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Coordination chemistry of rare earths: syntheses, structure, spectroscopy and chemical bonding

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Abstract - The molecular and electronic structure of mononuclear, dinuclear, polynuclear complexes and clusters of rare earths are discussed systematically, by an extended INDO method made applicable to treat 4f-compounds, with respect to the nature of chemical bonding and factors influencing the coordination number and structural types of lanthanide complexes and organometallics. Some recent investigations in our laboratory on the synthesis, molecular and electronic structure of some novel peroxy-bridging tetranuclear lanthanide complexes will also be discussed.

INTRODUCTION

In recent years the coordination and organometallic chemistry of rare earths have become one of the most fruitful and exciting fields of study. The successful syntheses of numerous novel rare earth compounds and their peculiar optical, magnetic, superconducting and catalytical properties not only attract extraordinary interests from experimental chemists but also give a great challenge in theoretical aspects.
The partially filled 4f-subshell of lanthanide compounds exhibits special optical and magnetic behaviour. The theoretical analysis of these phenomena is usually undertaken in terms of ligand field theory. However, for the study of chemical behaviour, such as the catalytic activities and the long-standing controvercy over the nature of chemical bonding of 4f-organometallics, and also for the prediction of new lanthanide compounds, it is more appropriate to use the molecular orbital theory.

In order to apply the molecular orbital theory for the calculation of the electronic structure of lanthanide compounds, we have extended the INDO formalism to 4f orbitals, derived all the expressions needed for the SCF MO calculations involving 4f atomic orbitals and evaluated VOIP, Slater and Racah parameters from the most recent spectral data (ref.1-3). An INDO program suitable for the lanthanide compounds was written and published (ref.2). It is well-known that the choice of the basic set of atomic orbitals is very important in ab initio as well as approximate MO calculations. Therefore we have proposed a set of double zeta wave functions of the 4f orbitals for the whole series of lanthanides. The optimized Slater exponents and the corresponding extension coeficients were obtained to fit the best Hartree-Fock numerical 4f orbitals of lanthanide elements (ref.4).

MONONUCLEAR COMPLEXES AND ORGANOMETALLICS

There are several long-standing controversies and questions in 4f-coordination and organometallic chemistry. They are: (1) What is the nature of lanthanide-ligand bonding, covalent or ionic? (2) If covalent, which orbitals contribute to bonding, 5d, 6s, 6p or 4f? (3) Why the coordination number of Ln atom or ion can vary in such a wide range from 3 to 12? What factors determine the C.N.? (4) Under what conditions it will be possible to form polynuclear Ln complexes and clusters?

1. Mononuclear complexes with C.N. = 3 are very scarce. Bradley et al. in 1973 (ref.5) synthesized

$$Ln(N(SiMe_3)_2)_3,\ Ln=Sc,Y,Ce,Pr,Nd,Sm,Eu,Gd,Ho,Yb,Lu$$

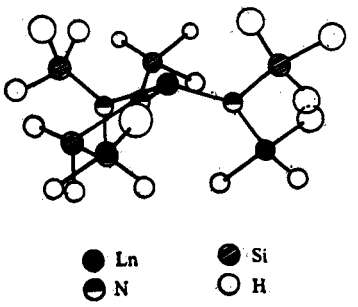

Fig.1 Structure of LnL_3

$L = N(SiMe_3)_2$

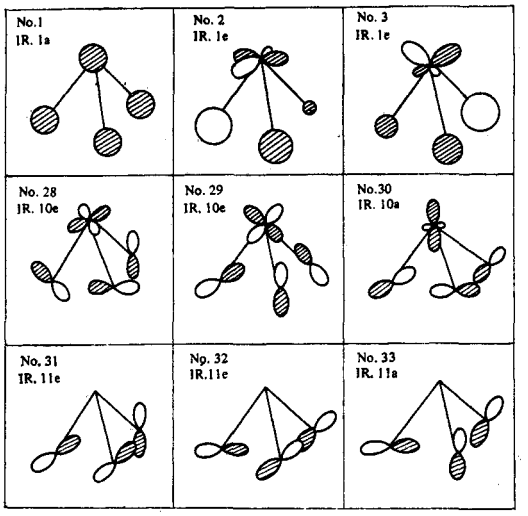

Fig.2 Schematic Diagram of Some MO's of NdL_3

Table 1 Theoretical Explanation of the Pyramidal Structure of NdL_3

Bond Angle of N-Nd-N/ Degree	Overlap Integral of Nd-N	Mulliken Bond Order				Net Charge on N
		Nd(6*s*)-N	Nd(6*p*)-N	Nd(5*d*)-N	Nd-N	
120	−0.172	0.079	0.116	0.435	0.630	0.637
115	0.386	0.084	0.111	0.452	0.641	0.503
100	0.438	0.094	0.103	0.457	0.654	0.421
90	0.293	0.095	0.100	0.456	0.651	0.415
80	0.055	0.093	0.097	0.452	0.642	0.433

Fig.1 shows the molecular structure of LnL_3.We have studied the electronic structure and chemical bonding of this compound by INDO method (ref.6).The results may be summarized as follows:(a)The net charge on Nd atom is only 0.254,so that the Nd-N bonds are mainly covalent in character.(b)The covalency of the bond is due to the participation of 5d,6s and 6p orbitals of the central Nd atom,while the three 4f electrons are more than 99% localized at the Nd atom.(c)Table 1 shows that the Mulliken bond order of the Nd-N bond is maximum at bond angle of N-Nd-N equal to 100°,which explains the pyramidal structure of the molecule.(d)Since the central lanthanide atom has nine valence orbitals: (5d),(6s) and (6p),it tends to assume high coordination number by polymerization or reaction with other neutral ligands such as solvent molecules unless there are bulky substituent groups R in the amide ligand NR_2.Therefore the presence of the bulky trimethyl silicon group R is a very important criterion for the existence of the discrete lanthanide complex LnL_3 with coordination number as small as three due to the steric hindrance against self polymerization.

2. Mononuclear complexes with C.N. = 4 are also scarce. Hart et al. in 1968 first reported a purely sigma bonded derivative,$Li(LnPh_4)$ (ref.7);but after structure determination,it was found that the anion $LnPh_4^-$ is not a discrete complex with C.N.=4,but polymerize to higher C.N.In 1972,F.A.Cotton,F.A.Hart et al.(ref.8) reported the synthesis and structural determination of tetrakis(2,6-dimethylphenyl) lutetiate anion.This was the first complex of lanthanides with C.N.=4,arranged in tetrahedral configuration.We have studied the electronic structure and chemical bonding in this anion complex by INDO method (ref.8).Fig.3 shows the schematic diagram of some MO's of

$$Lu(2,6\text{-dimethylphenyl})_4^-$$

Fig.4 gives the charge distribution of the simplified complex anion $LuPh_4^-$. It may be seen that the net charge on Lu atom is 0.948,so that the Lu-C bond is mainly covalent with about 31% ionic character.The Mulliken bond order of Lu-C is 0.497.

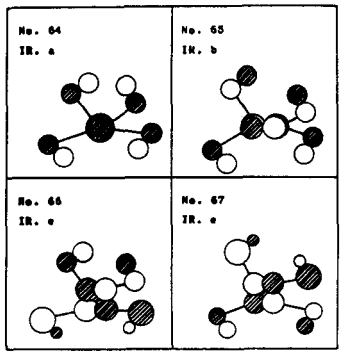

Fig.3 Schematic Diagram of Some MO's of $Lu(2,6\text{-dimethylphenyl})_4^-$

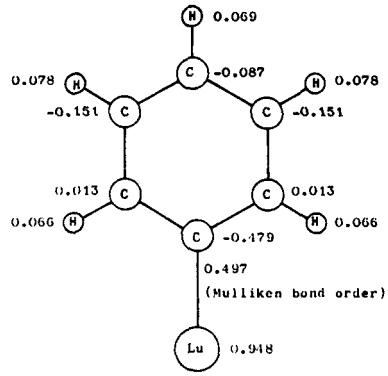

Fig.4 Net Charge Distribution of $LuPh_4^-$

3. Mononuclear complexes with C.N. = 5 are also scarce. The following complex may be an example,but its structure has not been reported yet.

$$LnCl_3(\text{phenanthroline})$$

4. Mononuclear complexes with C.N. = 6 are not common also. The anion

$$Er(NCS)_6^{3-} \text{ in } ((C_4H_9)_4N)_3Er(NCS)_6 \quad \text{(Martin et al.,1968)}$$

is an example.Here the presence of the bulky tetrabutylammonium cation is an important criterion for the existence of this lanthanide complex.

5. Mononuclear complexes with C.N. = 7 In our laboratory,as a part of a project to study the rare earth complexes with neutral organophosphorus extractants,Huang et al.(ref.9) have synthesized a neodymium complex with C.N.=7, $Nd(NCS)_3(Ph_3PO)_4$. The crystal and molecular structure have been determined by a Nicolet Model R3 Four-circle X-ray Diffractometer.The crystal is monoclinic with space group P21/c.The unit cell parameters are

a=13.211(7) Å	beta = 102.19(5)°	Z = 4
b=23.544(14) Å	F(000) = 2924 e	d_{calc}=1.370 g/cm^3
c=22.821(18) Å	V = 6943 Å^3	d_{expt}=1.375 g/cm^3

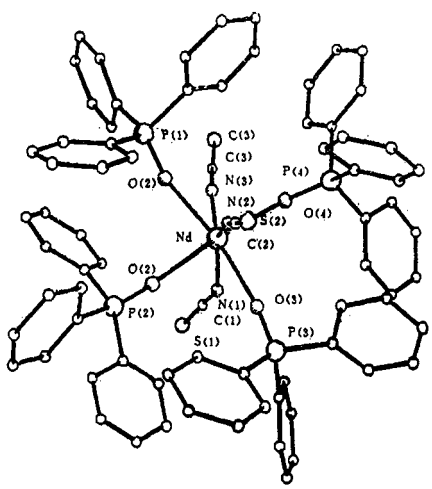

Fig.5 Structure of $Nd(NCS)_3(Ph_3PO)_4$

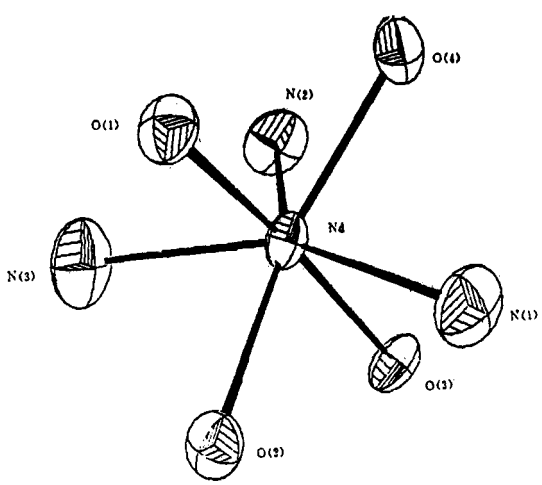

Fig.6 The Coordination Sphere of Neodymium

The molecule has an approximate Cs symmetry as shown in Fig.5. It has three covalent Nd-N bonds with an average bond length of 2.50 Å and four dative covalent bonds with neutral triphenyl phosphine oxide ligands, the average length of the dative Nd-O bond is 2.39 Å. Fig.6 shows the coordination sphere of Neodymium.

6. Mononuclear complexes with C.N. = 8 Li, Ni, Xu and Ren (ref.10) have studied the electronic structure and chemical bonding in the 15-crown-5 complex of lanthanum trichloride having C.N.=8.

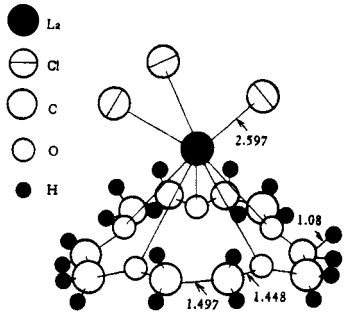

Fig.7 Molecular Structure of $LaCl_3$(15-crown-5)
(Numbers in the figure are bond lengths in Å)

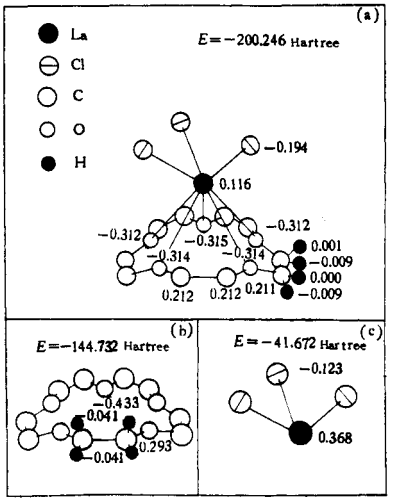

Fig.8 Charge distribution of
(a) $LaCl_3$(15-crown-5)
(b) 15-crown-5
(c) $LaCl_3$

7. Mononuclear complexes with C.N. = 9 Huang et al.(ref.11) have prepared a neodymium complex, $Nd(NO_3)_3(Ph_3PO)_2(C_2H_5OH)$, and determined its crystal and molecular structure having C.N.=9. But we shall only discuss the electronic structure and chemical bonding in a pi-bonded complex, trisindenyl samarium, with C.N.=9.(ref.12).

Fig.9 shows the molecular structure of $Sm(ind)_3$, Fig.10 gives the schematic diagrams of some MO's of $Sm(ind)_3$.

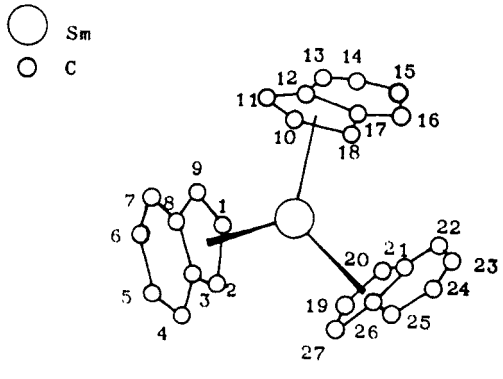

Fig.9
Molecular structure of $Sm(Ind)_3$

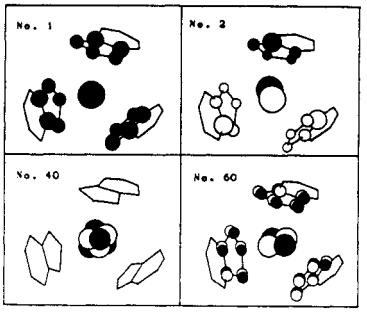

Fig.10
Schematic diagrams of some MO's of $Sm(C_9H_7)_3$

From Fig.10 it may be seen that the MO No.1 of the lowest energy is due to the overlapping of the 6s orbital of Sm and the C 2p pi-orbitals of the five membered rings of the three indenyl ligands,while the four other C 2p pi-orbitals of the six-membered ring do not participate to the bonding with Sm. MO No 2 is due to the overlapping of 6p orbitals of Sm with the five-membered rings of indenyl ligands.MO No.60 is of much higher energy and due to the overlapping of 5d of Sm,while the Mo No.40 is strongly localized to 4f of Sm, without any interaction with the ligands.The net charge on Sm atom is only 0.471,so that the Sm-ligand pi-bond s are mainly covalent in character.Other details of the electronic structure may be refered to ref.12.

8. Mononuclear complexes with C.N. = 10 D.R.Rogers et al.(1980) synthesized $Cp_3Gd(THF)$ and determined its structure,which has C.N.=10.We have studied its electronic structure and bonding (Ren and Xu,to appear).

9. Mononuclear complexes with C.N. = 11 are very rare.One example worthwhile to mention is $LaCp_3(CH_3CN)_2$.

10. Mononuclear complexes with C.N. = 12 In our laboratory,Huang et al.(ref.13) synthesized $((C_4H_9)_4N)_3Nd(NO_3)_6$ and determined its molecular and crystal structure and found that the nitrate ligands are bidentate,so that the C.N. of Nd is 12.That means there are 24 valence electrons surrounding the central Nd atom,but INDO calculation (Ren,Huang and Xu,to appear) reveals that the 4f orbitals of Nd remain strongly localized,only nine valence orbitals, 5d,6s and 6p particpape to bonding with the bidentate nitrate ligands,the six excess valence electrons being located at the nonbonding orbitals of the ligands.

DINUCLEAR COMPLEXES AND ORGANOMETALLICS

1. Dinuclear complexes with C.N. = 5 or less are rather rare.The following oxygen bridging,sigma-bonded complex is an example.Here,as in the mononuclear complexes,the presence of bulky ligands is very important for low C.N.

$$La(N(SiMe_3)_2)_3 + Ph_3PO + O_2 \longrightarrow$$

$$(Ph_3PO)(N(SiMe_3)_2)_2La(mu\text{-}O)_2La(N(SiMe_3)_2)_2(Ph_3PO)$$

(Bradley et al.,1974)

2. Dinuclear complexes with C.N. = 8 are rather common.M.L.Ely et al.synthesized $Cp_2Yb(mu\text{-}Me)_2YbCp_2$ and J.Holton et al.(ref.14) determined its structure as shown in Fig.11.We studied its electronic structure (ref.15).Fig.12 shows the schematic diagram of the MO's corresponding to the bridging methyl bonds. Fig.13 gives the charge distribution of the complex.

The carboxylate bridging lanthanide complexes usually crystallize in polymeric chains.Zhang et al.(ref.16) have succeeded to prepare a dimeric Nd complex by using a bulky neopentanoic acid to prevent from polymerization. The structure was determined and shown in Fig.14.

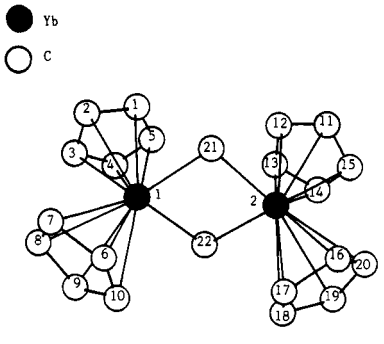

Fig.11 Structure of $(YbCp_2Me)_2$

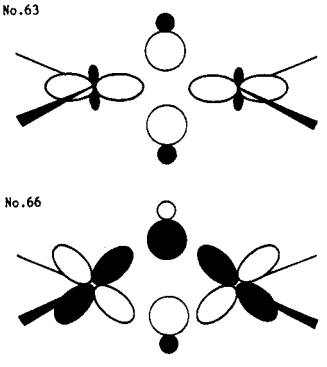

Fig.12 MO's of bridge bonds

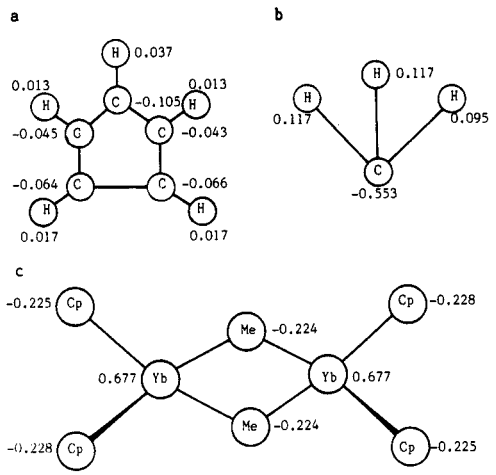

Fig.13 Charge Distribution of $(YbCp_2Me)_2$

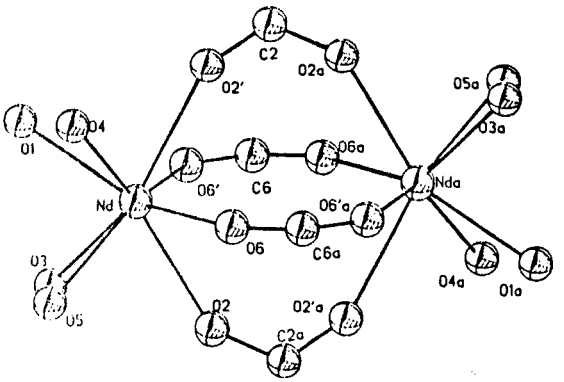

Fig.14 Structure of Dimeric Nd Complex with Neopentanoic Acid

3. Dinuclear complexes with C.N. = 9 The following complex is an example.

$(MeC_5H_4)_2(THF)Er(mu\text{-}H)_2Er(THF)(MeC_5H_4)_2$

(E.C.Baker et al.,1975; W.J.Evans et al.,1982)

4. Dinuclear complexes with C.N. = 11 is very rare.Huang et al. in our laboratory (ref.17) have prepared a compound,in which there is a novel eleven-coordinate nitrate bridging dinuclear neodymium complex,the structure of which has been determined as shown in Fig.15.Using a localized INDO program,we also studied the electronic structure and bonding of this interesting complex. Figs. 16 and 17 show the contour diagram of the bonding between the two Nd atoms and the bridging nitrate group.

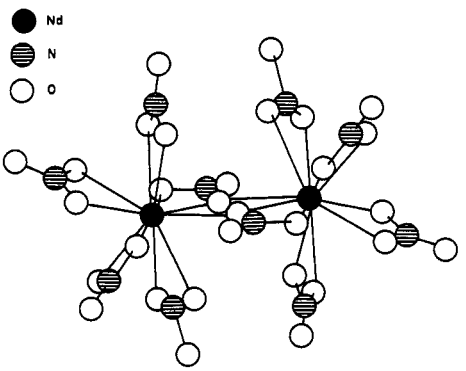

Fig.15 Structure of $Nd_2(NO_3)_{10}^{4-}$ in $(Me_3C_{16}H_{33}N^-)_4(Nd_2(NO_3)_{10}^{4-})$

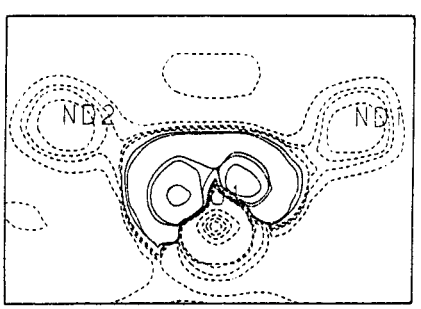

Fig.16 Contour diagram of the nitrate bridge bond between two Nd atoms (a)

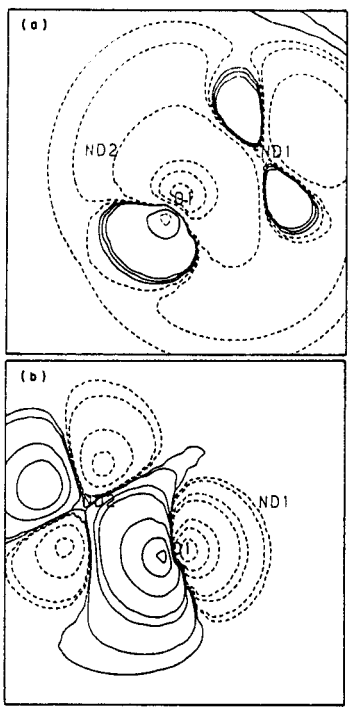

Fig.17 Contour diagram of the nitrate bridge bond between two Nd atoms (b)(c)

POLYNUCLEAR COMPLEXES AND CLUSTERS

1. Dioxygen bridging tetranuclear complexes In our laboratory,we have recently synthesized four novel series of complexes having the following formulations (ref.18):

$Ln_4O_4Cl_8(THF)_8(H_2O)_2 \cdot 2THF$ $Ln_4O_4Cl_8(THF)_6(H_2O)_4 \cdot 2THF$

$Ln_4O_4Cl_8(THF)_2(H_2O)_8 \cdot 4THF$ $Ln_4O_4Cl_8(THF)_2(H_2O)_8 \cdot 2H_2O$

where Ln=Pr,Nd,Sm and THF is tetrahydrofurane. The crystal and molecular structure of them have been determined by x-ray diffraction method.

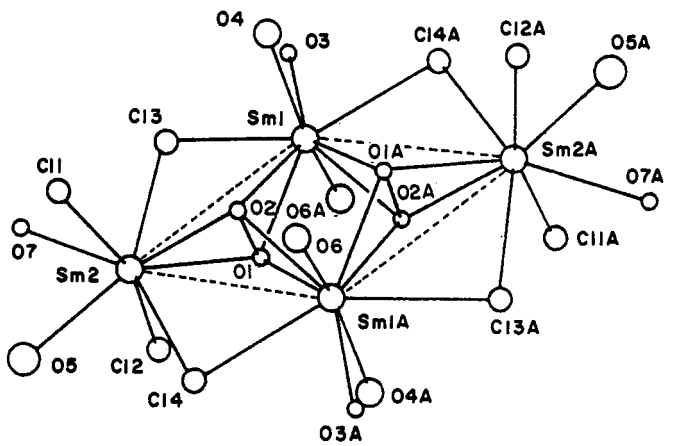

Fig.18 Structure of $Sm_4O_4Cl_8(THF)_6(H_2O)_4$

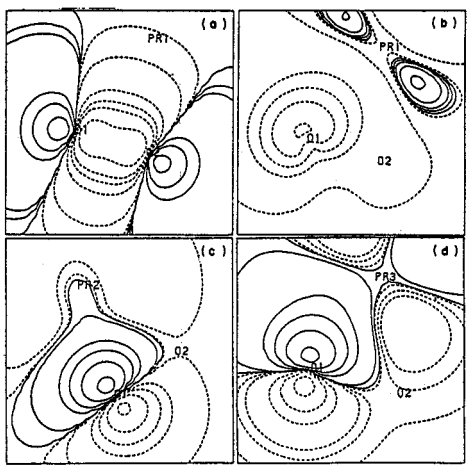

Fig.19 Contour maps of dioxygen bridge to three Ln atoms (ref.19)

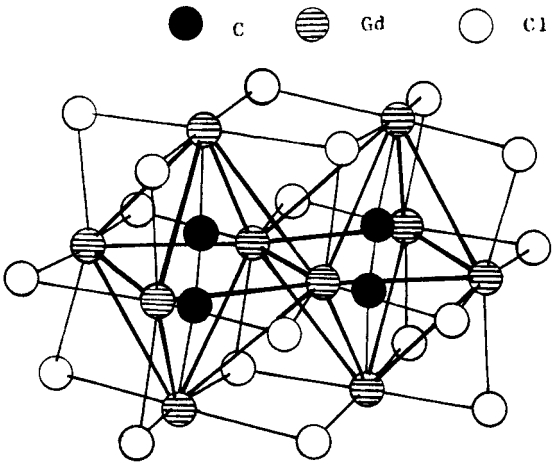

Fig.20 Structure of $Gd_{10}C_4Cl_{18}$

2. Polynuclear lanthanide clusters The electronic structure and chemical bonding in the cluster,$Gd_{10}C_4Cl_{18}$,whose structure was determined by E.Warkentin et al. (ref.20) as shown in Fig.20,was studied by us (ref.21).The results show that the bonding is covalent in character rather than ionic. Mulliken population analysis gives that the net charges on all atoms in the cluster are nearly neutral.The contribution to covalent bonding is mainly due to the 5d,6s and 6p orbitals of Gd,while the 4f orbitals are strongly localized.The C_2 unit in the center of each Gd octahedron,in which there is a C-C single bond,is combined with six neighboring Gd atoms by two Gd-C single bonds and eight Gd··C "half bonds",so that the total valence of C remains equal to 4.The Mulliken bond order between Gd··Gd is only o,265.

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