

Pseudopotential Calculations. 5. Results for Group 2A and 2B Dimethyls and Chlorides

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Abstract: Ab initio valence-only molecular orbital calculations, using an ab initio pseudopotential to represent the cores, are reported for (CH₃)₂Mg, (CH₃)₂Zn, ZnCl₂, MgCl₂, CH₃MgCl, and ZnF₂, all at experimental (electron diffraction) geometries. The calculations were performed in an attempt to study the effects on the bonding of the full 3d and 3p orbitals which distinguish these compounds. We find that, as expected, the bonding is nearly all of σ type; the d electrons in Zn seem unimportant for these bicoordinate species. Orbital energies and population analysis are contrasted with expectations based on electronegativities and Pearson's hard-soft principle; the latter seems slightly more helpful. The somewhat unusual bond distances reported in the literature are briefly discussed.

I. Introduction

One ultimate aim of molecular electronic structure calculations is, in Mulliken's words, to provide knowledge of what electrons really are doing in molecules. Since much of this knowledge, like much of descriptive inorganic chemistry, is relative rather than absolute (the prediction and explanation of changes with a homologous series or a row or a column of the periodic table), it is clearly extremely useful to produce ab initio self-consistent field calculations for such series of molecules. The core electrons, however, greatly impede performing such calculations, since they lead to great increases in the amount of computer time required. Although such comparative studies have been performed for a few special cases,^{2,3} and semiempirical arguments of the same type have proven very useful,⁴ there have not yet been enough high-quality, large basis calculations to provide much comparison of rigorous (orbital energies) or helpful (Mulliken populations) quantum mechanical results with such very useful concepts as atomic electronegativities, "hardness or softness", bond ionicity, covalent and ionic radius, etc. It is the aim of the present work to discuss such correlations for six simple compounds of the group 2 metals Mg and Zn, based on pseudopotential Hartree-Fock-Roothaan (HFR) calculations on (CH₃)₂Mg, CH₃MgCl, MgCl₂, ZnCl₂, ZnF₂, and (CH₃)₂Zn.

The essential difference between Mg and Zn is the presence of full 3p and 3d shells in Zn; qualitatively, the metals exhibit similar chemical properties in that the only really common oxidation state is plus two, the compounds tend to be colorless and ionic, the metals are good broad-band conductors, a well-defined set of coordination complexes exists, aquo ion pK_as differ by only one unit, the thermodynamics of atomization are similar, both have a number of organometallic derivatives, etc. There are, of course, significant differences brought about by the full p, d shells, the most striking of which is the larger ionic radius⁵ ($r_{\text{ionic}} = 0.74, 0.67 \text{ \AA}$ for Zn²⁺, Mg²⁺, respectively), which results, among other things, in Mg being "harder", less electronegative, and less prone to high coordination number than Zn. We wished to compare these trends of empirical inorganic chemistry with the results of our calculations on halides and organometallics of these metals. (We chose to compare Mg, rather than Ca, with Zn, because similarities between Zn and Mg are much greater than between Zn and Ca (or, indeed, between Ca and Mg). In particular, the ionic radii and the nature of the compounds formed are very similar for Mg and Zn; Ca(OH)₂ is far more soluble than the hydroxides of Zn or Mg, etc.)

The pseudopotential method explicitly calculates only the

valence electrons (1 for H, 4 for C, 7 for Cl or F, 2 for Mg, 12 for Zn); the effects of the atomic cores are replaced by an angular momentum dependent pseudopotential operator.^{6,7} These calculations thus lend themselves easily to comparison with ordinary concepts of valence. The pseudopotential method, the basis sets, and the chosen geometries are outlined very briefly in section II, while section III presents some results of our computations, some comparisons with ordinary bonding and valence concepts, and a short discussion.

II. Methodology. Pseudopotentials, Basis Sets, and Geometries

The ab initio effective potential method (which is called the pseudopotential scheme for convenience, although it is not really a pseudopotential in the ordinary sense)^{2b} provides a procedure for calculating explicitly the valence electron wave function for any given atom, molecule, or solid. The effects of the core are subsumed in a one-electron operator which is added to the Hamiltonian for the valence electrons. The pseudopotential scheme was first introduced into molecular structure theory by Hellmann⁸ and by Gombas.⁹ The pseudopotentials we employ were developed by Topiol et al.⁷ based on a formal procedure developed by Melius, Kahn, and Goddard.⁶ It is one of a rapidly growing number^{2b,3,10} of angular momentum dependent pseudopotentials being employed with conspicuous success by a number of groups. We have calculated a number of main-group and transition-metal species using this method in Hartree-Fock-Roothaan valence-only ab initio calculations, and have obtained results in excellent agreement with all-electron ab initio calculations, and one-electron energies in good agreement with photoemission spectra for several species.¹¹⁻¹⁶

The full formalism for development and use of the pseudopotential method is presented in extenso elsewhere.^{2b,6,7} To illustrate very briefly, we consider the case of an atomic calculation. The pseudopotential procedure replaces the Fock operator for the valence electrons

$$F_{\text{val}}(i) = h(i) + \frac{1}{2} \sum_{j \neq i=1}^{Z_{\text{core}}+Z_{\text{val}}} (2J_{ij} - K_{ij}) \quad (1)$$

where J_{ij} and K_{ij} are the usual Coulomb exchange operators,¹⁷ the sum on j runs over all electrons except i , and where

$$h(i) = \frac{-Z_{\text{core}}}{r_i} - \frac{Z_{\text{val}}}{r_i} - \frac{\hbar^2 \nabla_i^2}{2M_{\text{el}}} \quad (2)$$

by an effective Fock operator

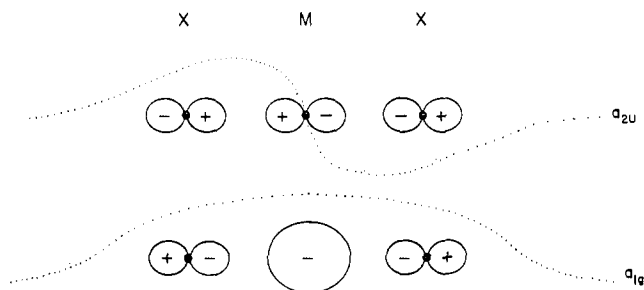


Figure 1. Simple schematic three-orbital picture of the σ bonding in MX_2 systems. Note that, by symmetry, the metal d_{σ} can contribute only to the a_{1g} bonding species. Solid lines represent atomic basis orbitals, dotted lines give molecular orbital contour. There are additional contributions from ligand s and metal s, d, which are omitted for clarity.

Table I. Metal-Ligand Bond Lengths (\AA)

M	X	Molecule	Distance (exptl)	Ionic radius sum ^a	Covalent radius sum ^a
Mg	F	MgF ₂	1.77 ^b	2.03	
Mg	Cl	MgCl ₂	2.18 ^b	2.48	2.45
Mg	C	(CH ₃) ₂ Mg	2.26 ^c		2.15
Zn	F	ZnF ₂	1.81 ^b	2.10	2.61
Zn	Cl	ZnCl ₂	2.05 ^b	2.05	2.30
Zn	C	(CH ₃) ₂ Zn	1.83 ^d		2.00

^a From ref 5. ^b From ref 19. ^c From ref 20. ^d From ref 18.

$$F_{\text{val}}'(i) = h'(i) + \frac{1}{2} \sum_{j \neq i, \text{core}+1} (2J_{ij} - K_{ij}) + V_{\text{pseudo}}(i) \quad (3)$$

Here

$$h'(i) = h(i) + \frac{Z_{\text{core}}}{r_i} \quad (4)$$

is the effective one-electron operator including only the nuclear charge Z_{val} , and only the Z_{val} valence electrons are included in the sum in eq 3. The pseudopotential, which includes both Coulomb and Pauli effects of the core on the valence, is given by

$$V_{\text{pseudo}}(r_i) = \sum_{L,M} |LM\rangle \langle LM| V_L(r_i) \quad (5)$$

$$V_L(r_i) = \sum_j A_j(L) e^{-\alpha_j(L)r_i^2} r_i^{\beta_j(L)} \quad (6)$$

$$V_{L > L_{\text{max}}}(r) \equiv V_{L_{\text{max}}}(r) \quad (7)$$

The coefficients in the pseudopotential expansion for any given angular momentum L are determined by reproducing the atomic eigenvalue (and, depending on the scheme, either matrix elements⁷ or orbital amplitude).² The approximation of eq 7 is required if the resulting pseudopotential is to be practical and to result in any real diminution of computational effort. It says that the effect of the core density is the same for all valence orbitals whose angular momentum is not present in the core, and are therefore not constrained by the Pauli principle to be orthogonal to the core. It has been extensively tested in atomic systems⁷ and for HF, and has been proven both necessary and accurate.¹³ The Gaussian form in eq 6 has been chosen for computational simplicity; values of the parameters A , α , and β are tabulated elsewhere.⁷

The valence basis sets employed in the present calculations are of double- ζ quality on C, H, and Zn (including two 4p-type functions on Zn) and of double ζ plus polarization quality on Mg, Cl, and F. The basis functions have been taken from a number of sources, and, for the valence functions, consist of

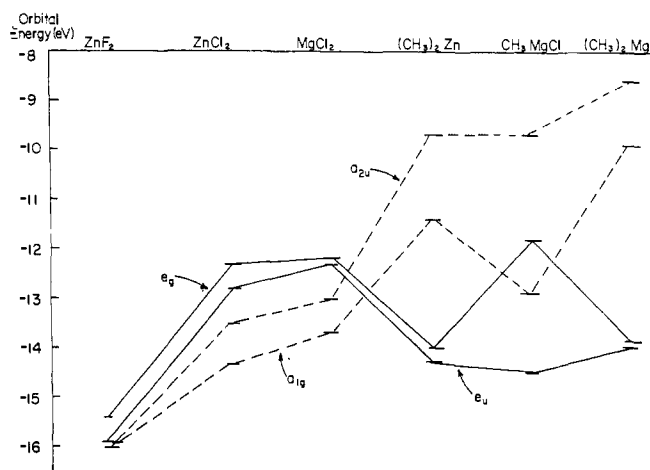


Figure 2. Calculated molecular orbital energies for the four highest occupied molecular orbitals.

n primitives contracted ($n - 1, 1$), where $n = 3, 4, 5$, based on atomic calculations;⁷ the basis sets and their sources are summarized in Appendix A.

We have not optimized geometry, but have instead employed bond lengths^{1,18} based on electron diffraction¹⁹ and crystallographic²⁰ measurements; the lengths employed are 2.26, 2.18, 1.83, 2.05, 1.81, and 1.098 \AA for Mg-C, Mg-Cl, Zn-C, Zn-Cl, Zn-F, and C-H bonds, respectively. These bond distances do not seem internally consistent (for Mg, the M-Cl bond is shorter than the M-C, whereas for Zn the M-Cl is longer; Mg-F is given as shorter than Zn-F, but Mg-Cl is longer than Zn-Cl), and do not fit the sums of either ordinary covalent or ionic radii, but are the best we have been able to obtain. The electron diffraction work¹⁹ from which these geometries (except for C-H, Zn-C, and Mg-C) were obtained gives only small error bars (± 0.02 \AA); the C-H distance in methyl groups is very well known. The Mg-C distance is based on crystallographic results.²⁰ Since all of the compounds are fairly polar, the bond distances found in the crystal might be very different, owing to Madelung effects, from those in the vapor-phase molecule. A theoretically determined (by energy minimization) calculation would seem the best way around this, but we have not yet completed such a study. The use of slightly dubious bond lengths may have some effect on our conclusions, or perhaps they may be explicable in terms of altered bonding (vide infra).

III. Results and Discussion

Tables II and III present the calculated orbital energies and the Mulliken population analysis for the six molecules we have calculated. The orbitals are labeled according to the irreducible representations of D_{3d} . For CH_3MgCl , there is no parity operation in the point groups, and therefore only the a_1 and e representation labels occur; we have assigned the levels in this molecule to correspond to the D_{3d} labels largely on the basis of orbital ordering, population analysis, and intuitive orbital shapes.

A. Role of π Bonding and of d-Orbital Participation. The most naive bonding picture for these linear MX_2 molecules ($X, Y = \text{CH}_3, \text{F}, \text{Cl}; M = \text{Mg}, \text{Zn}$) is a four-electron two-orbital one, similar to the Hückel description of allyl or to Pimentel's description²¹ of trihalide species. In this picture, the bonding is entirely σ , and arises firstly from the σ_g orbital of a_{1g} symmetry, which contains, in addition to the ligand contributions, only s and d contributions from the central metal, and secondly from the σ_u orbital of a_{2u} symmetry, which contains ligand plus only p contributions from the metal. The a_{1g} is, formally, bonding both in a two-center and in a three-center

Table II. Calculated Orbital Energies (eV)

Species	ZnF ₂	ZnCl ₂	(CH ₃) ₂ Zn	(CH ₃) ₂ Mg	CH ₃ MgCl ^a	MgCl ₂
Bond length	1.810 Å	2.049 Å	1.830 Å (Zn-C)	2.260 Å	2.260 Å 2.180 Å	2.180 Å
-ε(e _g)	15.43	12.27	14.01	13.93	11.75	12.19
-ε(e _u)	15.92	12.82	14.37	13.95	14.46	12.30
-ε(a _u)	15.97	13.46	9.67	8.56	9.71	13.00
-ε(a _{1g})	15.92	14.34	11.43	9.93	12.92	13.77
-ε(a _{1g}) ^b	23.79	23.90	20.48			
-ε(e _g) ^c	23.59	24.12	20.86			
-ε(e _g) ^b	23.85	24.39	21.17			
-ε(a _{2u}) ^d	40.35	29.03	24.25	23.72	24.27 ^e	28.47
-ε(a _{1g}) ^d	40.64	29.68	24.99	23.78	28.01 ^f	28.59

^a For this C_{3v} species, the (e_g, e_u) labels become simply e, and (a_{1g}, a_{2u}) become a₁. ^b Largely d electrons on metal. ^c Largely d electrons on metal. For dihalides, the symmetries are b_{1g}, b_{2g}. ^d Largely ligand s electrons. ^e Mostly on CH₃. ^f Mostly Cl s.

Table III. Mulliken Population Analysis

Molecule		ZnF ₂	ZnCl ₂	(CH ₃) ₂ Zn	MgCl ₂	(CH ₃) ₂ Mg	CH ₃ MgCl	
a _{2u}	M	s					16.3	
		p					10.7	
		d					0.5	
	X	C-2s			2.6		3.5	2.0
		C-2p			72.9		76.0	63.6
		H-1s			5.5		3.7	3.9
		Cl/F s	0.8	1.6		1.1		
X	Cl/F p	93.7	84.5		86.4		3.1	
	Cl/F d	0.1			0.3			
a _{1g}	M	s	15.4	22.3	36.0	18.1	36.6	12.6
		p						3.7
		d	8.0	3.1	4.0	0.6	1.7	0.6
	X	C-2s			0.5		1.0	
		C-2p			54.7		56.5	0.6
		H-1s			4.9		4.2	0.2
		Cl/F s	0.6	1.8		2.0		1.5
X	Cl/F p	75.0	72.4		79.0		80.6	
	Cl/F d		0.3		0.4		0.3	
e _u	M	s						1.9
		p	3.3	4.6	2.0	4.1	1.0	
		d						2.6
	X	C-2s						
		C-2p			53.0		52.6	
		H-1s			45.0		46.3	
		Cl/F s						
X	Cl/F p	96.6	95.2		95.8		95.3	
	Cl/F d		0.2		0.2		0.1	
e _g	M	s						0.5
		p						
		d	3.4	1.4	3.0	5.3	1.1	0.6
	X	C-2s						
		C-2p			51.4		52.5	53.0
		H-1s			45.6		46.5	45.9
		Cl/F s						
X	Cl/F p	96.5	98.5		94.6			
	Cl/F d				0.1			
Gross charge	M	1.36	0.92	0.65	0.71	0.60	0.64	
	Cl		-0.46		-0.36		-0.38	
	F	-0.68						
	C			-0.73		-0.71	-0.69	
	H			0.14		0.14	0.15	

sense, while the a_{2u}, which has a node at the metal, is bonding only for the single M-Y bonds (Figure 1). Qualitatively, this picture indeed describes most of the bonding interactions, although there is some minor additional contribution from metal-ligand π bonds. The orbital energies of the four highest molecular orbitals are plotted in Figure 2. The π_g(e_g) and π_u(e_u) orbitals consist very largely of density on the ligands,

with little overlap density with the metal d functions, indicating little metal-ligand π bonding. The very small splittings between the e_g and the e_u orbitals, one of which is π bonding and the other π nonbonding in the sense of a delocalized (three-center) bond, again illustrates the minor role of π bonding. Numerically, an effective Hückel-type resonance integral β_π for π bonding can be defined; the splittings for MgCl₂ and

$(\text{CH}_3)_2\text{Mg}$ would result in values of this parameter (just half the $\pi_u-\pi_g$ splitting) of 0.05 and 0.01 eV, respectively; the analogous β_σ would be (splitting over $\sqrt{2}$) 0.50 and 0.98 eV. The changes on going from Mg to Zn are much greater for the σ than for the π orbitals, again because the π 's are largely localized on the ligands. The Mulliken populations show that among these six compounds, the largest $d\pi$ -orbital participation is in MgCl_2 , and that even there it is only 5.3%. Thus it seems fair to conclude that, at least for the bicoordinate geometry, the role of π bonding in Zn and Mg alkyls and chlorides is very minor. Similar conclusions for the Zn case have been put forward previously,¹⁶ based on the success of a two valence electron Zn pseudopotential. When higher coordination numbers are considered, the π orbitals should be more important (for oxidative addition reactions, etc.), but for the compounds under consideration here, the σ bonds clearly dominate. These conclusions indicating little bonding role for the d electrons in linear Zn species have been drawn previously, both on theoretical and on experimental¹⁸ grounds, but the present theoretical results provide a quantitative indication of just how small the π character is. The only molecule studies here for which the π orbitals differ substantially in energy is CH_3MgCl , and there the lower π MO is almost pure Cl $2p\pi$, and the higher simply a CH_3 π function. The orbital energies are essentially those of the ligands, and no important π bonding effects are seen.²²

B. σ Bonding. The orbital energies are generally lower for the Zn compounds than for the Mg, due primarily to the lower metal atomic levels (-20.8 and -7.8 eV for Zn 3d, 4s, but -6.9 eV for Mg 3s). This is more pronounced for the σ orbitals, which contain considerable metal contribution, than for the (nearly pure ligand) π orbitals. Likewise, the dimethyl derivatives have σ orbitals much higher than the dichlorides (Cl s, p at -29 , -13.4 eV; C s, p at -19.2 , -11.8 eV). Conversely, the π orbitals lie higher for the dichlorides, where they consist principally of Cl 3p (-13.4 eV in atom), than in the dimethyls, where they are largely C 2p (-11.8) and H 1s (-13.6). This atomic orbital energy data would, in itself, imply that the dichloride π might lie below the dimethyl π . The population analysis, however, suggests that the relevant orbital would belong to $\text{Cl}^{-0.4}$ rather than Cl; this would give a Cl atomic energy of roughly -10 eV, which is above C 2p or H 1s, and indeed, fairly close to the e_g molecular orbital energy.

The difference in the σ bonding orbitals confirm some of the classical valence concepts, but seem sharply at variance with others. If we look first at overall charge balance, we see that in accord with Pauling's electroneutrality principle²³ the formal +2 charge on the central metal is never found—even ZnF_2 has an effective charge on Zn, from the population analysis, of only 1.36, while the other species all have formal charges on the metal between 0.5 and 1.0. Employing either Pauling²³ or Allred-Rochow²⁴ electronegativity differences, we observe (Table III) that the overall metal charge follows the electronegativity difference monotonically, but not linearly, for compounds of the same metal. In comparing the two metals, however, we note that the population analysis shows, both for the dimethyl and dichloro species, that the Mg compound exhibits a less polar charge distribution than the Zn compound. The rather polar nature of the RMgX material is consonant with the observation of Gilman²⁵ that CH_3MgCl heated to 100°C undergoes metathesis to the (less polar and less associated) $(\text{CH}_3)_2\text{Mg}$, which sublimes. The major factor rendering the metal-carbon bond less polar than the metal-halogen bond is the bonding a_{1g} orbital, which includes much larger metal s-orbital population for the dimethyls than for the dihalides. This can be rationalized from the perturbation theoretic viewpoint: the valence s-orbital energies²⁶ for Mg and Zn for -6.9 and -7.8 eV in the present basis, and are much closer to C 2p at -11.8 eV than to Cl 3s at -29 eV or Cl 3p at -13.5 .

Therefore we would expect greater metal s participation in the a_{1g} for dimethyls than for dichlorides. The match is even worse for Zn 4s with F 2s or 2p, and therefore there is less metal contribution to the a_{1g} in ZnF_2 than in ZnCl_2 . The generalization that reactivity of metal alkyls decreases as the metal electronegativity increases²⁸ may relate to the higher σ orbital energies found for $\text{Mg}(\text{CH}_3)_2$ than for $\text{Zn}(\text{CH}_3)_2$, but the relationship between orbital energy and reactivity is certainly not firm.

It is interesting to attempt further comparison of the observed orbital energies and populations with some of the qualitative valence concepts so useful in inorganic chemistry. We have seen that for comparing the differing ligands on either metal the empirical electronegativity scales correlate fairly well with the gross Mulliken populations. For the CH_3MgCl , the charge on Cl^- is half again as great as on the methyl, consonant with higher Cl electronegativity. The higher bonding a_1 orbital in CH_3MgCl is strongly Mg-C bonding, and has roughly 64% of its density on the electronegative C atom. The lower a_1 is strongly Cl-Mg bonding, but is even more polar (82% on Cl), owing to the higher electronegativity difference. For predicting relative polarity of Mg-X and Zn-X bonds, however, the Mulliken populations and the electronegativities disagree. (The older concept of carbon-metal bond ionic character as calculated by Hannay and Smyth²⁹ is simply contradictory to the Mulliken populations; they obtained 27 and 20% ionic character for C-Mg and C-Zn, respectively.) Part of these disagreements must spring from the rather arbitrary charge partitioning inherent in the Mulliken analysis, and some from our use of uncertain bond lengths. But even allowing these sources of error, the large differences in calculated and expected charge balance seems to require some further explanation.

Some help is available from Pearson's notion³⁰ of hard and soft acids and bases. Pearson, extending some notions of Chatt,³¹ pointed out that uncharged or slightly charged polarizable species with available low-lying excited orbitals, which he called "soft" acids and bases, will tend to interact with each other rather than with small, charged, low-polarizability (hard) species. By "interact" we mean form a complex by the general Lewis acid-base mechanism. Pearson and many others have applied this concept to interpretations of mechanisms, thermodynamics, complex formation, adsorption, precipitation etc., while theoretical justifications of the general principle have been given by several workers.³⁰ Now in Pearson's nomenclature Mg^{2+} is a hard acid, CH_3^- a soft base, Cl^- a rather hard base, F^- a very hard base, and Zn^{2+} a borderline acid. We would thus expect, on the general interaction principle, that the interaction strength in our molecules would run roughly $\text{Cl-Mg} \gg \text{F-Zn} > \text{Cl-Zn} \sim \text{CH}_3\text{-Zn} > \text{CH}_3\text{-Mg}$. The mechanism of interaction is considered, in the hard-soft classification, to be largely covalent between soft species, and largely ionic between hard. Thus the hard-soft principle would suggest:

1. The soft-borderline $\text{CH}_3\text{-Zn}$ interaction should be stronger than the soft-hard $\text{CH}_3\text{-Mg}$. This agrees with the larger $\sigma_g-\sigma_u$ splitting in the Zn species.
2. The hard base bonds involving F and Cl should be more polar than the soft base bonds involving CH_3 . This holds, both for the symmetric molecules and for CH_3MgCl .
3. The softer metal, Zn, should be less highly charged than the harder Mg. This is in agreement with electronegativity, in disagreement with the population analysis.
4. Because hard interactions are more ionic than covalent, the $\sigma_g-\sigma_u$ splitting should be larger for the ZnX_2 than for the MgX_2 , and larger for the dimethyls than for the dichlorides. This agrees with the observed orbital energies.
5. Because the harder Cl^- should interact more strongly with hard Mg^{2+} than will the soft base CH_3 , we expect the lower

lying σ bonding orbital in CH_3MgCl to consist largely of density on the Cl^- , the upper σ to be largely on the methyl (the stronger interaction lowers the energy of the bonding combination). This is in agreement with the population analysis, which shows 82% on Cl and 69% on CH_3 , for the lower and higher, respectively.

6. Although the experimental bond distances we have used correlate smoothly with neither ionic nor covalent radii, some can be rationalized by the hard-soft principle. The strong hard-hard interaction renders MgCl_2 abnormally short, while the unfavorable hard-soft interaction leads to normal or long (compared with radius sums) ZnCl_2 and Mg-CH_3 distances. As shown in Table I this is precisely what is observed.³²

These arguments are all based on the solution characteristics of the ionic species Mg^{2+} , Zn^{2+} , and X^- . In the gas phase or in media with very low dielectric constant, for which our calculations are relevant, the covalent, rather than ionic, criteria may be relevant (indeed, Pearson remarks³³ that in some cases relative softness and hardness may invert in going from solution to vapor phase). It is therefore tempting to argue that the greater metal charge in $(\text{CH}_3)_2\text{Zn}$ than in $(\text{CH}_3)_2\text{Mg}$ is due to Mg in fact being slightly softer as judged by its covalent radius (1.4 Å) than by its ionic radius (0.67 Å) compared to Zn ($r_{\text{cov}} = 1.2$ Å, $r_{\text{ion}} = 0.74$ Å). This still would not entirely explain the Mulliken charge balance in the dichlorides.

It must always be remembered that calculations such as these, which utilize rather small basis sets, are subject to several inherent limitations. For the present arguments, the most serious difficulty relates to the calculated Mulliken populations. Since all the Mg calculations were done with the same Mg basis sets and all Zn calculations with the same Zn basis, comparison of the relative populations of the three Zn or the three Mg compounds among themselves is meaningful. Since, however, the Mg and Zn bases are not strictly comparable, direct comparison of Mg to Zn populations may be misleading and we note above that such comparisons, with the present results, are contrary to expectations based on electronegativity and on chemical intuition. Thus we feel that, while our energies and relative populations within the compounds of one metal are useful and meaningful, the population comparison between metals is more tenuous. One solution to this difficulty, which has been utilized by Pople and co-workers, involves the use of specially designed "balanced" basis sets.³⁴

We feel that the present calculations, though somewhat fragmentary, are highly suggestive. To further increase our understanding of the bonding in these d^0 and d^{10} systems, additional quantities, such as density matrix elements, dissociation energies, force constants, and particularly density differences, should be calculated and compared to experiment. These can all be done within the pseudopotential scheme, and efforts in these directions are continuing. The comparisons with electronegativity and hard-soft arguments may also be slightly premature (especially considering the uncertain bond distances employed),²⁰ but we feel that one important function of electronic structure calculations is to aid in the establishment of general conceptual schemes of this type by pointing out where disagreements occur. These computations do permit strong statements concerning the small role of π bonding for a number of bicoordinate d^0 and d^{10} complexes, and, together with comparisons with photoemission spectra and all-electron Hartree-Fock-Roothaan calculations,^{2,6,7,10-16} help to establish the validity and accuracy of the present pseudopotential method.

Acknowledgments. We are grateful to Professor Max Goldstein of the ERDA Courant Computer Center for a particularly generous grant of computer time, and to the National Science Foundation for sponsorship of the Northwestern research. We also thank D. F. Shriver, J. A. Ibers, G. M. Ban-

croft, H. Basch, C. F. Melius, and L. R. Kahn for helpful conversations.

Appendix A. Basis Sets Employed

Atom	Basis	Reference
Zn	s(3/2,1)	7
	d(5/4,1)	35
	p(2/1,1)	35
F	s(4/3,1)	2
	p(5/4,1)	36
	d(1/1)	Present work
Cl	s(3/2,1)	2
	p(4/3,1)	7
	d(1/1)	34 ^a
Mg	s(3/2,1)	7
	p(3/2,1)	7
	d(1/1)	34

^a We have averaged the HCl (0.53) and Cl_2 (0.44) exponents of Pople et al.³⁴

References and Notes

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The Shapes and Other Properties of Non-Transition Element Complexes. 1. AB_6

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Abstract: Qualitative MO methods are used to study the properties of six-coordinate complexes of the main group elements of the periodic table. The hexahalides are emphasized. The simplest possible AO basis set is used to form MOs. No d orbitals are considered. MO correlation diagrams are presented to compare energies of AB_6 complexes in octahedral (O_h) and trigonal prismatic (D_{3h}) geometries. The O_h and D_{3h} conformations possible for AB_6 complexes are compared to the staggered and eclipsed conformations of ethane. The qualitative MO model predicts that 12-electron complexes (PF_6^- , SF_6 , ClF_6^+ , for example) should be rigidly octahedral but the 14-electron complexes (XeF_6 and isoelectronic species) should be considerably less rigidly octahedral. For the 14-electron series there should be a trend of increasing ease of distortion from octahedral shape with decreasing difference in electronegativity between the central atom and the ligands. No ten-electron complexes are known. The qualitative model predicts these to be open-shell cases and octahedral. Complexes with six and eight electrons should be trigonal prismatic. Reported examples are LiH_6^+ and $BF_2H_4^+$. MO correlation diagrams describe the dissociation of AB_6 complexes into $AB_4 + B_2$. Qualitative MO arguments are used to explain the differences in bond lengths and strengths between 12- and 14-electron complexes and to rationalize trends in complex stabilities as related to ligand substitution.

Introduction

Our object in this paper is to explain, rationalize, or predict as many of the properties of selected AB_6 complexes as possible using qualitative arguments within the framework of molecular orbital (MO) theory and relying on a single well-defined model that can be applied to other classes of complexes. Many of the properties discussed here have already been explained, perhaps even more simply, by using a diverse set of models. The point here is unity. One justification for this is aesthetics: it is pleasing to have a single model that explains a large number of facts and MO theory does provide a well-defined connection between the qualitative concepts and the basic laws of physics that underlie chemistry. A more practical reason is that MO theory is the most successful and convenient method for the quantitative application of quantum mechanics to chemistry. Therefore, a powerful computational method exists for testing the arguments and conclusions of the qualitative MO model. Such checks are not always possible or convenient for other qualitative models.

For the complexes to be considered here, the central atom A will be one of the main group elements of the periodic table. To limit our study further we will consider only those complexes in which the ligands B are individual atoms. In most cases the ligands are halogens, although a few oxides are known. We will also mention some real and hypothetical examples which involve hydrogen ligands. We omit transition metal complexes in order to avoid discussion and representation of d atomic orbitals, although similar arguments could be

applied to them. We will compare octahedral (O_h) and trigonal prismatic (D_{3h}) structures. In a recent paper Hoffmann, Howell, and Rossi³ have used extended Hückel calculations and qualitative MO arguments to rationalize the preference of most AB_6 complexes for octahedral geometry. They also consider a bicapped tetrahedral structure. Hoffmann, Howell, and Rossi have studied the transition metal complexes and the effect of d atomic orbitals, topics we have ignored. Besides the 12-valence electron complexes of the main group elements reviewed by Hoffmann and co-workers, we consider structures for 6-, 8-, 10-, and 14-electron complexes. We also discuss other properties including dissociation mechanisms, bond lengths and strengths, and relative stabilities of AB_6 complexes. Urch has also published an important qualitative study of the relative stabilities of non-transition element AB_6 complexes.⁴

Many of the rules of qualitative MO theory have already been discussed elsewhere,² but in this and subsequent papers we will use additional arguments which we present here. The qualitative MO model follows the formalism of the extended Hückel method.⁵ The MOs ϕ_k are formed by linear combinations of normalized atomic orbitals (AOs) χ_r : $\phi_k = \sum_r c_{rk} \chi_r$. The MOs must be normalized:

$$\langle \phi_k^2 \rangle = \sum_r c_{rk}^2 + 2 \sum_{r < s} c_{rk} c_{sk} S_{rs} = 1 \quad (1)$$

where S_{rs} is the overlap between AOs χ_r and χ_s . The total energy E of a molecule is the sum of the energies ϵ_k of occupied MOs: $E = \sum \epsilon_k$, where the summation is over the valence electrons. The orbital energy ϵ_k can be calculated as $\epsilon_k =$