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Model Chemistry Methods for Molecular Dications: The Magnesium Dication Affinity Scale

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High-level ab initio calculations, including the recently formulated CP-dG2thaw methodology, are used to explore the bonding between Mg^{2+} and a representative assembly of small inorganic and organic molecules. Assessment of existing and novel computational techniques shows that both Mg 2s and 2p electron correlation, and correction for basis set superposition error (BSSE), have a significant influence on calculated magnesium dication affinity (MgDA) values. These two effects are opposed, so that techniques which neglect both (such as G2) are actually found to perform better than techniques in which innervalence correlation, but not BSSE, is treated (such as G2thaw). As shown by comparison of sodium cation affinity (SCA) and MgDA values, we find that Mg^{2+} has a somewhat greater propensity for binding to "soft" ligands containing second-row donor atoms than does Na^+. This trend is attributable to the increased influence of the ion/induced dipole term with increasing cation charge. Dipole induction is, in some circumstances, sufficient to very significantly lengthen other bonds to the donor atom: for example, the $F-CH_3$ bond is extended by over 0.25 Å upon coordination to Mg^{2+}, while structural factors substantially dampen the corresponding effect for the $HO-CH_3$ and H_2N-CH_3 bonds.

1. Introduction

In solution, the thermochemistry of hydrated metal dications such as $Mg^{2+}{}_{(aq)}$ is well-established, while the boundaries of the solvation sphere are uncertain.[1−4] The reverse is true of gas-phase measurements, through which techniques such as electrospray ionization[5] can offer a clear insight into the (mass-spectral) distribution of water molecules in partially hydrated metal ions[6−9] but at rather poor energy resolution. Precise measurement of such a fundamental parameter as the binding energy of one water molecule to any metal dication,

$$M^{2+} + H_2O \rightarrow M(OH_2)^{2+} \quad (1)$$

remains elusive despite continuing impressive advances in the laboratory study of gas-phase dications.[7−16] One way in which this impasse might effectively be sidestepped is by resort to ab initio calculations, but herein lies a quandary. If there are currently no examples of molecular dications whose thermochemistry has been precisely characterized by laboratory methods, how can we have confidence in the reliability of the theoretical methods which we might employ on such species? The most reasonable approach, we would suggest, is to choose methods which have been well-tested for the purpose of computing ligand binding energies to metal monocations, so as to ensure as far as possible that our computational tools are sensitive to the particular demands of cationic complexes in which induced electrostatic forces dominate the metal/ligand interactions. This is the rationale behind the present work, which seeks to apply recent refinements in metal-ion computational methodology (developed in the first instance for sodium-containing molecular cations)[17,18] to the analogous but more experimentally elusive magnesium-containing molecular dications. The ultimate aim of such a task is to establish a reliable "magnesium dication affinity" (MgDA) scale to complement and augment future experimental measurements of Mg^{2+}−ligand binding energies.

Many of the Mg^{2+} adducts investigated here have been subjected to previous theoretical study. This is most notably so for the aquo complex $Mg(OH_2)^{2+}$;[13,19−40] conversely, for some other complexes presented here, such as $Mg(CH_4)^{2+}$, $Mg(C_2H_2)^{2+}$, $Mg(CO_2)^{2+}$, and $Mg(FCH_3)^{2+}$, no previous results appear to exist.

2. Theoretical Methods

1. Description of Nonstandard Computational Methods. The CP-dG2thaw method and other computational techniques employed here are all variants on the widely used G2 model chemistry method.[41] These variants have been described in detail in previous studies,[18,42−44] but a brief overview is of benefit so as to readily identify how each method differs from G2 itself:

(i) The "thaw" suffix[42] denotes an expansion of the correlation space used in single-point calculations, so as to include the "innervalence" orbitals of the metal atom[43,45−47] (in this case, the 2s and 2p orbitals of Mg). These orbitals would otherwise (for example, in a standard G2 calculation)[41] lie within the "frozen core".

(ii) The "d" prefix indicates use of a modified metal-atom basis set[18,44] in the single-point calculation involving the B4G basis set. (Throughout this paper we use the abbreviation "B4G" to represent the 6-311+G(3df,2p) basis set, which is the largest of the four basis sets used in G2's constituent single-point calculations).[41] In "d" method calculations, the B4G basis is

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TABLE 1: Counterpoise Correction Terms Obtained for Small $Mg^{2+}\cdot X$ Adduct Ions at Various Levels of Theory

	MP2/B4G[a]		QCISD(T)/B4G[a]		QCISD(T)/dB4G[a]			
ligand	CP(Mg^{2+})[b] mHartree	CP(X)[c] mHartree	CP(Mg^{2+})[b] mHartree	CP(X)[c] mHartree	CP(Mg^{2+})[b] mHartree	CP(X)[c] mHartree	$\Delta_{(QCI-MP2)}$[d] kJ mol^{-1}	$\Delta_{(dB4G)}$[e] kJ mol^{-1}
H_2	−0.33	−0.20	−0.34	−0.17	−0.14	−0.18	0.05	0.49
He	−0.25	−0.24	−0.26	−0.26	−0.10	−0.26	−0.05	0.41
CH_4	−1.08	−0.57	−1.13	−0.57	−0.46	−0.61	−0.14	1.68
NH_3	−1.00	−1.21	−1.04	−1.25	−0.34	−1.30	−0.20	1.70
H_2O	−2.01	−1.66	−1.96	−1.72	−0.38	−1.79	−0.03	3.96
HF	−2.03	−1.58	−1.98	−1.67	−0.37	−1.69	−0.08	4.15
Ne	−1.61	−1.63	−1.53	−1.69	−0.20	−1.76	0.04	3.33
PH_3	−1.73	−1.46	−1.65	−1.49	−0.35	−1.51	0.14	3.34
H_2S	−1.75	−1.71	−1.67	−1.81	−0.34	−1.85	−0.07	3.40
HCl	−1.68	−2.13	−1.60	−2.28	−0.30	−2.33	−0.20	3.29
Ar	−1.64	−1.29	−1.56	−1.42	−0.26	−1.46	−0.13	3.29

[a] Level of theory used for the indicated counterpoise correction calculations. In all instances a "thawed" correlation space (i.e., including the 2s and 2p electrons of any Mg atoms present) was employed. The B4G basis set is 6-311+G(3df,2p), while the dB4G basis set is as identified in the text. [b] Counterpoise correction for Mg^{2+} in the presence of the ligand's basis functions. [c] Counterpoise correction for the ligand X in the presence of the Mg atom's basis functions. [d] Difference between QCISD(T)/B4G and MP2/B4G values of the total counterpoise correction for the indicated $Mg^{2+}\cdot X$ adduct ion. [e] Difference between QCISD(T)/dB4G and QCISD(T)/B4G values of the total counterpoise correction for the indicated adduct ion.

TABLE 2: Calculated Values of IE(Mg^+) at Various Levels of Theory

	IE(Mg^+)/eV	
method	excluding HLC[a]	including HLC[a]
CBS-Q		14.719
G2(MP2)	14.719	14.724
G2	14.719	14.724
G2(QCI)	14.719	14.724
G2thaw	14.891	14.896
G2thaw(QCI)	14.902	14.907
dG2thaw	14.908	14.913
dG2thaw(QCI)	14.922	14.927
G3	14.927	14.959
G3(QCI)	14.943	14.976
exptl[b]	15.035	

[a] HLC is the "higher level correction" as defined for the G2,[41] G2(MP2),[78] G2(QCI),[50] or G3[53] method. The HLC value for each nonstandard method is taken to be equal to that for the most closely related "standard" method. [b] from the NIST Physical Reference Data website: http://physlab2.nist.gov/cgi-bin/AtData/.

used for all nonmetallic atoms, but for the metal atom (here Mg) the second set of contracted s functions, and the second set of contracted p functions,[48] are expanded out (i.e. "decontracted"); this basis set modification is denoted "dB4G" in the discussions which follow. Further details on this basis set modification can be found in our previous studies.[18,44]

(iii). The "CP-"prefix indicates inclusion of a counterpoise correction[49] for basis set superposition error in determination of the metal dication/ligand binding energy. This counterpoise correction is determined using the B4G basis set (or dB4G for "dG2"-type methods) at the same level of theory employed in the regular single-point total energy calculation using this basis set:[17,18] that is, MP2 for G2-type calculations, or QCISD(T) for G2(QCI)-type[50] calculations.

2. An Exploratory Assessment of the Nonstandard Computational Methods for Mg-Containing Dications. Previous studies on metal (mono)cation affinities[17,18,44] have shown that MP2-level counterpoise corrections correspond very closely to those obtained at higher levels of electron correlation (e.g. QCISD(T)) using the same basis set. The counterpoise correction (CP) values listed in Table 1 indicate that this close correspondence holds true also for the magnesium dication affinities of various small ligands. This can be seen by comparing the CP values obtained at MP2/B4G and at QCISD(T)/B4G. The parameter Δ(QCI-MP2), which is the difference between total counterpoise corrections at these two levels of electron correlation, never exceeds ±0.2 kJ mol^{-1} for the examples surveyed: this is very much less than the target accuracy of G2-type methods, which is typically ±8 kJ mol^{-1}, and is also generally rather less than the satisfactorily small discrepancy (i.e., the deviation from the "additivity assumption")[41,50] between MgDA values calculated using G2-derived methods and those determined using the corresponding G2(QCI)-derived technique. Table 1 also provides an indication of the merit of basis set decontraction for magnesium: a comparison of the Mg^{2+} component of the counterpoise correction, at the QCISD(T)/B4G and QCISD(T)/dB4G levels of theory, reveals that the latter correction is much smaller than the former, typically by a factor between 2 and 6. This degree of improvement matches that seen for Na^+ counterpoise corrections in similar calculations for sodium ion adducts,[18] while the absolute magnitude of the Mg^{2+} counterpoise corrections is generally somewhat greater than the corresponding value for Na^+ at either level of theory. The significance of this last point is that neglect of basis set superposition error, in calculations on Mg-containing molecular dications, would appear to result in a somewhat larger error than would ensue from such neglect[17] in calculations on Na-containing cations. Also in accord with our previous experience in CP calculations on sodium-containing ions[18] is that the ligand component of CP is very slightly enlarged upon metal atom basis set decontraction: however, as can readily be appreciated from the $\Delta_{(dB4G)}$ values, which measure the difference in total CP between QCISD(T)/dB4G and QCISD(T)/B4G calculations, the reduction in the Mg^{2+} CP component very much overrides the small increase in the ligand component resulting from this basis set decontraction. Since it is expected that the counterpoise correction will generally overestimate the true basis set superposition error,[49] it is desirable to use a method offering as small as practicable a total counterpoise correction. In the present context, then, the CP-dG2thaw method can be seen to fulfill this criterion better than CP-G2thaw.[51]

A second measure by which to assess the reliability of the various methods for Mg^{2+}-containing species is to compare their accuracy in determining IE(Mg^+), the second ionization energy of the magnesium atom (see Table 2).[52] The "frozen-core" methods G2, G2(MP2), G2(QCI) and CBS-Q all underestimate IE(Mg^+) by ~0.3 eV, indicating the necessity for inclusion of Mg 2s and 2p electron correlation. Much better performance is given by all of the "thawed" and "full correlation" methods, even G3 (in which only the “G3Large” basis set single-point calculation does not adopt a frozen core). In fact, the closest agreement with the experimental value is given by G3 and by its more computationally intensive variant, G3(QCI), although a large part in the improvement of these values over all the G2-related methods stems from the rather larger unpaired-electron HLC (higher level correction) value for G3 (1.185 mHartree)[53] compared to that for G2 (0.19 mHartree).[41] The difference in G2-based and G3-based HLC values means that the G3-based IE(Mg^+) values are “ramped up” by ∼25 meV more than their G2-based counterparts, and when HLCs are discounted the difference between the best G2-based method and G3 is much less. Despite G3's good performance on this criterion, we have not pursued G3 calculations on the Mg dicationic adducts for several reasons. First, the combination of “frozen-core” and “full correlation” single-point calculations in G3 is problematic − as we have previously reported,[18] inappropriate assignment of “core” and “valence” orbitals arises in some complexes of Na^+ with O-, F-, and Ne-containing ligands, with the result that G3 significantly underestimates the binding energy to such ligands despite the inclusion of a full-correlation calculation at the MP2/G3Large level of theory. It is quite possible that similar problems arise when Mg^{2+} is combined with such ligands. This problem could be avoided by use of a thawed correlation space in a modified G3 approach, but this presents a second problem since the HLC in such a case becomes ambiguous: the higher level correction is determined from the number of α and β valence electrons, but are the Mg 2s and 2p electrons genuinely “valence” or should they still be treated as “core” for HLC purposes? (While such a quandary also arises in principle for G2thaw and other G2-related methods, it is of no consequence in such cases because, in spin-conserving metal-ion ligation reactions, there is no change in the total HLC upon adduct formation; in G3, however, the HLC is determined differently for atomic (e.g., Mg^{2+}) versus molecular (e.g., $MgHe^{2+}$) species). Furthermore, it is not apparent as to what extent the HLC is able to compensate for neglect of BSSE in metal ion/ligand complexes. Since a “thawed G3” method for determining MgDA values would involve inclusion of an empirical correction factor (which, in any case, is calibrated chiefly using examples of covalently bonded compounds, and therefore probably quite inappropriate for electrostatically bound adduct ions) for which the value is ambiguous, it would appear that there can be little, if any, advantage in pursuing G3-variant methods, rather than G2-based approaches, for the purposes of determining metal ion/ligand binding energies.

All calculations reported in the present work were obtained using the Gaussian98 suite of programs.[54]

TABLE 3: Magnesium Dication Affinities Obtained at G2 and Higher Related Levels of Theory

	MgDA/kJ mol-1[a]					
ligand	G2	G2 (QCI)	G2thaw	G2thaw (QCI)	dG2thaw	dG2thaw (QCI)
He	25.4	25.4	26.8	26.9	26.4	26.5
Ne	45.3	45.8	48.4	49.0	47.7	48.4
H_2	85.3	84.7	88.9	88.5	88.7	88.3
Ar	118.8	118.0	126.4	125.8	123.2	122.9
N_2	167.0	167.0	173.6	173.8	172.1	172.3
CH_4	194.9	194.7	203.7	203.8	202.5	202.6
CO	199.0	198.9	206.2	206.3	205.3	205.4
HCl	219.9	218.7	229.6	228.6	226.6	226.0
HF	219.3	220.7	225.5	227.1	224.3	225.9
CO_2	248.4	248.6	256.3	256.6	254.9	255.3
C_2H_2	277.8	278.3	288.1	288.5	287.6	288.0
H_2S	302.4	301.1	314.3	313.3	311.4	310.7
CH_3F	321.1	321.9	329.3	330.4	328.4	329.4
H_2O	320.2	321.2	327.6	328.8	326.8	328.0
PH_3	347.6	346.3	360.9	359.8	358.4	357.5
H_2CO	366.8	367.9	375.4	376.7	374.2	375.5
HCN	369.1	369.3	377.7	378.2	376.1	376.5
CH_3OH	376.9	377.6	385.9	386.9	384.9	386.0
NH_3	383.5	383.3	392.6	392.8	391.5	391.7
CH_3NH_2	424.2	424.3	434.8	435.4	433.6	434.2

[a] Magnesium dication affinity value, at 0 K and corrected for zero-point energy, at the indicated level of theory. See text for a brief description of nonstandard methods used.

TABLE 4: Comparison of Metal−Ligand Bond Distances Obtained at the MP2(full)/6-31G* and B3-LYP/DB4G [a] Levels of Theory

	Mg-X bond length/Å	
ligand	MP2/6-31G*	B3-LYP/dB4G
He	2.054	1.909
Ne	2.058	2.066
H_2[b]	2.049	2.012
Ar	2.396	2.345
N_2	2.131	2.069
CH_4	2.169	2.138
CO	2.233	2.201
HCl	2.374	2.357
HF	1.883	1.867
CO_2	1.912	1.871
C_2H_2[b]	2.267	2.254
H_2S	2.453	2.468
CH_3F	1.819	1.800
H_2O	1.948	1.913
PH_3	2.543	2.546
H_2CO	1.882	1.841
HCN	2.016	1.961
CH_3OH	1.916	1.880
NH_3	2.081	2.042
CH_3NH_2	2.071	2.035

[a] See text for a description of the dB4G basis set. [b] For this adduct ion (which has C_{2v} symmetry), the metal−ligand separation shown is from Mg to the ligand’s bond midpoint.

3. Results and Discussion

Calculated magnesium dication affinity (MgDA) values, at levels of theory ranging from G2 to dG2thaw(QCI), are listed in Table 3. Table 4 offers a comparison between dicationic Mg-ligand bond distances at the MP2/6-31G* and B3-LYP/dB4G levels of theory, while counterpoise-corrected MgDA values are given in Table 5. Inspection of the values in Tables 3 and 5 show that the conclusions drawn from our recent study of sodium cation affinity values[18] apply about equally well to these dicationic magnesium adducts. Comparison of the G2 and much more computationally expensive G2thaw(QCI) values is illuminating. The G2 method, with an inadequate correlation space (for Mg) and no treatment of BSSE, almost invariably delivers MgDA values which are closer to our “best level” (the counterpoise-corrected, expanded correlation space, and modified Mg basis set techniques CP-dG2thaw and CP-dG2thaw-(QCI)) than does G2thaw(QCI). This result arises principally from the cancelation of errors due to G2's lack of both Mg innervalence correlation[43] and of any correction for basis set superposition error.[17] The G2thaw(QCI) technique appears to deliver MgDA values which are substantially too high (typically by around 6 kJ mol^{-1}): a significant observation, since this level of theory has previously been proposed as an acceptable method for MgDA calculation.[33,38] While G2 itself does perform better than this, it is not absolutely reliable: in many cases, it is seen to give MgDA values around 4 kJ mol^{-1} lower than CP-dG2thaw. The neglect of both innervalence Mg correlation

TABLE 5: Counterpoise-Corrected Dication Affinities Obtained at Various Levels of Theory

	CP-corrected MgDA/kJ mol^{-1}			
ligand	G2thaw[a]	dG2thaw[a]	dG2thaw (QCI)[a]	dG2thaw(QCI)// B3-LYP/dB4G[a]
He	25.5	25.6	25.6	25.9
Ne	39.9	42.8	43.3	43.1
H_2	87.5	87.8	87.5	87.0
Ar	118.7	119.0	118.4	118.2
N_2	166.9	167.1	167.3	167.0
CH_4	199.3	199.8	199.8	200.4
CO	198.1	201.3	201.4	202.1
HCl	219.6	220.1	219.1	219.3
HF	216.0	219.1	220.5	220.8
CO_2	246.7	249.9	250.2	250.6
C_2H_2	282.2	283.1	283.7	282.3
H_2S	305.2	306.0	304.9	306.3
CH_3F	318.6	322.0	322.9	320.6
H_2O	318.0	321.3	322.3	322.5
PH_3	352.6	353.6	352.7	353.0
H_2CO	365.5	368.9	370.1	369.1
HCN	371.5	371.9	372.4	372.1
CH_3OH	376.1	380.6	380.4	379.8
NH_3	386.8	387.3	387.4	387.3
CH_3NH_2	428.4	429.1	429.5	429.4

[a] See text for description of the identified method.

and BSSE (in G2) is not, finally, an acceptable substitute for treatment of both these factors (as in CP-dG2thaw).

Magnesium basis set modification, in the dG2thaw calculations, is seen to deliver a slight reduction from the G2thaw values. This corresponds mainly to the improvement in description of the atomic dication Mg^{2+} by the dB4G basis set compared to B4G. An interesting and somewhat puzzling dichotomy is seen when counterpoise corrections are applied (see Table 5). For ligands containing an O, F, or Ne, the CP-G2thaw MgDA value is always 2.9 kJ mol^{-1} or more below the CP-dG2thaw counterpart, while for all other ligands the discrepancy between these two methods is always less than 1 kJ mol^{-1}.[55] The discrepancy between CP-G2thaw and CP-dG2thaw cannot be resolved by comparison with precise experimental values, since no such values currently exist for monoligated Mg^{2+}; however, the dB4G basis clearly leads to systematically smaller counterpoise corrections than B4G, which should equate to a tendency to better approximate the "true" complete-basis-set value, and dB4G also leads to a better IE-(Mg^+) value than does B4G.

Alcami et al.[33] have suggested that hybrid DFT methods such as B3-LYP tend to yield optimized dicationic Mg−ligand separations which are significantly too short, on the basis of comparison with QCISD(full)/6-311G** geometries. In contrast, MP2 calculations and nonhybrid methods such as B-LYP offer substantially better agreement with QCISD geometries. Our own calculations using B3-LYP/dB4G have delivered Mg−ligand bond distances which are substantially shorter again than the B3-LYP/6-311G** values of Alcami et al.,[33] but it is not at all clear that our B3-LYP/dB4G bond lengths are in fact underestimates as the latter study[33] would suggest. The choice of QCISD(full)/6-311G** as a "benchmark" for dicationic metal−ligand bond lengths is somewhat questionable: while this level represents a reasonably advanced treatment of electron correlation, values obtained by this method are not expected to be completely accurate and may well be subject to some systematic discrepancy of their own. Such a systematic discrepancy might arise through comparatively poor treatment of the Mg 2s and 2p "innervalence" electrons in calculations using the 6-311G** basis set, and/or through neglect of basis set superposition error in geometry optimizations. It is very interesting to note, in this context, that while the agreement between B3-LYP/dB4G and QCISD(full)/6-311G** geometries for MgX^{2+} (X = H_2O, NH_3, CO, H_2CO and HCN) is comparatively poor, the agreement between B3-LYP/dB4G and *counterpoise-corrected* QCISD(T)(full)/6-311+G** optimized geometries for $MgHe^{2+}$, $MgNe^{2+}$, and $MgAr^{2+}$ is excellent,[56,57] and is much better than that seen between MP2 and the CP-corrected QCISD(T) values. Notwithstanding the possibility that BSSE considerations may be significant in determining the optimized geometries for dicationic Mg/ligand complexes, it remains to be stated that the calculated MgDA values are in fact *not that sensitive* to the level of theory used in geometry optimization (see Table 5). Of the 20 ligands for which we present MgDA values, only C_2H_2, H_2S, and CH_3F show discrepancies exceeding 1 kJ mol^{-1} between MP2/6-31G*-optimized geometries and B3-LYP/dB4G structures when the same level of theory (e.g., CP-dG2thaw-(QCI)) is used in the single-point calculations on both sets of structures. The differences between MP2/6-31G* and QCISD/6-311G** geometries have also previously been shown to be fairly unimportant in influencing the final MgDA value. We conclude that the inclusion of Mg 2s and 2p electron correlation, decontraction of the Mg basis set, and treatment of BSSE are much more significant considerations in this context than is the geometry optimization method.

Having discussed the issues affecting computational accuracy, we turn now to an examination of overall trends and wider implications of the tabulated values. The preferences for Mg^{2+} ligation by larger rather than smaller, and polar rather than nonpolar ligands, are readily apparent in Table 5; as previous studies have noted,[26,27,29,32,33,38,58,59] the metal/ligand binding in these complexes is dominated by the electrostatic effects of ion/dipole and ion/induced dipole attraction. This may, incidentally, help to explain why the calculated MgDAs are comparatively insensitive to minor variations in optimized geometries, in contrast to the very large geometry-dependent discrepancies which have been noted in a few instances for covalently bonded molecular dications:[60] for the latter class of compounds, the bond length is at once more subject to variation with different levels of theory, and more critical in influencing the total energy of the molecular dication, than is the case for dicationic metal/ligand adducts.

Comparison between our CP-dG2thaw values and those obtained by other correlated or DFT methods is possible for most of the ligands surveyed. Agreement with the binding energies of Breckenridge and co-workers[56,57] for the noble-gas adducts MgX^{2+} (X = He, Ne, Ar) is very good: following correction for zero-point energy, the D_e values obtained by their counterpoise-corrected, large-basis-set QCISD(T) parametrization of the Mg^{2+}/X potential energy curves[56,57] yield MgDA values for He, Ne, and Ar of 27.8, 43.7, and 120.6 kJ mol^{-1}, respectively. Other studies have also employed QCISD(T) or CCSD(T) single-point calculations on several of the ligands explored herein, notably H_2O:[32,33,38,40,61] such studies have frequently employed "thawed" or "full" correlation spaces[33,38,61] but have not employed counterpoise corrections, with a range of "high-level" QCISD(T) and CCSD(T) MgDA(H_2O) values from 317.6 kJ mol^{-1} [40] to 332.3 kJ mol^{-1} [61] having been previously reported. As is consistent with our experience in the present study, the lower values are obtained in "frozen-core" calculations[32,40] while the higher values arise in calculations which explicitly treat Mg 2s and 2p electron correlation.[33,38,61] Consistent also with our present work is the finding that the "frozen core" calculations fortuitously show better agreement

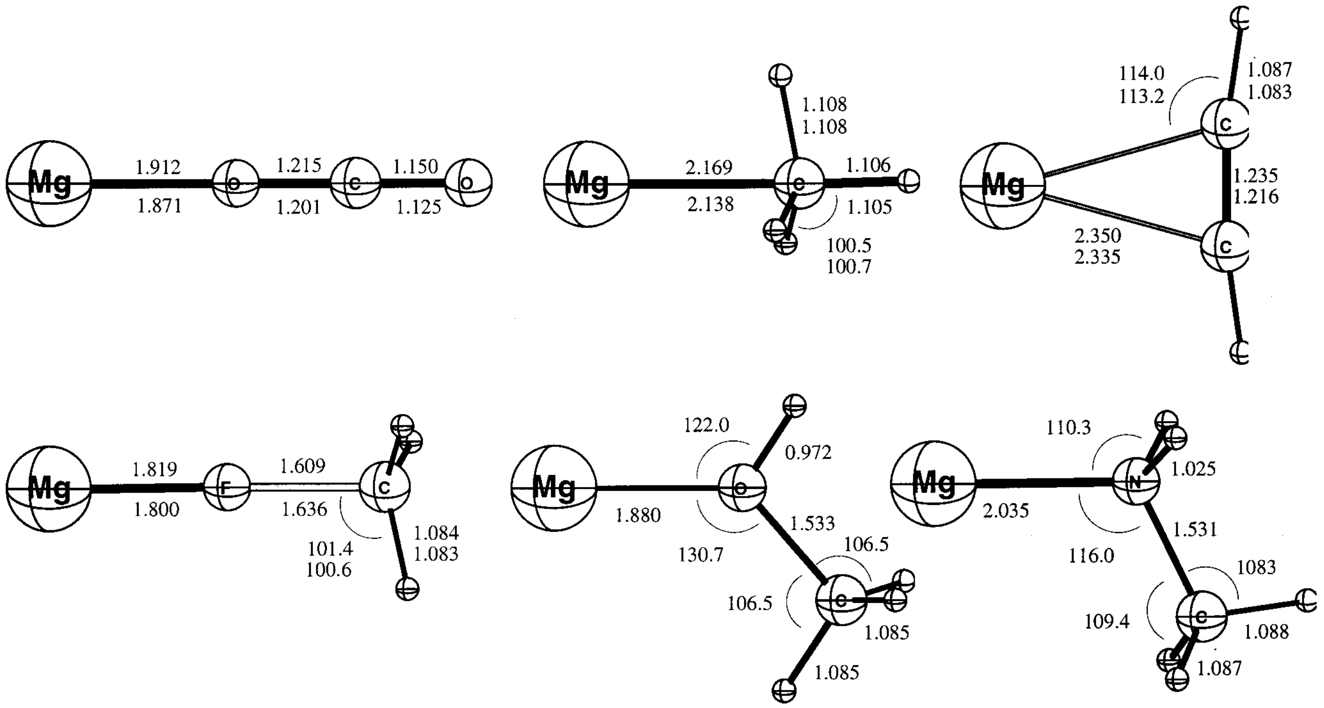

Figure 1. Optimized geometries for the Mg^{2+} adduct ions with CO_2, CH_4, C_2H_2, CH_3F, CH_3OH, and CH_3NH_2. For the first four of these species, bond lengths (in Ångstroms) and bond angles (in degrees) are reported at both the MP2(full)/6-31G* and B3-LYP/dB4G levels of theory; while for the CH_3OH and CH_3NH_2 adducts we give only the B3-LYP/dB4G values since previous studies[32,33] have already reported the MP2/6-31G* values.

with our CP-corrected values than do the calculations with a more extensive correlation space.

Alcami et al.[33] have recently assessed the reliability of several DFT and hybrid DFT methods, using the 6-311+G(3df,2p) ("B4G") basis set, for calculating metal dication/ligand binding energies. Although we suggest that their chosen method of assessment, viz., agreement with QCISD(T)thaw/B4G and CCSD(T)thaw/B4G calculations, neglecting correction for BSSE, is not in itself highly reliable, we remain in agreement with their conclusion that the G96-LYP functional performs significantly better than other methods, notably B-LYP and B3-LYP. For the six Mg^{2+}/ligand complexes common to their study and ours, the G96-LYP MgDA values exceed our CP-dG2thaw values by 3.4 (H_2O), −2.0 (H_2CO), 6.3 (HCN), 6.0 (CH_3OH), 8.5 (NH_3), and 12.3 (CH_3NH_2) kJ mol^{-1}, while for the same series of ligands the B-LYP values exceed ours by respectively 17.6, 18.1, 21.0, 23.2, 24.8, and 32.0 kJ mol^{-1}, and the apparent performance of B3-LYP is marginally worse again. It would seem, from these values (which are expressed in order of increasing ligand MgDA), that the density-functional methods show a fairly consistent tendency to overestimate not only the absolute MgDA values, but also the differences between MgDA values, i.e., the spacings on the MgDA "ladder". One result from the study of Alcami et al.,[33] which may warrant further investigation, is that the combination of the Becke three-parameter exchange functional[62] (B3) with either of the P86[63] or PW91[64] correlation functionals shows a markedly lower overestimation of MgDA values than does the B3-LYP[62,65] functional combination, and it may well be that the G96-P86 or G96-PW91 methods (which to date appear not to have been tested for metal dication/ligand binding energies) also yield values closer to CP-dG2thaw than does the G96-LYP method. This is, however, a topic which we choose not to explore further in the present study.

Of the species surveyed here, only the Mg^{2+} adducts of CH_4, CO_2, C_2H_2 and CH_3F appear not to have been subjected to previous theoretical study, and for these species we present full structural details in Figure 1. The lack of previous calculations on $Mg(CO_2)^{2+}$ is somewhat ironic, since this is one of the first—and remains one of the few—monoligated Mg^{2+} complex ions to have been experimentally observed;[10] in contrast, the much-calculated[10,13,19−36,38−40,59,61,66,67] species $Mg(H_2O)^{2+}$ has eluded detection until very recently.[16] We find that the $Mg(CO_2)^{2+}$ complex is a linear structure, with O-atom σ-coordination to Mg^{2+}; the CP-dG2thaw $MgDA(CO_2)$ value of 249.9 kJ mol^{-1} is significantly larger than the corresponding values for the linear σ-donors N_2 (167.1) and CO (201.3), with the increase being most likely due to the higher polarizability of CO_2 (see below). The adduct with CH_4 is perhaps best regarded as a van der Waals complex, since its structure does not formally permit σ- or π-donation to Mg^{2+}; the relevant MgDA value of 199.8 kJ mol^{-1} is notably much larger than that determined for the smaller analogous complex $Mg(H_2)^{2+}$ of 87.8 kJ mol^{-1}. The sole π-complex included in the present study, $Mg(C_2H_2)^{2+}$, has a binding energy of 283.1 kJ mol^{-1}, much larger than that determined for singly charged metal ion adducts of acetylene,[18,68] while the binding energy of Mg^{2+} to CH_3F exceeds that to HF by slightly more than 100 kJ mol^{-1}, a much greater "methyl effect" than that seen between H_2O and CH_3OH (59.3 kJ mol^{-1}) or NH_3 and CH_3NH_2 (41.8 kJ mol^{-1}).

Several previous studies[27,39,59,61,69] have contrasted the ligand-binding tendencies of Na^+ and Mg^{2+}, using computational results obtained at lower levels of theory than those employed here. In general our MgDA and sodium cation affinity[18] (SCA) results, depicted graphically in Figure 2, are in agreement with the previously identified trends. One example of the differences in ligand preference of the two metal ions Na^+ and Mg^{2+}, apparent from Figure 1, is that $MgDA(HCl) \approx MgDA(HF) \ll MgDA(PH_3)$, while $SCA(HCl) \ll SCA(HF) \approx SCA(PH_3)$, a relationship which is also evident (though not explicitly stated) in the recent B3-LYP/6-311+G** results of Remko and Rode.[59] The graphical presentation of these and other cation affinity values in Figure 2 makes plain the general feature that Na^+ shows a greater preference than does Mg^{2+} for ligands contain-

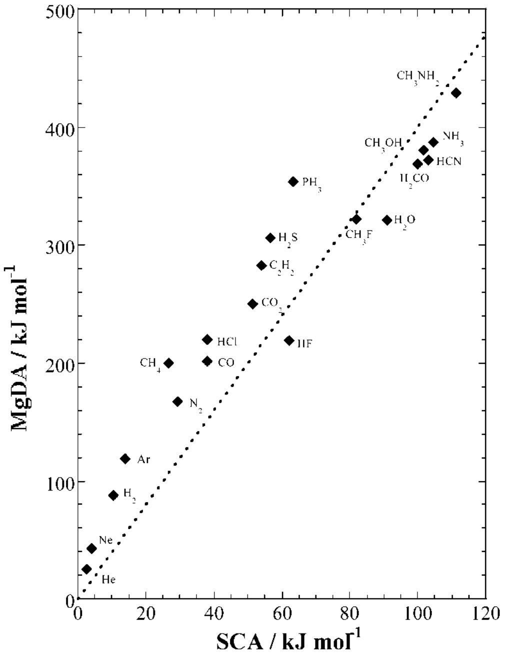

Figure 2. A graphical comparison of trends in magnesium dication versus sodium cation affinity, using values obtained at the CP-dG2thaw level of theory for both parameters.[18] The dotted line, which has a slope of 4:1, is shown as a visual aid and is not intended as a fit to the data.

ing first-row, rather than second-row, donor atoms. As previous comparative studies have also indicated,[27,59] this preference relates to the difference in relative importance of ion/dipole ($z\mu/r^2$) and ion/induced dipole ($z^2\alpha/r^4$) terms in the ion/ligand electrostatic attraction, where z is the ion charge, μ is the ligand's dipole moment and α is its polarizability. Clearly the ion/induced dipole term increases in importance with increasing ion charge z. If, to a first approximation, we discount any difference between Na^+ and Mg^{2+} metal/ligand separations (since the ionic radii for these metal cations are not greatly different), we would naively expect that MgDA(X) = 4SCA(X) for nonpolar ligands (in which only the ion/induced dipole term can contribute to the binding energy), with a lower MgDA:SCA ratio evident for polar ligands due to the involvement of both dipolar and induced-dipole terms. In fact, since $r(Mg^{2+}) < r(Na^+)$, all of the nonpolar ligands in Figure 2 lie above the line of slope 4:1, as do all the ligands containing second-row donor atoms and the weakly polar CO ligand; the only ligands which lie below this line are strongly polar species possessing a first-row donor atom. These results, in essence, present a quantification of the somewhat greater preference by Na^+, compared to Mg^{2+}, for binding to "hard" (first-row, small polarizability) rather than "soft" (second-row, large polarizability) ligands.[59,70]

The interaction of structural and electrostatic parameters can also help to account for the observation, made above, that the increase in MgDA value from HF to CH_3F is much greater than that seen between H_2O and CH_3OH or between NH_3 and CH_3NH_2. The difference in dipole moments between any of the hydrides NH_3, H_2O, or HF and their methylated analogues is not substantial, while the increase in polarizability upon methylation is more-or-less constant for all three hydrides; notably, the lack of hydrogenation of the F donor atom in CH_3F ensures that for this species the axis of coordination is aligned with both the ligand's dipole moment and its principal axis of polarizability. This alignment of the coordination axis and the ligand's major axis (in all cases, its principal axis of symmetry) is seen also in the minimum-energy structures obtained for the $Mg(NH_3)^{2+}$, $Mg(OH_2)^{2+}$, and $Mg(FH)^{2+}$ adducts. In contrast, Mg^{2+}-coordination at the O of CH_3OH, or the N of CH_3NH_2, must occur in conjunction with the steric demands of the hydrogens attached to the donor atom, so that the coordination axis is angled very obliquely to the ligand's major axis. The magnitude of dipole induction in the $Mg(FCH_3)^{2+}$ adduct can be appreciated by comparing the molecular dication's F−C bond length of 1.636 Å (from optimization at B3-LYP/dB4G) with the bare ligand value of 1.388 Å. This substantial elongation also suggests that the molecular dication's structure can, in part, be described as a "fluoride-bound dimer" $Mg^{2+}\cdots F^-\cdots CH_3^+$; Mulliken charges ($q_{Mg} = +1.79$ $q_F = -0.64$, and $q_{CH_3} = +0.84$) lend some support to this description. While this phenomenon does not appear to have been noted in regard to Mg^{2+} coordination, similar effects have previously been discerned for metal ion/molecule complexes involving Li^+, Mg^+, and Al^+ among other cations,[71−73] although the "bond activation" effect seen for main-group metal monocations is generally rather weak when compared to the analogous proton-induced effect.[74,75] In contrast to the CH_3F bond activation, the O−C and N−C bond elongation seem upon Mg^{2+} complexation of methanol and methylamine is much less: the B3-LYP/dB4G values for the bare ligands (1.421 and 1.463 Å respectively) are increased by only 0.11 and 0.07 Å on coordination to Mg^{2+}.

Finally, the large magnesium dication affinity values reported here for many ligands do not, in themselves, provide an assurance of the dicationic adducts' thermodynamic stability. We have not considered the thermochemistry of any charge-separation processes such as partial charge transfer or methyl cation loss which, in several instances, may represent the most exothermic reaction pathways for reactions of the type $Mg^{2+} + X$. While the overall thermochemistry of such processes is quite readily accessible to methods such as CP-dG2thaw, these charge-separating reactions are routinely inhibited by Coulombic barriers arising from the electrostatic repulsion between proximate like-charged product ions.[40,76,77] Such barriers are difficult to quantify precisely, but we would envisage that for most, if not all, of the adduct dications investigated here these dissociative barriers are substantial and ensure that the molecular dications have at least a significant kinetic stability. In any event, the presence of Coulombic barriers for the charge-separating processes means that the thermochemistry of such processes is not readily measurable to high precision under laboratory conditions. Since a principal goal of the present study is to furnish a theoretical "ladder" of dicationic thermochemical values which can ultimately be verified (or proven inaccurate) by precise experimental measurements, we have restricted ourselves here to determining the parameters which appear best to meet such a criterion.

4. Conclusions

Our investigation of the impact of various factors on calculated magnesium dication affinity (MgDA) values has revealed that neglect of magnesium "innervalence" electron correlation has a significant effect on the binding energy. While previous studies have anticipated such a result, it has not previously been appreciated that neglect of basis set superposition error, at the levels of theory habitually employed in "high-accuracy" model chemistry methods such as G2, has a comparable and countervailing effect. Therefore, while G2 itself appears to deliver MgDA values which are somewhat too low (typically by ~4 kJ mol^{-1}), methods which include Mg 2s and 2p electron correlation but neglect a correction for BSSE usually overestimate the MgDA by a markedly larger margin.

Our "best" (CP-dG2thaw) values for the MgDA of a representative sample of small organic and inorganic ligands indicate that both the polarity and the polarizability of the ligand are important influences on the binding energy to Mg^{2+}, with the polarizability playing a proportionately larger role than is evident in similar calculations on Na^+-containing ions. The influence of the ligand's polarizability, which through the ion/induced dipole interaction has a tendency to divert electron density from more remote covalent bonds toward the ligand's donor atom, is evident in the substantial F−C bond elongation seen for CH_3F upon coordination to Mg^{2+}. More generally, the greater influence of polarizability on the binding energy to Mg^{2+} than to Na^+ has the result that Mg^{2+} shows a somewhat greater affinity for coordination to nonpolar species, and to second-row-containing species such as PH_3 and HCl; nevertheless, for both Na^+ and Mg^{2+} the binding energy to methylamine is found to exceed that for all of the other covalent ligands included in our sample.

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(52) We have chosen this parameter in preference to the value AE(Mg^{2+}), the appearance energy of the magnesium dication, because the latter quantity has a much larger (and more variable) "higher level correction" (HLC) in the various model chemistry methods. Since there is no HLC applicable to the MgDA values obtained by any G2-derived (or G3-derived) computational method, it is appropriate to examine IE(Mg^+) as the atomic ionization parameter for which the smallest possible HLC value is defined.

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(55) This observation suggests strongly that some effect arising from the energetic proximity of Mg and ligand atomic orbitals is operating here, since O, F, and Ne have valence orbitals (2s and 2p) which are closest, of any of the atoms represented in the ligand "test set", to the "valence" 2s and 2p orbitals of Mg^{2+}. This suggestion is consistent in some respects with our experience in determining sodium cation affinities,[18,43] where the proximity to the Na 2p orbitals of F and Ne 2s valence orbitals (and, to a lesser extent, those of O also) is problematic in calculations involving standard "frozen cores": calculations on Na^+ coordination to ligands not containing O, F, or Ne do not show such problems, while the F/Na orbital rankings substantially influence the calculated binding energies even when the ligand "donor atom" is not F itself.[43] In the present work, the apparently problematic influence of O, F, and Ne similarly extends to the calculated MgDA of CO, where the structure studied is the C-coordinated isomer (i.e., with no "direct" contact between Mg and O). It must be acknowledged, however, that population analyses for the various Mg dicationic adducts do not show any systematic dependence of mixing of Mg 2s, 2p and "donor atom" 2s, 2p orbital character on the presence or absence of O, F, and Ne in the ligands concerned, nor any particular dependence of orbital character on the use of the dB4G versus B4G basis set for magnesium. Furthermore, the counterpoise corrections for O-, F-, and Ne-containing ligands are not outstandingly different from those for the N-, P-, S-, and Cl-containing ligands, either for B4G- or for dB4G-derived counterpoise corrections. Thus, while some factors are suggestive of an effect arising from the energetic proximity of metal and ligand valence orbitals, the precise mode of operation of such a supposed effect remains unclear.

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