Al.[16] This also is rationalized by hard-soft acid-base theory whereby the soft base R will migrate more readily to the softer metals than to the harder ones. The tendency is now opposite to that shown in F migration.

Elimination of neutral HF is not detected for the present complexes or for the analogous complexes of the other lanthanides[13,14] although it is reported as low-abundance $[ML_2F - CF_3 - HF]^+$ from tpa complexes of Al, Cr, and Fe[16] and tpa and tta complexes of In.[15] The suggested mechanism involves transfer of F^- from the metal to the γ-hydrogen of the ligand,[16] which should be difficult with the strong M-F bond that the hard metals provide.[19]

Comparing the ligands for the CeL_4 complexes, one sees that for most fragments the relative abundance is greatest when L = tta and least when it is tba. As discussed above, fragmentation to $[CeL_2]^+$ and beyond is believed to proceed from the odd-electron $[Ce^{III}L_3]^{+\cdot}$ ion. Formation of this from the even-electron $[Ce^{IV}L_3]^+$ requires the ligand to reduce the metal. This ability should be in the order tta > tpa > tba since the aromatic ring in tta and tpa, especially with the sulfur atom in tta, should favor oxidation of the ligand to a radical.

Other mass spectrometric studies involving chelates with some of the present ligands confirm the trends already mentioned. These chelates are of the type EuL_3,[21,22] PdL_2, and UO_2L_2.[23]

Conclusions

The mass spectra of the present CeL_4 complexes are understandable in terms of an ion-fragmentation scheme dominated first by Ce(IV) and then by Ce(III) with extensive rearrangement.

Facile loss of L· from the molecular ion to form $[CeL_3]^+$ gives the base peak. In that the Ce(IV) state is maintained in this ion and in others such as $[CeL_2F]^+$, these complexes resemble the analogous complexes of the group 4 transition metals.

The availability of the Ce(III) state and the ability of these ligands, especially those with aromatic substituents, to provide a radical site permit reduction of Ce(IV) by the ligand. This is followed by expulsion of L· to give $[CeL_2]^+$.

Fragmentation beyond $[CeL_2]^+$ resembles that of the tris complexes of the other lanthanides. Nearly every step involves rearrangement, especially fluorine migration from ligand to metal, which is favored by the hard-acid character of the metal. This involves an even-electron ion losing an even-electron neutral such as CF_2, CO, or RF. For loss of the latter two species, new mechanisms are proposed.

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Registry No. $Ce(tba)_4$, 35654-86-5; $Ce(tpa)_4$, 42730-87-0; $Ce(tta)_4$, 36733-44-5.

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Contribution from the Gibbs Chemical Laboratory, Harvard University, Cambridge, Massachusetts 02138,
and Department of Chemistry, Auburn University, Auburn, Alabama 36849

Ab Initio Study of Additivity. 2

M. L. McKEE and W. N. LIPSCOMB*

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The addition of energy changes when correlation or polarization effects are included in a starting basis set is compared with the results when both effects are included, starting from several different basis sets. If the starting basis is STO-3G for a selected set of molecules, additivity holds quite well, but the relative total energies of these molecules are not accurate. This accuracy is improved if polarization corrections (STO-3G to STO-3G*) and correlation corrections (STO-3G to MP2/STO-3G), obtained at a single-ζ basis set level, are applied to the relative energies obtained at a double-ζ basis set level, 6-31G. This procedure allows tolerably good energies in moderately large molecular systems.

Method

In studies of molecular orbital energetics of complex molecules it is often impractical to include both polarization (d orbitals on first-row atoms, p orbitals on H) and correlation. Hence, some approximate methods must be employed. One such method is to obtain energies for a reaction or isomerization, a → b, at an appropriate starting level such a 6-31G (double-ζ) basis, to extend that basis with either polarization or correlation (double excitations CID, or MP2, or MP3), and then to add these two energy increments in order to approximate the much larger calculation in which both effects are included. In several studies[1-16] the errors of this "additivity" are usually small (a few kcal/mol) when the results are compared to the full calculation for the process a → b. In our systematic study[1] the reference wave function was CID/6-31G**, while the starting set for extension was 6-31G. Here, we examine the results for several processes a → b of basis set extension and correlation (CID, MP2, MP3) starting from either STO-3G or 6-31G basis sets (eq 1-6). Equation 7 is the additivity approximation.

$$(\mathrm{CID/6\text{-}31G^{**}} - \mathrm{6\text{-}31G})_b - (\mathrm{CID/6\text{-}31G^{**}} - \mathrm{6\text{-}31G})_a = \Delta_{\mathrm{pol-cor}} \quad (1)$$

$$(\mathrm{6\text{-}31G^{**}} - \mathrm{6\text{-}31G})_b - (\mathrm{6\text{-}31G^{**}} - \mathrm{6\text{-}31G})_a = \Delta_{\mathrm{pol}} \quad (2)$$

$$(\mathrm{CID/6\text{-}31G} - \mathrm{6\text{-}31G})_b - (\mathrm{CID/6\text{-}31G} - \mathrm{6\text{-}31G})_a = \Delta_{\mathrm{cor}} \quad (3)$$

$$(\mathrm{CID/STO\text{-}3G^{*}} - \mathrm{STO\text{-}3G})_b - (\mathrm{CID/STO\text{-}3G^{*}} - \mathrm{STO\text{-}3G})_a = \Delta_{\mathrm{pol-cor}} \quad (4)$$

$$(\mathrm{STO\text{-}3G^{*}} - \mathrm{STO\text{-}3G})_b - (\mathrm{STO\text{-}3G^{*}} - \mathrm{STO\text{-}3G})_a = \Delta_{\mathrm{pol}} \quad (5)$$

$$(\mathrm{CID/STO\text{-}3G} - \mathrm{STO\text{-}3G})_b - (\mathrm{CID/STO\text{-}3G} - \mathrm{STO\text{-}3G})_a = \Delta_{\mathrm{cor}} \quad (6)$$

$$\Delta_{\mathrm{pol}} + \Delta_{\mathrm{cor}} \approx \Delta_{\mathrm{pol-cor}} \quad (7)$$

In Table I we compare, for the reaction a → b, the energy increment from the STO-3G or 6-31G basis to a basis that includes

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Table I. Energy Stabilization for Both Polarization and CI (at CID, MP3, or MP2 Levels) over the 6-31G or STO-3G Level for the Reaction a → b (e.g., $B_2H_6 \rightarrow 2BH_3$) (Error Associated with Adding Increments in Energy due Separately to Polarization and CI in Parentheses; Values in kcal/mol; More Classical Species Given Last under Pair)

pair	basis[a]	CID	MP3	MP2
B_2H_6 vs. $2BH_3$	6-31G**	24.9 (2.9)	26.3 (3.4)	27.7 (4.2)
	6-31G*	24.2 (3.3)	25.4 (3.5)	26.4 (4.0)
	STO-3G*	26.1 (4.6)	27.0 (4.7)	27.1 (4.9)
$B_2H_5^+$ vs. $B_2H_5^+$[c]	6-31G**	18.2 (−0.1)	18.9 (0.4)	19.7 (1.1)
	6-31G*	18.8 (2.4)	19.3 (2.6)	19.5 (2.7)
	STO-3G*	22.0 (2.1)	22.3 (3.4)	21.9 (3.5)
B_2H_4 vs. B_2H_4[d]	6-31G**	33.2 (−1.7)	34.7 (−0.3)	37.7 (1.3)
	6-31G*	33.0 (0.9)	34.0 (1.9)	36.3 (2.8)
	STO-3G*	46.2 (1.4)	46.4 (2.8)	46.4 (3.4)
BH_5 vs. $BH_3 + H_2$[b]	6-31G**	23.4 (3.9)	24.5 (4.3)	25.2 (4.8)
	6-31G*	18.9 (3.0)	19.8 (3.3)	20.3 (3.6)
	STO-3G*	18.3 (3.8)	18.9 (4.1)	18.8 (4.4)
H_2O vs. H_2O[e]	6-31G**	10.7 (−2.1)	10.5 (−2.0)	10.2 (−1.8)
	6-31G*	11.9 (−3.7)	11.6 (−3.7)	11.3 (−3.6)
	STO-3G*	16.1 (−3.1)	15.7 (−2.6)	14.8 (−1.8)
NH_3 vs. NH_3[f]	6-31G**	8.3 (−0.4)	8.2 (−0.3)	8.0 (−0.1)
	6-31G*	8.5 (−1.1)	8.3 (−1.1)	8.1 (−1.0)
	STO-3G*	10.7 (−1.6)	10.4 (−1.4)	10.3 (−1.0)
F_2 vs. F_2[g]	6-31G*	3.1 (−0.4)	1.4 (0.0)	1.8 (−0.1)
	STO-3G*	12.1 (−4.6)	7.8 (−3.2)	3.9 (−2.4)
N_2 vs. N_2[h]	6-31G*	9.7 (0.1)	4.5 (2.1)	19.2 (−1.4)
	STO-3G*	10.1 (−0.6)	5.4 (1.7)	18.5 (−1.9)

[a] For example, the first entry, 24.9 kcal/mol, is for the reaction $B_2H_6 \rightarrow 2BH_3$, the energy difference between the CID/6-31G** value and the 6-31G value. The number in parentheses is the energy (CID/6-31G** − 6-31G) − {(CID/6-31G − 6-31G) + (6-31G** − 6-31G)}. [b] Single molecule vs. separated. [c] Double bridged vs. single bridged. [d] Double bridged vs. single B-B bond (eclipsed). [e] Linear vs. bent. [f] Planar vs. pyramidal. [g] F-F bond: 1.418 vs. 1.518. [h] N-N bond: 1.194 vs. 1.294.

Table II. Energy Lowering (kcal/mol) from a 6-31G or STO-3G When Polarization Is Introduced and Comparison of Single- vs. Double-ζ Basis Results

	basis set			
pair[a]	6-31G**	6-31G*	STO-3G*	STO-3G − 6-31G
$B_2H_6 \rightarrow 2BH_3$	7.7	6.6	11.4	2.2
$B_2H_5^+$ vs. $B_2H_5^+$	10.5	8.8	12.9	4.7
B_2H_4 vs. B_2H_4	12.7	9.8	14.2	36.6
BH_5 vs. $BH_3 + H_2$	8.9	5.3	7.2	−11.7
H_2O vs. H_2O	9.7	12.5	11.5	43.9
NH_3 vs. NH_3	7.7	8.6	9.1	11.6
F_2 vs. F_2	5.7	5.7	2.3	−16.9
N_2 vs. N_2	4.8	4.8	10.4	5.7

[a] See Table I. [b] Single- vs. double-ζ basis results.

Table III. Energy Lowering (kcal/mol) from a 6-31G or STO-3G Basis When Correlation Is Introduced

	6-31G			STO-3G		
pair[a]	CID	MP3	MP2	CID	MP3	MP2
B_2H_6 vs. $2BH_3$	14.3	15.2	15.8	10.1	10.9	10.7
$B_2H_5^+$ vs. $B_2H_5^+$	7.7	8.0	8.1	6.0	6.0	5.6
B_2H_4 vs. B_2H_4	22.3	22.3	23.7	30.6	29.4	28.8
BH_5 vs. $BH_3 + H_2$	10.6	11.3	11.4	7.3	7.7	7.3
H_2O vs. H_2O	3.1	2.8	2.3	7.7	6.8	5.1
NH_3 vs. NH_3	1.0	0.8	0.4	3.2	2.8	2.2
F_2 vs. F_2	9.2	7.1	7.6	19.0	13.3	8.5
N_2 vs. N_2	14.4	7.1	25.4	21.2	14.0	30.9

[a] See Table I.

both polarization and correlation. In parentheses the error in use of the approximate eq 7 is presented. The standard error is 2.0 kcal/mol with CID, 2.0 kcal/mol with MP3, and 2.6 kcal/mol with MP2 for correlation. Here, additivity is a good approximation. The STO-3G* basis has d orbitals with an exponent of 0.6 for B and 0.8 for O, N, and F. We recommend indication of the approximated energy increments (eq 7) by enclosing the basis set in brackets. For example [CID/6-31G**] indicates that correlation is calculated at the CID/6-31G level and polarization at the 6-31G** level starting from the reference 6-31G level. In moderately complex molecules even these two separate calculations, CID/6-31G and 6-31G**, may become formidable. Hence, we explore here the use of simpler basis sets.

The first decrease in level, from 6-31G** to 6-31G* omits polarization (p functions) on H atoms. In Table II we show that this change causes at most a difference of 3 kcal/mol in the polarization correction. In electron-deficient systems examined here, the 6-31G* basis accounts for about 80% of the polarization increment, as compared with the 6-31G** basis. Of course, the more similar the two structures, the smaller will be the correction. Also, the correlation corrections refer to the 6-31G basis and are therefore the same for use with either the 6-31G** or 6-31G* results.

A more severe decrease in level occurs when polarization and correlation corrections are made from the STO-3G basis. The limitations of a minimal basis set are well-known. Fairly large errors can be seen in Table II, where the effect of adding polarization on the first-row atoms is shown upon comparison of the last two columns. Even when d orbitals are added to a minimal basis set to give angular flexibility, the in–out flexibility is insufficient when only a single exponent is available. In Table III, we summarize the energy lowering obtained by introducing correlation (CID, MP3, MP2) into the 6-31G or the STO-3G basis sets.

In the cases considered, the difference between 6-31G and STO-3G energies was as large as 44 kcal/mol (Table II, last column). In comparison, with the polarization increment (STO-3G to STO-3G*) and correlation increment (STO-3G to CID/STO-3G; STO-3G to MP3/STO-3G; STO-3G to MP2/STO-3G)

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Table IV. Total Reaction Energies (kcal/mol) from Different Schemes for Estimating Polarization and Correlation

		[(CID, MP3, MP2)/6-31G*]			[(CID, MP3, MP2/STO-3G*]			{(CID, MP3, MP2)/STO-3G}[b]		
pair[a]	CID/ 6-31G**	CID	MP3	MP2	CID	MP3	MP2	CID	MP3	MP2
B_2H_6 vs. $2BH_3$	38.6	34.6	35.5	36.1	37.4	38.2	38.0	35.2	36.1	35.8
$B_2H_5^+$ vs. $B_2H_5^+$	19.2	17.5	17.8	17.8	15.2	15.2	14.8	19.9	19.8	19.4
B_2H_4 vs. B_2H_4	13.2	14.2	14.3	12.9	38.2	39.4	40.0	1.6	2.8	3.4
BH_5 vs. $BH_3 + H_2$	6.1	13.6	12.9	12.7	26.6	26.3	26.6	15.0	15.0	15.0
H_2O vs. H_2O	37.0	41.9	41.6	41.1	89.4	88.5	86.8	45.5	44.6	42.9
NH_3 vs. NH_3	7.1	8.3	8.1	7.8	22.6	22.2	21.7	11.0	10.6	10.0
F_2 vs. F_2	1.8	1.4	3.5	3.0	5.1	10.8	15.6	−11.8	−6.1	−1.3
N_2 vs. N_2	28.6	28.6	36.0	17.8	21.8	29.0	12.1	27.6	34.7	17.9

[a] See Table I. [b] Correlation estimated using CID, MP3, or MP2 treatment at STO-3G level and polarization estimated at STO-3G* level are added to relative energies at 6-31G level.

Table V. Sum of Polarization and Correlation Increments Estimated from 6-31G Basis ($\{\Delta_{pol} + \Delta_{CI}\}_{6\text{-}31G} - \{\Delta_{pol} + \Delta_{CI}\}_{STO\text{-}3G}$ in Parentheses), All Values Being Given in kcal/mol

	$(\Delta_{pol})_{6\text{-}31G^{**}} + \Delta_{CI}$			$(\Delta_{pol})_{6\text{-}31G^{*}} + \Delta_{CI}$		
pair[a]	CID	MP3	MP2	CID	MP3	MP2
B_2H_6 vs. BH_3	22.0 (0.5)	22.9 (0.6)	23.5 (1.3)	20.9 (−0.6)	21.9 (−0.4)	22.4 (0.2)
$B_2H_5^+$ vs. $B_2H_5^+$	18.3 (−1.6)	18.5 (−0.4)	18.6 (0.0)	16.4 (−2.5)	16.7 (−2.2)	16.8 (−1.8)
B_2H_4 vs. B_2H_4	34.9 (−9.9)	35.0 (−8.6)	36.4 (−6.6)	32.1 (−12.7)	32.1 (−11.5)	33.5 (−9.5)
BH_5 vs. $BH_3 + H_2$	19.5 (5.0)	20.2 (5.4)	20.4 (6.0)	15.9 (1.4)	16.5 (1.6)	16.7 (2.3)
H_2O vs. H_2O	12.8 (−6.4)	12.5 (−5.8)	12.0 (−4.6)	15.6 (−3.6)	15.3 (−3.0)	14.9 (−1.7)
NH_3 vs. NH_3	8.7 (−3.6)	8.5 (−3.3)	8.1 (−3.2)	9.6 (−2.7)	9.4 (−2.5)	9.1 (−2.2)
F_2 vs. F_2				3.5 (−13.2)	1.4 (−9.6)	1.9 (−4.3)
N_2 vs. F_2				9.6 (−1.1)	2.3 (−1.3)	20.6 (0.1)

[a] See Table I.

in conjunction with the STO-3G energy, reaction energies were predicted up to 52 kcal/mol (89.4–37.0; Table II) in error when compared to the CID/6-31G** reaction energies (Table IV). That the difference in the 6-31G to STO-3G reaction energy is primarily responsible for this discrepancy can be seen by comparing the polarization and correlation increments from the 6-31G basis and from the STO-3G basis.

The largest difference in the polarization increment (6-31G polarization increment minus the STO-3G polarization increment) is 5.6 kcal/mol for N_2 (4.8–10.4; Table II). In fact, the polarization increment from the STO-3G basis (adding d orbital on first row) is closer to the polarization increment predicted when d orbitals are added to first-row atoms and p orbitals to hydrogen (6-31G**) than when only d orbitals are added to first-row atoms (6-31G*; Table II).

When correlation increments from the 6-31G basis and from the STO-3G basis are compared, the largest difference is 9.8 kcal/mol for F_2 (9.2–19.0; Table III). If we leave out F_2, N_2, and B_2H_4, three difficult cases, the largest difference drops to 5.1 kcal/mol (15.8–10.7; Table III).

Interestingly, the difference in the polarization increment starting from 6-31G as compared to starting from STO-3G is often of different sign from that of the difference in the correlation increment estimated at 6-31G compared to STO-3G. Therefore, one finds better agreement between the sum of the polarization and correlation increments starting from 6-31G as compared to starting from STO-3G than is shown by either of the increments separately. The agreement between the sum of polarization and correlation increments from the 6-31G and STO-3G basis sets is demonstrated in Table V. If B_2H_4 and N_2 are omitted, the largest error is found to be 6.4 kcal/mol for H_2O (Table V). Thus, the STO-3G basis usually provides a good estimate of polarization and correlation *increments* but not of reaction energies that require a better in–out flexibility in the basis set for the molecules that we have examined here.

If polarization and correlation estimates are to be made for a large system, it may be permissible to make the corrections at the STO-3G* and the MP2/STO-3G levels and then apply these corrections to the relative energies at the 6-31G level. This procedure is based on the assumption that additivity can be taken one step further and that the effect due to in–out flexibility in the basis is somewhat independent of the angular flexibility and electron correlation. Of course, this approximation is somewhat drastic, and it may have only limited application; but, in the case of electron-deficient boron hydrides it seems to hold reasonably well.

For B_2H_6, a more typical boron hydride, the difference in the methods of estimating polarization and correlation increments is less than 1 kcal/mol. It can therefore be hoped that increments from the STO-3G level will have some utility in calculating boron hydride reaction energies and, perhaps, a wider application.

Conclusion

We have found that application of polarization increments at the 6-31G* level and correlation increments at the MP2/6-31G level leads to reaction energies that deviate by only ±2 kcal/mol (excluding N_2) from reaction energies calculated at the CID/6-31G** level. This additive method can yield energies in about one-tenth of the computational time of single calculations in which both polarization and correlation are included.

The effects of additivity have been explored here at lower levels. We have found that estimates of polarization and correlation corrections at the single-ζ level provide tolerable accuracy if they are added to relative energies at the double-ζ (SCF) level. For electron-deficient systems the standard error (based on CID/6-31G** results) is approximately ±5 kcal/mol.

Additivity for molecules with large numbers of lone pairs, N_2 and F_2, seems to be obeyed (see Table I); however, for these molecules there is a large variation in relative energies when various basis sets and correlation methods are used (see Table IV).

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