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The Nature of Seat-ligand Fitting in Coordination Space.
Part 3. Ligand Exchange and Rearrangement Due to Awkward Packing

LI XING-FU*, SUN PENG-NIAN, GUO AO-LING and LU JING-CI

Application Department, The Institute of High Energy Physics, Academia Sinica, Beijing P.O. Box 2732, China

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Abstract

Steric effects are considered as the driving factors in ligand exchange reactions for the first time. Under weak ligand field interaction, various types of improper packing of ligands will induce packing rearrangements. The ligand mixing reaction, the nonintegral metal–ligand ratio in compound compositions, the even–odd effect and related phenomena are analysed in the light of the steric packing of the ligands. The extended Seat-ligand Least Fitting Method and the extended Maximum Difference Isomer Criterion are proposed for the quantitative treatment of ligand exchange.

Introduction

Steric packing is really the interaction of nonbonding repulsions among the atoms and groups due to their geometrical factors. Steric effects and bonding effects are two tendencies which attain equilibrium in stable molecular structures and which become unbalanced in chemical reactions. Nevertheless the steric effect exhibits itself only via action to strengthen and to weaken the bonding. The quantitative study of steric effects has been neglected until recently, for only steric hindrance was considered instead of the possibility of them being the driving factor for chemical processes.

Tolman made the first attempt to correlate the steric effects of phosphine ligands with the reaction rates of some catalytic reactions. However, his meritorious work was not continued. It may be that strong electronic effects interfere with steric effects so that the quantitative study is difficult [1, 2].

More recently, the introduction of the three dimensional solid angle and other steric concepts [3–13] in coordination chemistry has created a great potentiality for the understanding of this field from a new point of view.

In the present paper, we have, for the first time, reported the close similarities between packing rearrangements and the ligand exchange effect among metal ions under weak ligand field interactions. The Packing Saturation Rule and the Uniform Packing Rule [3–8] are followed in such exchanges. It is thus assumed that the driving force for the ligand exchange is due to the improper steric packing. The steric parameters adopted in the quantitative calculation are cited in refs. 3–6 and 14.

In packing articles in a box, it frequently happens that one cannot get proper packing. However, by exchanging the articles with those in another box, more reasonable packing may be achieved. Such a phenomenon not only exists in the packing of luggage but also in chemistry. Coordination space is limited to a 4π ster. solid angle which can be visualized as a box. If the ligands cannot be accommodated around the metal centre due to their awkward size and shape, apart from dissociation, association, substitution and other processes, through which more appropriate coordination is achieved, redistribution of the labile ligands among the metal centres is also possible, promoted by thermal vibration and by collision with the solvent molecules. The driving forces for such redistributions are the local and overall non-bonding repulsions caused by the improper packing.

The Seat-ligand Least Fitting Method and the Maximum Difference Isomer Criterion suggested in our preceding two papers [15] are also applicable to the ligand redistributions. The only difference emphasized here is the 'general' or 'extended' fitting instead of the fitting around one centre only. The minimum of seat function must be calculated among all the metal centers associated in the ligand redistribution. The following equation is used instead of the equation in our first paper [15a]

$$F(S) = \sum_{j=1}^{m} \sum_{i=1}^{n} k(S_i - \theta_i)^2 \qquad (1)$$

for calculation and to compare the minima of all the redistribution possibilities. Here m refers to the number of central ions participating in the redistribu-

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*Author to whom correspondence should be addressed.

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tion. The other terms are the same as those explained in our first paper [15a]. With the same considerations, in calculating the differences between the largest vacant seat and the smallest occupied seat for testing the isomers, using the same arguments, the vacant seats and the occupied seats are not necessarily at the same metal centre.

In order to avoid complexity added by other factors, we restrict our discussion to some of the most simple reactions of the f-block elements, for which ligand field interactions are at a minimum and contribute very little to the kinetic stabilities. There is little gain or loss of ligand field stabilization energy involved in the ligand exchanges.

1. Normal Ligand Exchange Reactions – Ligand-mixing Reactions

Normal ligand exchange reactions are expected when starting with two or more simple coordination compounds, and ending with one mixed-ligand compound by exchange processes shown in Fig. 1. The reactions are characteristic in that the two starting materials comprise sterically overcrowded and sterically undercrowded compounds respectively. Both metal centres, after exchanging the bulky* ligands for the small ones, become moderately crowded. A set of well known exchange reactions are those involving the exchange of cyclopentadienyl ligands for chloride ions, such as the following:

$$3UCp_4 + UCl_4 \xrightarrow{thf} 4UCp_3Cl \qquad [16, 17]$$

$$UCp_4 + 3UCl_4 \xrightarrow{thf} 4UCpCl_3(thf)_2 \qquad [16, 17]$$

$$UCp_3Cl + 2UCl_4 \xrightarrow{thf} 3UCpCl_3(thf)_2 \qquad [16, 17]$$

The first starting compound, UCp_4, is a little overcrowded with the estimated value of *SAS* equal to 0.84; the second starting compound, $UCl_4(thf)_2$ is somewhat sterically undercrowded with the estimated value of *SAS* equal to 0.73. The optimal ligand packing range is 0.80 ± 0.10 for uranium(IV) [4]. By giving up the more space demanding cyclopentadienyl groups for the relatively smaller chloride ions, both products, UCp_3Cl and $UCpCl_3(thf)_2$, are packed more closely to the optimal packing standard. Their *SAS* values are 0.77 and 0.815 respectively (Fig. 2).

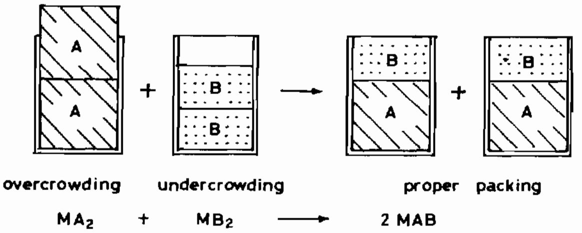

Fig. 1. Ligand mixing reaction: rearrangement to achieve proper packing.

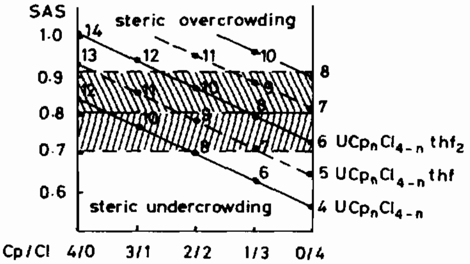

Fig. 2. Steric packing of the Cp–Cl–thf ternary ligand system of uranium(IV) for estimation of the products of ligand exchange.

In seat analysis, although the seat function calculated for UCp_4 is very low, the seat function calculated for $UCl_4(thf)_2$ is rather high. Even at optimal packing, the seat assigned for tetrahydrofuran, 45°, seems too large for the ligand. After exchanging one chloride ion for the large cyclopentadienyl ligand the seat for tetrahydrofuran is compressed so that the seats and the ligands fit better.

$$UCp_4 + UCl_4(thf)_2 \xrightarrow{thf} UCp_3Cl + UCpCl_3(thf)_2$$

The details of the seat functions are given together with the seat level diagrams in Fig. 3. The calculation is carried out in the same way as in our preceding paper [15], but the reported ligand parameter *FA* is used instead of the pre-bonding consideration**. It should be stressed that such redistributions are not due to random mixing because the most probable compound 'UCp_2Cl_2' does not appear in the above reactions.

Similar reactions occur by exchanging the cyclooctatetraenyl group with chloride:

$$K[Ln(C_8H_8)]_2 + LnCl_3 \xrightarrow{thf} [LnC_8H_8Cl \cdot 2thf]_2 + KCl \qquad [16]$$

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*Here 'bulky' refers to the greater space demanded in the first order steric packing.

**The calculation is carried out under the following conditions. 1. In $UCl_4(thf)_2$ the two thf molecules are *trans* to each other. 2. In $UCpCl_3(thf)_2$ one of the ligands is *trans* to the ring. 3. Values of the ligand FA are adopted from ref. 4. 4. Due to the secondary steric effect of tetrahydrofuran, which is complicated to estimate, we have simplified the calculation by letting the two thf have their largest possible seats. In this way, the seat function of $UCpCl_3(thf)_2$ is not the minimum. Such an approximation does not interfere with our estimation of the packing rearrangement.

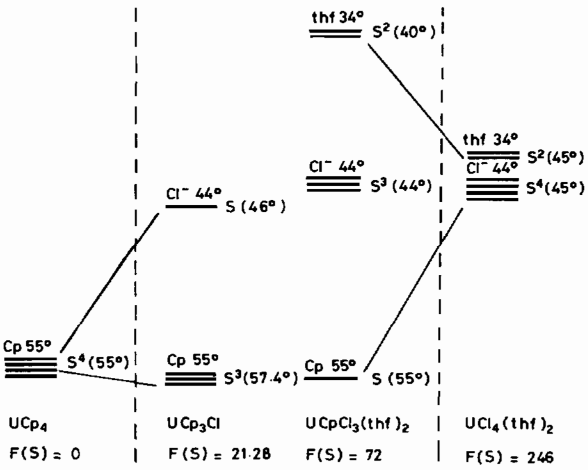

Fig. 3. Splitting of seat levels due to ligand exchange.

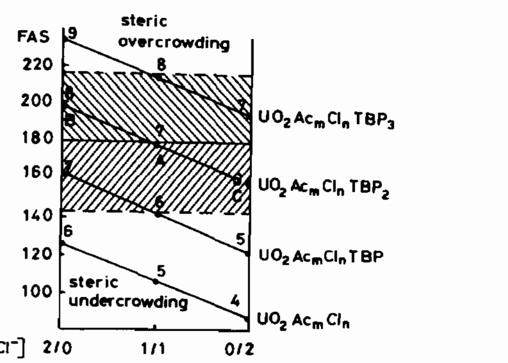

Fig. 4. Steric packing in the Ac^-–Cl^-–TBP ternary system of uranium(IV) complexes with $m + n = 2$. The tendency is for A to form on mixing B and C.

The complexes of phosphine oxides and tri-n-butyl phosphates with uranyl chloride, $UO_2Cl_2L_2$, are sterically undercrowded in the equatorial plane [18] whereas the corresponding complexes with uranyl acetate, $UO_2Ac_2L_2$, are sterically overcrowded [19]. By exchanging the bidentate acetate for the monodentate chloride ion, the product, UO_2AcClL_2, is expected to be more properly packed.

It is therefore expected that the ligand exchange reaction should occur (see Fig. 4):

$$UO_2Cl_2L_2 + UO_2Ac_2L_2 \longrightarrow 2UO_2AcClL_2$$

Although the reaction is also favoured by the entropy change, without the steric effect as the driving force the exchange will not reach completion. The direction of the ligand exchange can be studied quantitatively using the extended Seat-ligand Least Fitting Method. The seat level diagrams of the starting compounds, $UO_2Cl_2L_2$ and $UO_2Ac_2L_2$, are drawn on the left and the right hand sides respectively in Fig. 5. Each seat is represented by a short line with the fan angle of the seat inserted on the right. The ligand accommodated in the seat is written above the line.

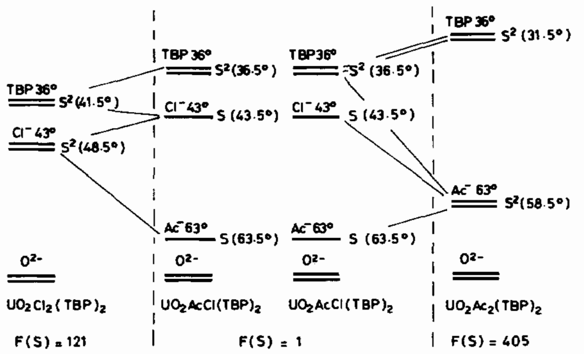

Fig. 5. Seat analysis for the ligand exchange reaction $UO_2Ac_2(TBP)_2 + UO_2Cl_2(TBP)_2 \rightarrow 2UO_2AcCl(TBP)_2$. The seat function is greatly decreased after the exchange.

The steric parameters of the ligands, $FA_{Cl^-} = 43°$*, $FA_{Ac^-} = 63°$ and $FA_{TBP} = 36°$, are adopted from ref. 3b. For simplicity we have omitted the uranyl oxygen.

It is clearly seen that in $UO_2Cl_2L_2$ both the chloride and the neutral ligands occupy seats which are too large for their sizes. Therefore even under the optimal packing conditions the seat function is still as high as 121. It is also clearly seen that the packing is too crowded in $UO_2Ac_2L_2$. Even at the optimal fitting, both the seats for the acetate groups and the seats for the neutral ligands are smaller than the respective ligands. We suggested in our second paper [15] that when the seat is smaller than the ligand, due to the steep increase in the repulsion, the packing coefficient would be higher than the unit and we had tentatively adopted a value of $k = 5$ in the calculation. The seat function so calculated for $UO_2Ac_2L_2$ is as high as 405. By exchanging the ligands, the seats assigned for the neutral ligands have been averaged in the reaction product and they just fit the ligand sizes. The seat assigned for the chloride ion is no longer too large for the ligands as in $UO_2Cl_2L_2$, whereas the seat assigned for the acetate group is no longer too small for the corresponding ligands as in $UO_2Ac_2L_2$. The seat function for UO_2AcClL_2 is as low as 1 for each molecule. The exchange reaction is thus expected to reach completion. Experimentally we have not confirmed the prediction but also observed the synergistic effect in solvent extraction on mixing chloride and the acetate solutions [20].

The ligand mixing rearrangements occur only when the product is stable because of steric packing. For example, the following reactions:

$$4LnCp_3 + 2LnCl_3 \longrightarrow 3[LnCp_2Cl]_2$$

$$LnCp_3 + 2LnCl_3 \xrightarrow{thf} 3LnCpCl_2(thf)_3$$

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*The fan angle of the chloride ion in uranyl compounds is a little different from that in uranium(IV) compounds [3b].

proceed only with the middle and the late lanthanides but are prohibited with the early lanthanides [16]; the instability of the exchange product for the early lanthanides, as explained in our previous paper [6], is due to the instability of the products which are not in the proper packing arrangement, so that the exchange does not occur.

2. Reverse Exchange of Ligands

Such an exchange might be more precisely called ligand disproportionation, which is the reverse of ligand mixing processes. The starting compound is actually non-existent, with a fictitious structure. In the products, metal ions with different coordination environments co-exist under the same conditions. In particular, when the charged ligands are distributed unequally in these different coordination environments, the product will be a complex salt. The disproportionation can be classified in various patterns.

2.1. Non-integral Coordination

The product of such a disproportionation characteristically has a non-integral metal–ligand ratio in the formal chemical composition, for example:

$UX_4L_{2.5}$ (X = chloride or bromide; L = amide) [21, 22]

$LnCl_3L_{3.5}$ (L = amide) [23]

$An(NO_3)_4 \cdot \frac{8}{3}L$ (An = uranium(IV) or thorium(IV); L = trimethylphosphine oxide) [23–26]

$UCl_4 \cdot \frac{2}{3}$dcc (dcc = dicyclohexyl-18-crown-6) [27]

$Ln(NO_3)_3 \cdot \frac{2}{3}$dcc [28]

$Ln(NO_3)_3 \cdot \frac{3}{4}$(18-crown-6) [28]

The major factor which leads to non-integral coordination might be the incapability of attaining proper packing with an integral number of ligands, for example, when the steric packing is somewhat undercrowded with *n* ligands whereas it is somewhat overcrowded with (*n* + 1) ligands. There is a potential possibility that after the ligand rearrangement illustrated in Fig. 6, each centre is, in fact, coordinated to an integral number of ligands whereas the total formal coordination number appears to be non-integral.

The phenomena are easily explained by the method of seat analysis. After the exchange of ligands the small vacant seats, which were scattered on two or more metal centres, have been collected together to make a large vacant seat to accommodate one extra ligand (see Fig. 7). Such a process can be explained using the compound pattern $UCl_4L_{2.5}$ as an example. The uranium(IV) centre, coordinated to four chloride ions and two molecules of amide (*N,N*-dimethylacetamide), still has vacant seats which are nevertheless not large enough to hold another amide ligand. If one chloride ion of the first metal centre is exchanged for the smaller amide ligand, the vacant seats in the first metal centre will expand so that it is large enough to hold another amide molecule. The first centre thus becomes $UCl_3L_4^+$. On the other hand, the vacant seat at the second centre, by exchanging the small amide molecule for a more space demanding chloride ion, will be blocked. The total result of the ligand exchange is that one additional ligand has coordinated to the metal ion by collecting the vacant seats from two metal centres.

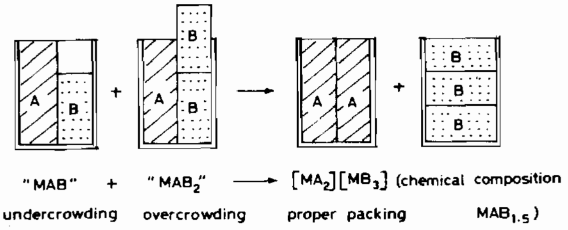

Fig. 6. Box/particle non-integral packing: an illustration for the non-integral metal–ligand complex.

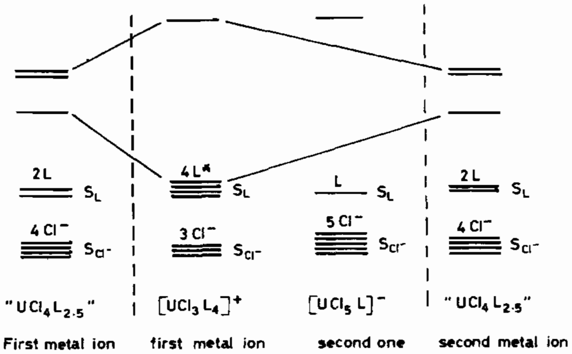

Fig. 7. The vacant seats of two metal ions are concentrated in the first one by the ligand rearrangement. *The additional amide is included.

The detailed mathematical treatment for each of the disproportionation possibilities is rather tedious and complicated. A simple method of predicting the optimal disproportionation products is suggested here using $UCl_4L_{2.5}$ as the example. Sterically, UCl_4L_2 is a little undercrowded with the value of $SAS = 0.76$, while UCl_4L_3 is a little overcrowded with the value of $SAS = 0.86$. The compound of chemical composition $UCl_4L_{2.5}$ has been characterized by chemical analysis. A structure involving bridging chloride seems unlikely because the estimated value of *SAS* is 1.00 for eight coordinated chloride bridging structures [44]. There are various combinations of the possible complex cations and anions with the same chemical composi-

TABLE I. Structural Possibilities for Compound $UCl_4(dma)_{2.5}$ in Relation to Steric Crowding

	Cation–anion combination					
	1	2	3	4	5	6
Complex cation	$[UCl_3L_4]^+$	$[UCl_2L_5]^{2+}$	$[UClL_5]^{3+}$	$[UCl_3L_3]^+$	$[UCl_3L_5]^+$	$[UCl_2L_4]^{2+}$
Coordination number	7	7	6	6	8	6
SAS	0.82	0.78	0.64	0.72	0.92	0.68
Complex anion	$[UCl_5L]^-$	$[UCl_6]^{2-}$	$[UCl_7]^{3-}$	$[UCl_5L_2]^-$	$[UCl_5]^-$	$[UCl_6L]^{2-}$
Coordination number	6	6	7	7	5	7
SAS	0.80	0.84	0.98	0.90	0.70	0.94
Difference between cation and anion						
Charge	2	4	6	2	2	4
Coordination number	1	1	1	1	3	1
SAS	0.02	0.06	0.34	0.18	0.22	0.26

tion (see Table I). According to the uniform packing principle, only those cation–anion combinations are possible which offer the least difference of the values of *SAS* in steric packing between the cation and the anion. It is therefore expected that $[UCl_3L_4]^+$-$[UCl_5L]^-$ is the optimal combination. This is in agreement with the structure determination [28].

In Table I it can be seen that both differences in the charge distribution and in the formal coordination numbers between the cations and the anions are less important in comparison with the differences in steric packing. The major influence of the geometrical factors can also be seen by adjusting the structural patterns simply according to the size of the ligand relative to the metal ion. The complex with the 1:2.5 metal–ligand ratio will change to the 1:3 complex by using the larger thorium(IV) instead of the uranium(IV) ion, or by tuning the ligand size to a less bulky amide, e.g. $CHCONMe_2$ [29, 30]. On the other hand, the complex with 1:2 metal–ligand ratio will form by changing the ligand to a more bulky amide, such as $CHMe_2CONMe_2$ and CMe_3CONMe_2 [31].

The complex with the non-integral metal–ligand ratio, when caused by improper packing, is thus characterised by the properties that: (a) of all the disproportionation products, only those are stable which satisfy the Packing Saturation Rule and the Uniform Packing Principle; (b) the metal–ligand ratio can be changed from non-integral to the neighbouring integral complexion by adjusting the relative size of the ligand to the metal ion.

Another type of ligand exchange occurs when the Packing Saturation Rule and the charge balance cannot be simultaneously achieved in a single metal centre. For example, macrocyclic ligands form complexes with non-integral metal–ligand ratios. When the macrocyclic ligands have coordinated to the metal ions, the remaining coordination space does not have enough seats left to hold the anions so that the charge is unbalanced in the coordination sphere. Some anions therefore have to transfer to another metal centre for coordination. Thus the first metal centre becomes the complex cation, and the second one the complex anion, forming complex salts of different cation:anion ratio according to the charges of the cation and anion (see Table II).

Steric characters displayed in this particular ligand exchange are:

(a) Transfer of the anions is accompanied by other types of unusual structures. It is expected that to achieve the charge balance in a single metal centre the steric packing would be overcrowded. There are three possibilities. Firstly, if the metal ion is sufficiently large and the steric overcrowding is, nevertheless, tolerable, the anions might be compelled to enter the coordination sphere, forming very disordered bonding and resulting in extra-ordinarily long bond lengths. For example, in the structure of $[Nd(18\text{-crown-}6)(NO_3)_3]$ the metal–nitrate bond lengths range from 2.566 to 2.598 Å, which are considerably longer than the corresponding bond lengths of 2.42 Å in $[Nd(18\text{-crown-}6)(NO_3)_2]^+$ [32]; also, in the structure of $[UCl_3dcc]^+$, the metal–chloride bond lengths range from 2.62 to 2.66 Å which are longer than the normal uranium(IV)–chloride bond length. Secondly, if the space is limited and the coordination ability is rather weak for the anions, another possibility is that the ligand anion will be forced out of the coordination sphere. For example, $Eu(ClO_4)_3(2,2,2)MeCN$ [34], in which the perchlorate anions are not all coordinated to the metal centre.

Finally, when the coordination space is limited and the ligand anion is strongly coordinated, the Packing Saturation Rule has to be followed for each individual ion centre whereas the charge balance is achieved in a general sense. A complex anion will

TABLE II. Ligand Rearrangements in Macrocyclic Complexes

Characteristics	Metal:Ligand	Structural examples and values of *SAS*
Transfer of the anions to form complex salts	4:3	$[LnL(NO_3)_2]_3[Ln(NO_3)_6]$ $SAS_c = 0.79$ $SAS_a = 0.93$ Ln = Nd, La L = 18-crown-6 [32] Ln = La L = $H_3CO(CH_2CH_2O)_5CH_3$ [33]
	3:2	$[LnL(NO_3)_2]_2[Ln(NO_3)_5]$ $SAS_c = 0.79$ $SAS_a = 0.78$ Ln = La L = dcc [36] (dcc = dicyclohexyl-18-crown-6)
	3:2	$[UCl_3(dcc)_2][UCl_6]$ [37] $SAS_c = 0.87$ $SAS_a = 0.78$
	2:1	$[SmL(NO_3)][Sm(NO_3)_5(H_2O)]$ $SAS_c = 0.80$ $SAS_c = 0.87$ L = (2,2,2) [38]
The anions have deformed structures due to steric overcrowding	1:1	$Nd(18\text{-}6)(NO_3)_3$ [35] The average bond length of Nd–O (NO_3^-) is 2.587 Å. $SAS = 0.92$
The inner sphere–outer sphere	1:1	$Eu(ClO)_3(2,2,2)MeCN$ [34] $SAS = 0.80$

form, which collects the remaining simple anions, in order to balance the positive charge of the complex cation.

(b) In the third case the metal–ligand ratio is closely associated with the ionic radii of the metals. For example, in crown ether complexes if the macrocyclic ligand is completely coordinated to the metal ion there would be two vacant seats located at the axial position for the anion accommodation. The structural pattern is decided by the complex anion. When the ionic radius of the metal is large, e.g. La^{3+}, it could hold more nitrate anions to form $La(NO_3)_6^{3-}$, resulting in the 4:3 metal–ligand complex type. If the metal ion holds only five nitrate ligands, the metal–ligand ratio will be 3:2 in chemical composition. When the cryptate is coordinated the ligand takes eight seats so that another anion has to be ejected from the centre of the complex cation. The positive charge of the complex cation will rise and the 2:1 metal–ligand ratio will form.

The steric packing due to the macrocyclic ligands is summarized in Table II and in Figs. 8–10. The way to use these figures is described in our previous work [6, 7, 14].

2.2. Ligand Exchange Due to Awkward Packing

It frequently happens in the packing of several particles that the volume of empty space is equal or even larger than that of the particle to be put in, but the particle will not fit in because of the awkward shape of the hole, as shown in Fig. 11. A more reasonable packing could then be achieved simply by exchanging the particles.

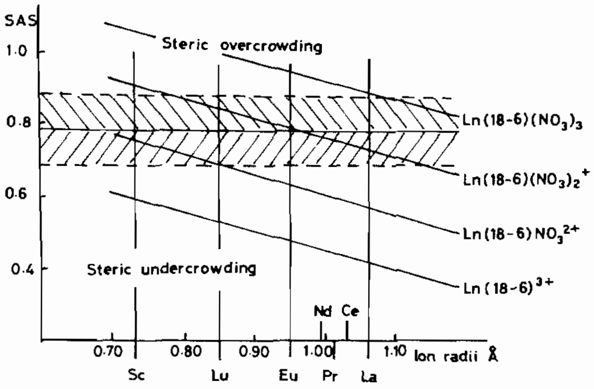

Fig. 8. Steric packing for the lanthanide crown ether complex cations.

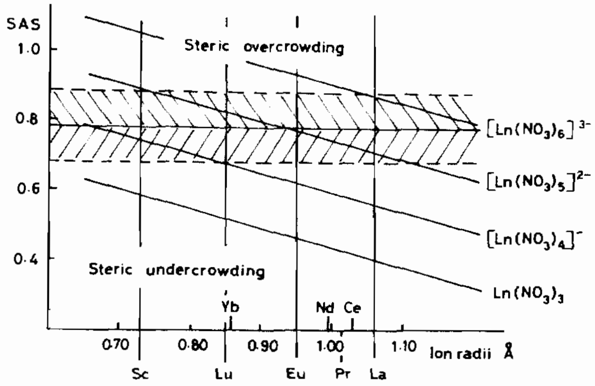

Fig. 9. Steric packing for the lanthanide nitrate complex anions in the corresponding crown ether compounds.

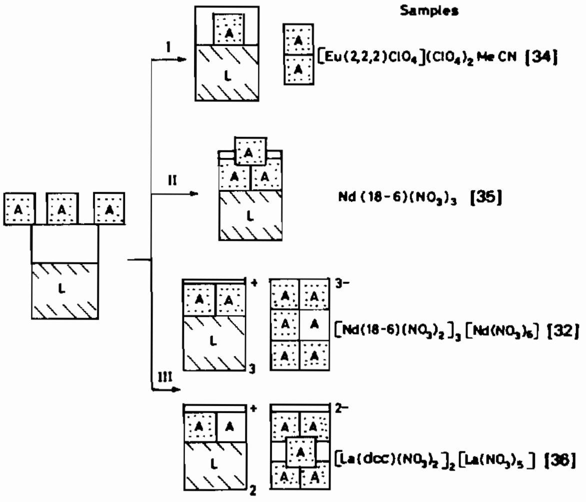

Fig. 10. Structure possibilities for lanthanide and actinide complexes of macrocylic ligands. I, inner sphere–outer sphere coordination conversion; II, distortion due to steric overcrowding; III, ligand exchange to achieve proper packing.

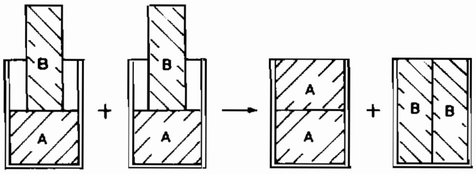

Fig. 11. Ligand rearrangement caused by awkward packing: 2'MAB' → $MA_2 + MB_2$.

In structural chemistry similar phenomena exist with odd number ligand packing. We have explained in our preceeding papers [15] that the difference between the smallest occupied seat and the largest vacant seat is usually large in the packing of an even number of ligands. However, the difference is minimized in odd number ligand packing. There are a series of small vacant seats useless for holding the ligands whereas the main seats, which are needed for ligand coordination, are not large enough. The space efficiency is rather low in odd number ligand packing except in delicately elaborated cases such as in MCp_3L_2 [45]. The problem is how to reorganize the vacant seats, which are usually scattered in the coordination sphere, and make them into an integral one.

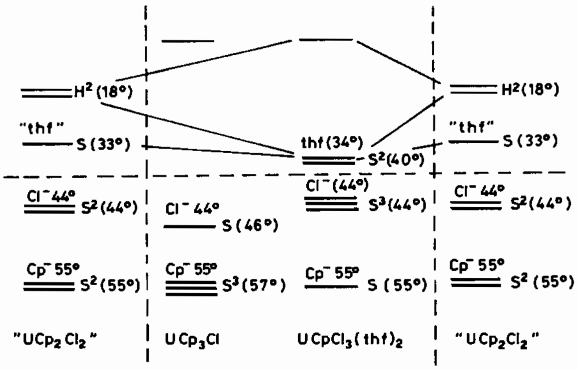

Fig. 12. Seat analysis for the disproportionation 2'UCp_2Cl_2' $\xrightarrow{thf}$ $UCp_3Cl + UCpCl_3(thf)_2$; an illustration of the reactions reorganizing the vacant seats for optimal packing.

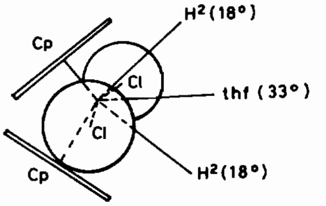

Fig. 13. Awkward packing in 'UCp_2Cl_2'.

The disproportionated compound, 'UCp_2Cl_2', is a good example (Fig. 12). Its existence had been long argued [16,39–43], but the disproportionation mechanism had not been clarified. If we place the two cyclopentadienyl groups and the two chloride ions in contact with each other at one side of the coordination sphere, a series of vacant seats will appear at the other side of the sphere. The largest vacant seat is located at the position of the C_{2v} rotation axis and its fan angle is calculated to be 33°*. The two next largest vacant seats are located beside the major one. Their fan angles are each 18°. The largest vacant seat is at the critical border for holding a new ligand and the two small vacant seats cannot cooperate with the major vacant seat for ligand accommodation (Fig. 13). On the contrary, the interlocking between the new ligand coordinated in the major vacant seat and the cyclopentadienyl group is obstructed by these two small vacant seats. Rearrangement is thus inevitable because of the awkward packing. If a cyclopentadienyl group in the first metal centre is exchanged for a smaller chloride ion, the extra room gained in the exchange, combined together with the original vacant seats, will lead to reorganization, producing two larger vacant seats. Each of the vacant seats is 40°, which is more proper for ligand packing as in $UCpCl_3(thf)_2$. The second metal centre, on obtaining the large cyclopentadienyl group and giving up the small chloride ion to form UCp_3Cl, becomes properly packed too because the vacant seats become smaller, the seat functions have greatly decreased. The seat analysis for the starting 'UCp_2Cl_2' and the exchange product is given in Fig. 12. Similar exchange occurred with the compound 'UCl_4dmso_3'. The formal chemical composition seems to be an odd number ligand packing whereas the actual structure showed it to be the complex salt of

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* $\dfrac{-\cos(\theta_{Cp} + \theta_{Cl})}{\cos\theta_{Cl}} = \cos(\theta_{Cl} + \theta_{thf})$

even number ligand packing, *i.e.* $[UCl_2L_6][UCl_6]$ [46].

In conclusion, if one places several balls in a box and shakes the box constantly, in the end the balls will arrange themselves in the most probable way of packing. Similarly, in chemistry the ligands tend to distribute themselves around the metal ion uniformly. If such packing homogeneity cannot be achieved within a single centre, exchange of labile ligands among several centres will occur.

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