectroscopic results for CaOH, other alkaline earth metal hydroxides, and CaSH have been presented in the literature as if linear geometry is to be correlated with electrostatic binding and bent geometry with covalence. Calculations on compounds considered most likely to entertain covalent binding give support to this view. Very careful calculations on two compounds not yet characterized spectroscopically show BeOH to have an inclination angle of 147° and MgOH, although linear, to have a very shallow bending potential.[27] Nevertheless, the radical adducts as a group seem to follow the same patterns of behavior as filled shell adducts, in which the quadrupole disposition of charge in H_2S, SH^-, and PH_2^- is the main reason for inclined conformations, with covalence playing only a subsidiary role. The hydroxides of both the filled shell and open shell cations are linear, BeOH being the single exception. This is not unexpected for a bond formed by an element usually placed in a class different from that of the elements below it.

In a recent molecular beam study, Pereira and Levy suggest that a linear ground state and low-lying excited states for CaOH are to be expected for "ionic states" but that "bent, covalent states involving p orbitals on the oxygen" are also expected.[4] Similarly, Scurlock et al. consider the bent structure found for the CaSH $^2A'$ ground state to be "indicative of a significant amount of covalent bonding".[2]

To test these suggestions, it is worthwhile to scrutinize the computational data for the adducts of all three cations but especially those of Ca(I). The MP2 wave function of the Ca(I)OH molecule in the (linear) ground state presents the unpaired electron in a mainly 4s orbital. Repulsion is severe because the Ca−O distance is so small, as usual in cation−anion adducts. The repulsion between the electrons of OH^- and the Ca 4s electron is reduced by a small amount of spσ hybridization, polarizing the unpaired electron away from the OH^- ion. Constraining the CaOH angle to values away from 180° produces no change in the p character of the unpaired electron, showing that it is determined purely by the need to reduce the repulsion. The effect of enforced bending of the molecule is the same as it is for adducts of closed shell cations. It strengthens the covalent interaction between the cation and the ligand, but not enough to displace the linear conformation as the most stable arrangement. The conformational energy change for CaOH is 9% of the binding energy of the preferred conformation, in the same range as that for the adducts of closed shell cations.

For CaSH the bent conformation is preferred. In this case the computational data show that covalent bonding, although not strong, takes a bigger share of the total binding energy, the ion−dipole energy contribution being smaller than for the hydroxide. The covalence comes from use of an almost unhybridized p orbital on sulfur resulting in an inclination angle close to 90°.

The electronic spectra of the Be^+, Mg^+,and Ca^+ compounds focus special attention on the excited states. Using the technique of interchanging occupied and virtual orbitals prior to the initial guess, an indication of the structure of the excited state molecules can be gained. Excited states in these radical compounds are considered to result from excitation of the unpaired 4s electron to 4pσ, 4pπ, or 3d orbitals, all strongly centered on the metal. The data show that both CaOH and CaSH are responsive to excitation of the s electron to a p orbital, binding energies, bond distances, and inclination angles being affected.

“Electrostatic-only” calculations are not possible for these compounds because of the extra electron outside the closed shell, but comparison of the covalence contributions in the radical and closed shell adducts can be made with the covalent bond orders calculated by natural resonance theory. As can be seen in Tables 3 and 4, the values for the Be^+, Mg^+, and Ca^+ adducts lie broadly between those of the mono- and divalent filled shell adducts of the same ligands. The conclusion to be made is that the dipole and quadrupole terms of the electrostatic energy compete in the radical adducts as they do in the closed shell compounds and that the inclined conformations are generally found when covalent bonding, never particularly strong, is nevertheless able to tip the scale away from aligned geometries.

Conclusions

Inclined conformations in single ligand adducts of main group cations occur most in adducts of the second row ligands and with the softer metal ions. The binding geometries seem to be mainly due to the relative size of the ion−quadrupole and ion−dipole contributions to the binding energy, as in the case of the H-bonded dimers.[10,11] For cations, however, covalence is a small additional influence favoring inclined structures. When the electrostatic terms are indecisive, covalence is sometimes enough to force the adduct into an inclined conformation. Radical adducts formed by Be^+, Mg^+, and Ca^+ demonstrate the same interplay between dipole, quadrupole, and covalence interactions as the compounds formed by the closed shell cations with the added influence of the location of the unpaired electron on the cation.

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