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Steric Packing and Molecular Geometry.
I. Simulation on Tetrahedral Structures of Weak Covalent Bonding

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Abstract

In the first attempt, the molecular geometries of more than 50 tetrahedral structures of f-block and group IVB transition metal organometallic compounds were simulated based on the uniform packing principle. The results are in good agreement with those obtained by X-ray diffraction. It thus provides clear evidence that steric packing plays the dominant role in structures of weak crystal field stabilization energy (CFSE).

Introduction

Molecular structures are actually determined by two major factors. Whereas the first one, orbital interactions, is well accepted and extensively applied in structural calculations, the second one, steric effects – effects of geometrical factors, e.g. size and shape of the bonded atoms and groups, has long been neglected in quantitative study, although it has been qualitatively and empirically acknowledged.

The influence of geometrical factors on molecular structure can be illustrated with toy building blocks. In a round box (Fig. 1) the two small blocks B can only be fitted into the two sides of the large blocks A. Such an effect due to packing in a limited space is called 'packing effect'. A similar effect occurs when ligands are arranged in the molecules of coordination and organometallic compounds. Coordination space around a central metal ion is not to exceed 4π for all the bondings. Therefore, besides the orbital interaction, 'steric interaction' due to packing of ligands in the three-dimensional 'toy block box' must be taken into consideration. The key problem is that the packing effect usually mixes and mutually interferes with orbital interactions. The actual structures might be a reflection of the combined effect of the two interactions.

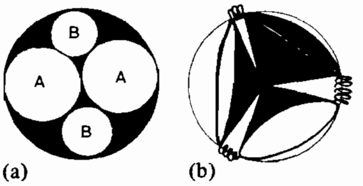

Fig. 1. (a) Block packing in a round box. (b) Ligand packing on a coordinating sphere.

In order to study steric effect in a more simplified way, the molecular structures of weak covalent compounds should be chosen to reduce the influence from orbital interactions. Ionic compounds which are ideally non-saturate and non-directional might be better candidates for these purposes.

Our recent study on the structures of lanthanides and actinides coordination and organometallic compounds has shown that ligand packing is of extreme importance in molecular geometry [1, 2]. The packing saturation rule and the packing centre rule were summarized based on quantitative analysis of more than 400 structures of lanthanide and actinide coordination and organometallic compounds. The uniform packing principle was thus assumed, and based on this principle we have designed 'CONPACKS', a computer program to simulate the molecular structures.

Steric Parameters of Ligands

In a simulation of molecular structure based on our recently developed cone-packing model, all ligands are mathematically treated to be equivalent to cones with their respective fan angles and solid angle factors. Molecular geometry is simplified as a problem of how these cones arrange when they join at the same apex. As long as certain packing regulations are established, the geometry is fixed. With the mathematical conditions given below, we have reported two sets of calculated results. Results A were those simulated by using the previously reported ligand fan angle (*FA*) and solid

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angle factors (*SAF*) [1, 2]. Bond angles so obtained could be used for the prediction of unknown structures. Results B were obtained based on *FA* and *SAF* of ligands in the actual structures. The second set of results has no predictive value, but it could be used to check the uniform packing principle adopted in our simulation.

Standardization must be made for irregular ligands, which are not of the standard cone shape. If a cone ligand has one substituting group only, e.g. $CH_3C_5H_4^-$, its fan angles are simplified as that of $C_5H_5^-$ because of the low energy barrier of rotating around the cone axis. The methyl group could move to holes among the ligands and does not have much effect on the ligand–metal–ligand bond angle. As a first attempt, which should be as simple as possible, we treated ligand cones with two substituting groups, such as $C_5H_3(SiMe_3)_2$ as if they were the same as cyclopentadienyl. We will report the refined simulation and the respective results in later papers.

We have written a computer program CONPACKS, using the method of lagrangian multiplier, and calculated the structures. In the program (its algorithm will be reported in a separate paper), the input data needed are the number of coordinated ligands, the fan angle of ligands, the initial positions and neighbours (i, j) that are inferred from the assumed structure pattern of the molecule being considered. After several cycles of the iterative fitting process, the convergence criterion is satisfied, then the program outputs the bond angle between ligands when the sum of square gaps approaches a local minimum. The 'uniform packing principle' as defined is mathematically expressed as:

TABLE I. Comparisons between the Calculated and the Reported Bond Angles in MA_3B

Structure	Bond angle	Reported (°)	Calculated by A (°)	Calculated by B (°)	Reference
$PrCp_3(NCC_6H_{11})$	Cp–Pr–Cp	118.9	118.3	118.0	4
	Cp–Pr–N	96.2	97.6	98.3	
$Nd(C_5H_4CH_3)_3$	Cp′–Nd–Cp′	117.4	116.6	117.9	5
	Cp′–Nd–C′	99.4	100.7	98.5	
$(YbCp_3)_2Py_2$	Cp–Yb–Cp	115.6–120	118.3	118.3	6
	Cp–Yb–N	94.6–102.5	97.6	97.8	
$LaCp_3thf$	Cp–La–Cp	117.7	118.2	118.3	7
	Cp–La–thf	99.5	97.8	97.6	
$PrCp_3thf$	Cp–Pr–Cp	117.6	118.2		8
	Cp–Nd–thf	99.0	97.8		
$NdCp_3thf$	Cp–Nd–Cp	117.0	118.2		8
	Cp–Nd–thf	100.2	97.8		
$GdCp_3thf$	Cp–Gd–Cp	117.5	118.2	118.1	9
	Cp–Gd–thf	99.2	97.8	97.9	
YCp_3thf	Cp–Y–Cp	117.4	118.2	118.0	7
	Cp–Y–thf	99.1	97.8	98.1	
UCp_3Cl	Cp–U–Cp	116.7	115.2	115.1	10
	Cp–U–Cl	101	102.8	103.0	
$U(C_5H_4CH_2C_6H_5)_3Cl$	Cp′–U–Cp′	117.1	115.2	115.7	11
	Cp′–U–Cl	100.0	102.8	102.2	
$UCp_3(p\text{-}Ch_3C_6H_4CH_2)$	Cp–U–Cp	115.6–120.6	115.5	115.9	12
	Cp–U–C	99.4–99.8	102.5	101.9	
$UCp_3(n\text{-}C_4H_9)$	Cp–U–Cp	115.8–118.1	115.5	115.7	12
	Cp–U–C	98.2–102.3	102.5	102.2	
$UCp_3C{\equiv}CPh$	Cp–U–Cp	116–119	115.5	114.5	13
	Cp–U–C	100	102.5	103.8	
$UCp_3[CH_3C(CH_2)_2]$	Cp–U–Cp	115–119	115.5	115.6	14
	Cp–U–C	97.5–102	102.5	102.3	
UCp_3F	Cp–U–Cp	117.2	117.9	117.9	15
	Cp–U–F	99.7	98.5	98.4	
$UCp_3(C{\equiv}CH)$	Cp–U–Cp	116–121	115.5		16
	Cp–U–C	94–99	102.5		

(1) Packing centre rule: the vector sum of the ligand solid angle factors should be equal to zero; *i.e.*, $\Sigma_{i=1}^{n} SAF_i\bar{r}_i = 0$.

(2) Square sum of gaps between the four ligands should be minimum; *i.e.*, $\Sigma_{i=1}^{n-1}\Sigma_{j>i}^{n} G_{ij}^2$ should reach to the minimum, where the gaps between two ligands A and B are defined as $G_{A,B}$ = bond angle AMB − ($FA_A + FA_B$) [3].

Explanations for the two conditions were given in our previous papers [1a, 3].

Results and Discussion

The output bond angles are listed in Tables I–VI without refinement. Manual calculations were also given in the structure of MA_3B because of the simplicity in mathematical treatment.

There are five patterns, *i.e.* MA_4, MA_3B, MA_2B_2, MA_2BC and MABCD in tetrahedral structures. All but the last pattern have been reported experimentally.

(1) MA_4

A tetrahedron structure is obviously packed more equally than the square plane structure. The vector sums of the ligand solid angle factors are zero for both structures. However, the distribution of gaps is not equal in a square plane structure. Gaps between ligands in the *trans*-position are larger than gaps between ligands in the *cis*-position. In spite of the fact that square plane structures are popular for certain transition metal organometallic compounds, they have not been reported in the f-block compounds. The structure of $U(C_5H_5)_4$ is tetrahedral [46].

TABLE II. Molecular Geometry of the Structural Pattern MA_2B_2. Case 1: A = $C_5H_5^-$; FA_A = 55°; M = Ln^{3+}, An^{4+}. B = other ligands. Case 2. A = $Me_5C_5^-$; FA_A = 63°. B = other ligands

FA_B	Bond angle (°)		
	A–M–A	A–M–B	B–M–B
Case 1			
10	175.98	91.98	20.25
20	164.80	97.11	41.40
25	157.27	100.18	52.46
30	149.05	103.10	63.75
35	140.62	105.52	74.81
40	132.31	107.33	85.07
45	124.27	108.55	94.23
50	116.60	109.25	102.30
55	109.47	109.47	109.47
60	103.09	109.26	115.94
70	93.33	107.77	127.19
80	87.64	105.58	136.28
90	84.82	103.44	143.30
Case 2			
10	176.86	91.55	20.11
20	168.09	95.59	40.20
25	162.11	98.10	50.03
30	155.41	100.65	59.62
35	148.29	103.02	68.85
40	136.57	106.16	82.47
45	133.65	106.78	85.61
50	126.46	108.07	92.97
55	119.54	108.94	99.72
60	113.06	109.40	105.94
70	102.22	109.69	117.20
80	95.02	107.54	126.99
90			

TABLE III. Comparisons between the Simulated and the Reported Bond Angles of the Structural Pattern MA_2B_2

Structure	Bond angle (°)	Reported (°)	Calculated by A (°)	Calculated by B (°)	Reference
1 $(ScCp_2Cl)_2$	Cp–Sc–Cp	–	124.3	124.7	17
	Cp–Sc–Cl	–	108.6	108.5	
	Cl–Sc–Cl	81.8	94.2	93.8	
2 $[Yb(CH_3C_5H_4)_2Cl]_2$	Cp′–Yb–Cp′	126.7	124.3	128.25	18
	Cp′–Yb–Cl	109.7	108.6	107.98	
	Cl–Yb–Cl	82.1	94.2	89.95	
3 $Li[YbCl_2(C_5H_4SiPh_2Me)_2](ether)_2$	Cp′–Yb–Cp′	135–140	124.3	127.2	19
	Cp′–Yb–Cl	–	108.6	108.1	
	Cl–Yb–Cl	87.14	94.2	91.1	
4 $Li[Yb(Me_5C_5)_2I_2](ether)_2$	Cp′–Yb–Cp′	135–140	133.7	104.9	19
	Cp′–Yb–I	–	106.8	105.1	
	I–Yb–I	86.1	85.6	81.7	
5 $Yb(Me_5C_5)_2AlCl_4$	Cp′–Yb–Cp′	135–140	133.7	140.85	19
	Cp′–Yb–Cl	–	106.8	105.1	
	Cl–Yb–Cl	73.36	85.6	78.11	

(continued overleaf)

TABLE III *(continued)*

Structure	Bond angle (°)	Reported (°)	Calculated by A (°)	Calculated by B (°)	Reference
6 $Yb(Me_5C_5)_2Py_2$	Cp′–Yb–Cp′	136.3	151.2	146.6	20
	Cp′–Yb–Py	108	102.1	103.6	
	Py–Yb–Py	82.5	65.21	70.64	
7 $[Yb(C_5H_5)_2(CH_3)]_2$	Cp–Yb–Cp	128.2	127.44	128.6	21
	Cp–Yb–CH_3	105.9–110	108.13	107.9	
	CH_3–Yb–CH_3	93.4	90.71	89.48	
8 $[Yb(C_5H_5)_2(CH_3)_2Al(CH_3)_2]$	Cp–Yb–Cp	133.1	127.4	130.9	22
	Cp–Yb–CH_3	104.5–107.8	108.1	107.6	
	CH_3–Yb–CH_3	87.1	90.7	86.8	
9 $[Y(C_5H_5)_2(CH_3)]_2$	Cp–Y–Cp	128.9	127.4	125.3	21
	Cp–Y–CH_3	105–110	108.1	108.4	
	CH_3–Y–CH_3	92.3	90.7	93.2	
10 $[Pr\{\eta^5\text{-}[C_5H_3(SiMe_3)_2]\}_2Cl]_2$	Cp′–Pr–Cp	130	124.3	131.9	23
	Cp′–Pr–Cl	102	108.6	107.4	
	Cl–Pr–Cl	78	94.2	85.4	
11 $[Yb\{\eta^5\text{-}[C_5H_3(SiMe_3)_2]\}_2Cl]_2$	Cp′–Yb–Cp′	130	124.3	129.1	23
	Cp′–Yb–Cl	100	108.6	107.8	
	Cl–Yb–Cl	80	94.2	89.0	
12 $[Sc\{\eta^5\text{-}[C_5H_3(SiMe_3)_2]\}_2Cl]_2$	Cp′–Sc–Cp′	131	124.3	128.6	23
	Cp′–Sc–Cl	101	108.6	107.9	
	Cl–Sc–Cl	79	94.2	89.8	
13 $Th(Me_5C_5)_2(CH_2SiMe_3)_2$	Cp′–Th–Cp′	134.9	133.7	130.2	24
	Cp′–Th–C	104.5	107.5	105.8	
	C–Th–C	96.8	88.9	85.6	
14 $[ErCp_2(C{=}C{-}CMe_3)]_2$	Cp–Er–Cp	130.2	127.4	127.2	25
	Cp–Er–C	108.3	108.1	108.1	
	C–Er–C	83.4	90.7	91.1	
15 $(AsPh_4)[Nd\{\eta^5\text{-}C_5H_3(SiMe_3)_2\}_2Cl_2]$	Cp′–Nd–Cp′	126.3	124.3	127.5	26
	Cp′–Nd–Cl	–	108.6	108.1	
	Cl–Nd–Cl	99.3	94.2	90.5	
16 $[Li(THF)_4]_2[U(C_2B_9H_{11})_2Cl_2]$	Cp′–U–Cp′	137	131.9	130.72	27
	Cp′–U–Cl	–	107.2	107.48	
	Cl–U–Cl	90.3	86.8	87.82	
17 $U(Me_5C_5)_2Cl_2$	Cp′–U–Cp′	–	135.11	–	28
	Cp′–U–Cl	–	106.48	–	
	Cl–U–Cl	95.3	84.05	–	
18 $[Nd\{\eta^5\text{-}[C_5H_3(SiMe_3)_2]\}_2(\mu\text{-}Cl)]_2Li(thf)_2$	Cp′–Nd–Cp′	–	124.26	–	29
	Cp′–Nd–Cl	–	108.55	–	
	Cl–Nd–Cl	82.1	94.23	–	

(2) MA_3B

According to the packing centre rule, on projection (Fig. 2) of SAF_A along the MB direction, there is the equation:

$$3SAF_A \cos(180 - \theta) = SAF_B$$

Bond angle θ (angle AMB) is derived from the known SAF_A and SAF_B. Another bond angle ϕ (angle AMA) can be derived as:

$$\phi = \cos^{-1}\left(\frac{3}{2}\cos^2\theta - \frac{1}{2}\right)$$

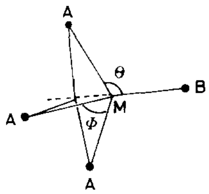

Fig. 2. Calculation of the structural pattern MA_3B.

Bond angle dependence on the ligand packing parameters is drawn in Fig. 3, using $M(C_5H_5)_3X$ as an example. Bond angles between cyclopentadienyls are close to 120° when the ligand X is very

TABLE IV. Molecular Geometry of Structural Pattern MA_2-BC for Case: $A = C_5H_5^-$, $FA_A = 55°$, B = thf, $FA_B = 33°$, C = X.

FA_B	Bond angle (°)			
	A–M–A	A–M–B	A–M–C	B–M–C
20				
25				
30	146.42	104.47	103.31	67.27
35	142.26	104.61	105.56	72.71
40	137.51	104.05	108.14	78.74
45	132.07	102.64	111.09	85.05
50	125.78	100.35	114.49	91.30
55	118.43	97.25	118.43	97.25
60	109.83	93.41	122.98	102.79
70				
80				

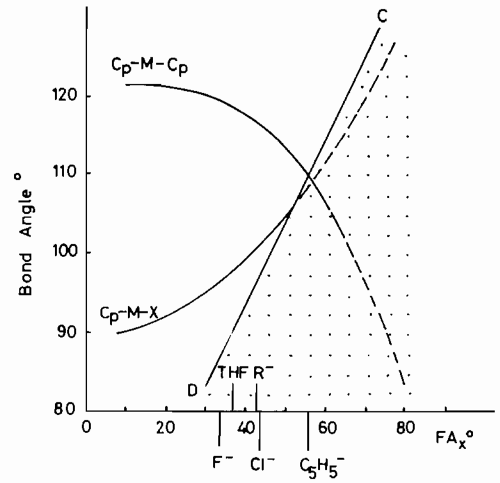

Fig. 3. Molecular geometry of the structural pattern MCp_3X (M = f-block element).

TABLE V. Comparisons between the Experimental and the Calculated Bond Angles of the Structural Pattern MA_2BC

Structure	Bond angle (°)	Reported	Calculated by A (°)	Calculated by B (°)	Reference
$LuCp_2(CH_2SiMe_3)thf$	Cp–Lu–Cp	130	132	130.03	30
	Cp–Lu–C	108	111	110.5	
	Cp–Lu–thf	105	102	104.5	
	C–Lu–thf	96	85.1	87.8	
$Lu(C_5H_5)_2(t\text{-}C_4H_9)thf$	Cp–Lu–Cp	125.6	124.1	132.5	31
	Cp–Lu–C	110	115.1	109.3	
	Cp–Lu–thf	106	100.2	104.9	
	C–Lu–thf	94.1	93.01	85.04	
$Yb(Me_5C_5)_2(thf)OCCo(CO)_3$	Cp′–Yb–Cp′	139.4	146.7	145.4	32
	Cp′–Yb–OC	–	104.22	104.1	
	Cp′–Yb–thf	–	102.7	103.5	
	thf–Yb–OC	83.3	70.81	72.8	
$Lu(C_5H_5)_2(C_6H_4\text{-}4\text{-}CH_3)thf$	Cp–Lu–Cp	128.8	133.7	125.3	30
	Cp–Lu–thf	107	103.7	102.8	
	Cp–Lu–C	108.5	109.8	113.1	
	thf–Lu–C	89.6	83.2	92.6	

small. They decrease gradually with increasing size of ligand X. Bond angle Cp–M–X increases gradually. At the point where $FA_X = FA_{Cp}$ all six bond angles are equal and the structure becomes a normal tetrahedron. The equation of the oblique line CD is $y = FA_{Cp} + FA_X$ which represents an assumed bond angle Cp–M–X when the two ligands, Cp and X, come in contact with each other. Gaps between the two ligands are positive above line CD and negative below line CD, which implies non-overlapping and overlapping between the two ligands, respectively. The curves describing the bond angle are drawn with a dotted line to indicate overlapping.

Comparisons between the calculated and the reported bond angles are listed in Table I.

(3) MA_2B_2

Bond angle dependence on the size of the second ligand was given in Table II, with M = Ln^{3+} or An^{4+}, $A = C_5H_5^-$ or $Me_5C_5^-$. These were illustrated in Fig. 4. It clearly shows that the two cyclopentadienyls are almost linear, like a sandwich, when ligand B is very small. Bond angle Cp–M–Cp decreases with increasing size of ligand B, whereas bond angle X–M–X gradually increases. Bond angle Cp–M–X also increases but rather slowly. It reaches a maximum when X is cyclopentadienyl or a ligand which exerts the same steric effects. The structure will then turn into a tetrahedron.

The fan angle of cyclopentadienyl is 55° both for uranium(IV) and for europium(III). The bond angles

TABLE VI. Comparisons between the Calculated and the Reported Bond Angles of some Group IVA Organometallic Compounds

Structure	Bond angle (°)	Reported (°)	Calculated by B (°)	Gaps	Reference
$TiCp_2Cl_2$	Cp–Ti–Cp	129.4	122.77	+9	33
	Cp–Ti–Cl	–	108.64	–	
	Cl–Ti–Cl	95.2	96.26	–4	
$(CH_3C_5H_5)_2TiCl_2$	Cp′–Ti–Cp′	130.2	122.50	+10	34
	Cp′–Ti–Cl	106.8	108.68	–3	
	Cl–Ti–Cl	93.15	96.52	–6	
$(Me_5C_5)_2TiCl_2$	Cp′–Ti–Cp′	137.4	129.32	+6	35
	Cp′–Ti–Cl	104.5	107.52	–10	
	Cl–Ti–Cl	92.94	90.59	–7	
$(C_5H_5)_2Ti(NCO)_2$	Cp–Ti–Cp	–	124.88	–	36
	Cp–Ti–N	–	108.38	–	
	N–Ti–N	94.7	94.09	–1	
$(C_5H_5)_2Ti(NCS)_2$	Cp–Ti–Cp	133.7	125.44	+5	37
	Cp–Ti–N	–	108.30	–	
	N–Ti–N	93.9	93.53	–1	
$(C_5H_5)_2Ti(N_3)_2$	Cp–Ti–Cp	132.2	125.84	+7	38
	Cp–Ti–N	106.1	108.24	–1	
	N–Ti–N	94.1	93.11	–1	
$(C_5H_5)_2Ti(CO)_2$	Cp–Ti–Cp	138.6	113.23	18.6	39
	Cp–Ti–C	105	109.4	–10	
	C–Ti–C	87.5	105.8	–26.3	
$(C_5H_5)_2ZrF_2$	Cp–Zr–Cp	127.8	130.63	+13	40
	Cp–Zr–F	–	107.54	–	
	F–Zr–F	96.2	87.60	+10	
$(C_5H_5)_2ZrI_2$	Cp–Zr–Cp	126.3	121.64	+10	40
	Cp–Zr–I	–	108.79	–	
	I–Zr–I	96.2	97.31	+1	
$(C_5H_5)_2ZrCl_2$	Cp–Zr–Cp	–	117.95		41
	Cp–Zr–Cl	–	109.14		
	Cl–Zr–Cl	97.1	101.01		
$(C_5H_5)_3Zr(\sigma\text{-}C_5H_5)$	Cp–Zr–Cp	117	115.77	–2	42
	Cp–Zr–C	99.3	102.04	3	
$(Cp_2TiCl)_2O$	Cp–Ti–Cp	129.61	123.26	9	43
	Cp–Ti–Cl	104.8	108.04	–2	
	Cp–Ti–O	108.1	109.14	–1	
	Cl–Ti–O	95.95	95.71	–2	
$Cp_2Hf(CO)_2$	Cp–Hf–Cp	141	117.91	25	44
	Cp–Hf–C	103.5	109.13	–7	
	C–Hf–C	89.3	101.08	–15	
$(C_5H_5)(Me_5C_5)TiCl_2$	Cp′–Ti–Cp	–	125.91	–	45
	Cp′–Ti–Cl	118.2	115.47	0.7	
	Cp–Ti–Cl	106.0	100.56	–3	
	Cl–Ti–Cl	94.8	92.97	–7	

between all four ligands would be less than their fan angle sum when the second ligand exerts steric effect greater than that of cyclopentadienyl. These mean that the ligands begin to overlap each other and the potential energy increases steeply afterwards. The compound is normally unstable at this stage, and the curves are drawn in dotted line. It is not difficult to understand that pentamethyl-cyclopentadienyl or any ligands larger than cyclopentadienyl rarely form compounds of the type MCp'_4, MCp'_3Cp, and MCp'_2Cp_2 etc.

Comparisons between the reported bond angles and the calculated ones are listed in Table III. The structures are classified into four groups:

(a) The ligand cones have regular cone shape, e.g. structures 4, 16, 17. The calculated results normally agree with the reported structures.

(b) Bridged structures

$Cp_2M(\mu\text{-}X)_2MCp_2$, e.g. structures 1, 5, 7, 8 and 9. The calculated bond angle only agrees with the reported ones when the bridging

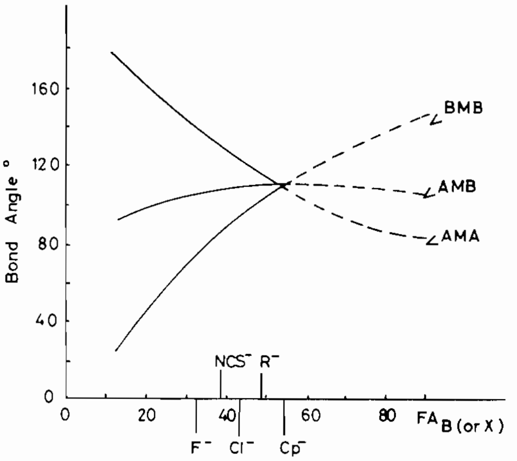

Fig. 4. Molecular geometry of the structural pattern MCp_2-B_2.

ligands are methyl groups. However, when chlorine ions are the bridging ligands, the calculated bond angles Cl–M–Cl are considerably higher than the experimental results. The error might come from the fact that we had to take the two chlorines as two independent ions regardless of their bridging character. Bridging chlorine is in fact an intermediate case between two free moving ions and two fixed ones in one group, such as the two oxygen atoms in bidentate nitrate ion; this results in a positive deviation. Nevertheless, the bond angles between the two cyclopentadienyls are still in good agreement.

(c) For bridging structures containing cyclopentadienyls with bulky substituting groups, such as structures 2, 3, 12, 15 and 18, not only are the bond angles X–M–X smaller than the calculated ones, but also the bond angles Cp′–M–Cp′ are larger than the expected bond angles.

(d) In structure 6, the bond angle between the two pyridines is greater than the calculated values. The reason for the under-estimation was that we took only the fan angle of nitrogen atom as the first order steric parameter in calculation for simplicity. Definitely, the pyridine ring exerts a second-order steric effect and causes a larger N–M–N bond angle and smaller Cp′–M–Cp′ bond angle.

(4) MA_2BC

Calculated bond angles of the structures $LnCp_2$-Xthf are listed in Table IV and their dependence on FA_X is illustrated in Fig. 5. The bond angle between tetrahedrofuran and X increased rapidly (curve I) while the bond angle between cyclopentadienyl and X increases rather slowly (curve II) as FA_X increases. The bond angles between the two cyclopentadienyls and between tetrahedrofuran and cyclopentadienyl (curves IV and III, respectively) decrease with increasing steric effect of group X. At the point $FA_X = FA_{thf}$, curves II and III cross each other. For $FA_X > FA_{thf}$, bond angle Cp–Ln–X is always greater than Cp–Ln–thf. The ligand X could be as large as cyclopentadienyl without causing steric overcrowding. At the point $FA_X = FA_{Cp}$, curves I and III, and II and IV cross each other, indicating that bond angle Cp–Ln–X is equal to bond angle Cp–Ln–Cp, and bond angle thf–Ln–X is equal to bond angle thf–Ln–Cp.

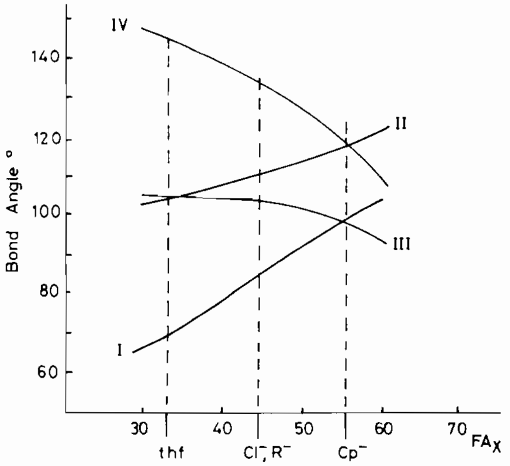

Fig. 5. Molecular geometry of the structural pattern Cp_2-LnX•thf. Curve I thf–Ln–X, curve II Cp–Ln–X, curve III Cp–Ln–thf, curve IV Cp–Ln–Cp.

The calculated and experimental results are listed in Table V. The bond angles between the two cyclopentadienyls and those between cyclopentadienyl and tetrahydrofuran are in good agreement with the reported bond angles, whereas the experimental bond angle between group X and tetrahydrofuran, which is very sensitive to fan angle changes of small ligands, is considerably larger than the calculated angles. This negative deviation might be due to the fact that only the oxygen atom, but not the whole ligand of tetrahydrofuran, has been considered in the calculation.

Besides the structures of f-block organometallic compounds, some tetrahedrons of the group IVA organometallic compounds have also been calculated as the first attempt to study the molecular geometry of d-transition elements in view of steric packing. The calculated results with the reported molecular structures were listed in Table VI for comparison. Since a universal set of standard steric parameters of ligands has yet not been published [47], we report here only the calculated results B. Nevertheless, the excellent agreement between the calculated and the reported bond angles in all but the compounds containing carbon monoxide provides clear evidence that the steric effect not only dominates in f-block organometallic compounds, but also has great influence on all structures of weak covalent bonding. The great deviation in the calculation for $Cp_2M(CO)_2$ suggests that:

(1) because of the electron delocalization, the electron density of the carbon atom in carbon monoxide is considerably lower than that of the free carbon atom, and 1.8 Å is not the proper value to be used for calculation of its van der Waals boundary.

(2) orbital interactions have a strong influence on the size and shape of ligands.

To give a clear indication of steric packing in group IVA tetrahedrons, the gaps between ligands are also listed in Table VI. First, it is clearly seen that the absolute values of gaps are normally less than 10°, implying a very close packing. Molecular structures calculated by optimizing the orbital interactions but disregarding the ligand size and shape might lead to overlapping of ligands, and hence to the increasing of potential energy. The actual structures are in an equilibrium between 'the most proper packing to reduce the repulsion energy' and 'optimum orbital interaction to increase the bond energy'. Secondly, large negative gaps are indications of strong electronic effect within the ligands.

Since the accuracy of van der Waals radii, which are used to locate the ligand boundaries, is quite limited, better simulation results have not been pursued. In conclusion, steric packing might play the dominant role in tetrahedron structures of weak CFSE.

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