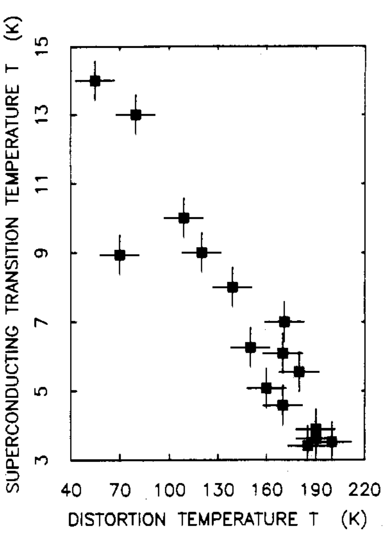

Figure 13. Superconducting critical temperature of the lead solid solution and the $M^{II}Mo_6S_8$ compounds as a function of the distortion temperature.

in a more symmetric environment about the Mo_6 cluster. These data are summarized in Table IV. Figure 13 contains a plot of the temperature of the anomaly, T_1, vs. the superconducting critical temperature for the solid solution as well as the data for Eu, Yb, Sr, Ba, and Sn. The correlation supports the hypothesis that the drops in the susceptibility are due to electronic instabilities that are related to the structural distortions observed in Eu, Sn, Ba, and Ca compounds.

By way of summary, a structural distortion in the $M^{II}Mo_6S_8$ compounds from a rhombohedral to a triclinic structure as reported by Baillif et al.[5] for the europium, barium, strontium, and calcium compounds was related to electronic instabilities in the lead, tin, and ytterbium compounds. A correlation between the temperature of the anomalies in the physical properties and the second ionization potential of the cation was demonstrated and explained in terms of increased covalent bonding of the ternary cation as the ionization potential increases. The anomaly was then shown to correlate with the superconducting critical temperatures of these compounds and also with anomalies in the pressure dependence of the superconducting critical temperature. This relationship results from the effects of electron-phonon coupling affecting both the superconducting critical temperature and the structural distortion. The correlation was extended to the $PbMo_6(S_{1-x}Se_x)_8$ solid solution, where anomalies in the magnetic susceptibility were shown to correlate with the superconducting critical temperature. This paper extends the relationship between structural and electronic instabilities and high-temperature superconductivity to yet another class of compounds.

Acknowledgment. This research was sponsored by the Air Force Office of Scientific Research, Grant No. AFOSR 80-0009, and was supported in part by the National Science Foundation and the Materials Science Center at Cornell University.

Note Added in Proof. A recent publication (Jorgensen, J. D.; Hinks, D. G. *Solid State Commun.* **1985**, *53*, 289) confirms the presence of a structural distortion in $PbMo_6S_8$ and $SnMo_6S_8$ below 100 K.

Registry No. $CaMo_6S_8$, 85714-04-1; $SrMo_6S_8$, 85704-51-4; $BaMo_6S_8$, 96866-36-3; $YbMo_6S_8$, 57485-88-8; $EuMo_6S_8$, 61642-20-4; $SnMo_6S_8$, 39432-50-3; $PbMo_6S_8$, 39432-49-0.

Contribution from the Max-Planck-Institut
für Festkörperforschung, 7000 Stuttgart-80, FRG

Interstitial Carbon Molecules, Metal-Metal Bonds, and Chemical Binding in $Gd_{10}C_4Cl_{18}$

S. SATPATHY* and O. K. ANDERSEN

Received August 22, 1984

By means of electronic structure calculations we study the chemical binding in the cluster $Gd_{10}C_4Cl_{18}$—a cluster that consists of a Gd edge-sharing double octahedron with Cl atoms bridging the remaining edges and with C_2 molecules occurring at the octahedral centers. This type of cluster is the basic unit of three compounds, $Gd_{10}C_4Cl_{18}$, $Gd_{10}C_4Cl_{17}$, and $Gd_{12}C_6I_{17}$. We find that in the $Gd_{10}C_4Cl_{18}$ cluster the Cl-like and the C_2 π_p*-like levels are occupied while the C_2 σ_p*-like and all Gd-like levels are empty. The cluster has no metal-metal bonds in the sense that there are no occupied molecular orbitals that are primarily metal-metal bonding in character. However, 1.7 electrons are contributed to each Gd atom through back-bonding from the occupied Cl-like (1.0 electron/Gd) and C_2-like (0.7 electron/Gd) states. The lowest unoccupied molecular orbital is a Gd molecular orbital in the basal plane—and concentrated along the shared edge—of the double octahedron. We expect that the binding in the cluster compound $Gd_{10}C_4Cl_{18}$ is like that in the isolated cluster and hence is predominantly ionic. For the cluster compounds $Gd_{10}C_4Cl_{17}$ and $Gd_{12}C_6I_{17}$ we find that the molecular-orbital schemes are essentially the same as in $Gd_{10}C_4Cl_{18}$; however, now an extra electron occupies the metal-metal bond concentrated along shared edges in the compound.

Introduction

Recently a novel class of cluster compounds involving rare-earth halides and carbon atoms has been synthesized.[1-4] The basic structural unit, $Gd_{10}C_4X_{18}$, of the compounds with which we shall be concerned is an edge-sharing double octahedron, $(Gd_4Gd_{2/2})_2 = Gd_{10}$, with halogen atoms, X_{18}, bridging the remaining edges of the double octahedron and with a C_2 molecule at the center of each octahedron (Figure 1). The occurrence of a molecule inside the metal octahedron is an unusual feature of these compounds. The two molecules of the double octahedron are well separated and, for each molecule, the C–C distance of 147 pm is slightly shorter than the C_2 single-bond length of 154 pm.

The crystal structures are such that the halogen atoms together with the C_2-containing Gd_6 octahedra form a face-centered cubic lattice. In the compounds $Gd_{10}C_4Cl_{18}$ and $Gd_{10}C_4Cl_{17}$ the clusters are well separated as far as distances between metal atoms are concerned: ($d^{\text{inter}}_{\text{Gd-Gd}} \geq 1.17$, $d^{\text{intra}}_{\text{Gd-Gd}} \approx 440$ pm). In $Gd_{10}C_4Cl_{17}$ two Cl atoms are shared between neighboring clusters.[2,3] In $Gd_{12}C_6I_{17}$ the double octahedra are parallel and are arranged in such a way that through the addition of linear Gd–C–C–Gd units between them third octahedra are formed, and the entire structure is then

---

(1) Simon, A. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 1 and references therein.
(2) Simon, A.; Warkentin, E.; Masse, R. *Angew. Chem.* **1981**, *93*, 1071.
(3) Warkentin, E.; Masse, R.; Simon, A. *Z. Anorg. Allg. Chem.* **1982**, *491*, 323.
(4) Simon, A.; Warkentin, E. *Z. Anorg. Allg. Chem.* **1983**, *497*, 79.

0020-1669/85/1324-2604$01.50/0 © 1985 American Chemical Society

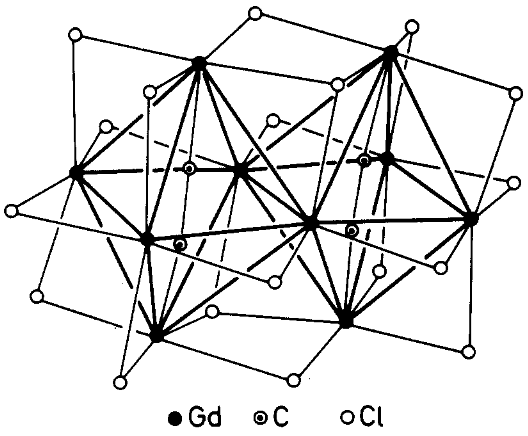

Figure 1. Structure of the isolated cluster $Gd_{10}C_4Cl_{18}$ (schematic). The Gd atoms form the edge-sharing double octahedron. Two C_2 molecules are located at the centers of the octahedra, and the eighteen Cl atoms bridge the free edges of the double octahedron.

composed of infinite zigzag chains of edge-sharing octahedra.

The fact that no compound has been found where an edge-sharing double octahedron occurs without the enclosed C_2 molecule indicates that the C_2 molecules might play a crucial role in the stabilization of the cluster. Basically two models have been proposed[3,4] to describe how the metal double octahedron and the two C_2 molecules interplay to bring about the structural stability.

A hypothetical, bare $Gd_{10}X_{18}$ cluster has, corresponding to the ionic formula $(Gd^{3+})_{10}(X^{1-})_{18}$, 12 electrons in Gd-like orbitals. Two isolated C_2 molecules have 8 s electrons in the σ_s and $\sigma_s{}^*$ orbitals and 8 p electrons in the bonding π_p orbitals. The bonding σ_p orbitals together with the antibonding $\pi_p{}^*$ and $\sigma_p{}^*$ orbitals are empty.

The first model,[3] from the observation that the metal atoms are arranged in octahedra, hypothesizes strong metal–metal bonds and supposes that the C_2 molecules strengthen these bonds by transferring electrons into them. Consequently in the compound $Gd_{10}C_4Cl_{18}$ one would obtain the observed C_2 single-bond distance by transferring the 12 π_p- and $\sigma_s{}^*$-like electrons into Gd-like orbitals, thereby making a total of 24 electrons occupying the valence orbitals of the 10 Gd atoms. Subsequently, this naive picture corresponding to the formula $(Gd^{0.6+})_{10}(C_2{}^{6+})_2(X^{1-})_{18}$ would be modified through covalent interaction between the C_2 and the Gd orbitals. A similar, but more plausible, model is obtained by assuming that in $Gd_{10}C_4X_{18}$ the π_p- and the σ_p-like levels are inverted such that σ_p is below π_p. The C_2 single bond now arises because σ_p is occupied and π_p is empty. Here, only 4 electrons would be transferred to the Gd-like orbitals, making a total of 16 electrons on the valence orbitals of the Gd atoms. (This happens to be the number of bonding electrons for single M_6X_{12} octahedral clusters[5]). The corresponding ionic formula is $(Gd^{1.4+})_{10}(C^{1+})_4(X^{1-})_{18}$. In the following we shall refer to the two models described above as models Ia and Ib, respectively.

According to the second model[3,4] the electron transfer is in the reverse direction and all 12 Gd electrons are transferred to the C_2 molecules, thus filling the σ_p- as well as the $\pi_p{}^*$-like orbitals. The facts that the C_2 bond is slightly shorter than a single bond and that the distance between a C atom and the apex Gd atom is unusually short (220 pm) should be caused by back-bonding to Gd orbitals. This—essentially ionic—model has no metal–metal bonds and corresponds to the formula $(Gd^{3+})_{10}(C_2{}^{6-})_2(X^{1-})_{18}$. It is consistent with the observation that the large anions (X^{1-} and $C_2{}^{6-}$) occupy a close-packed lattice in which the small cations (Gd^{3+}) gather in the octahedral holes around the most highly charged anions ($C_2{}^{6-}$).

The chemical binding of the compound $Gd_{10}C_4Cl_{17}$ differs from that of the compound $Gd_{10}C_4Cl_{18}$ in that now there is one more electron per cluster. The C–C distance is the same (147 pm), and so is the shortest C–Gd distance (220 pm). However, the average edge length of the Gd_{10} double octahedron is notably decreased (374 → 371 pm), in particular through shortening of the shared edge (321 → 312 pm) and the ones parallel to it (355 → 346 pm).[3]

The compound $Gd_{12}C_6I_{17}$ has one C_2 molecule more and one halogen atom less than $Gd_{10}C_4Cl_{18}$. Therefore, the former compound has 7 electrons more than the latter in Gd-like orbitals according to model Ia, and 3 according to model Ib. According to model II this compound is formally described as the ionic lattice $(Gd^{3+})_{12}(C_2{}^{6-})_3(I^{1-})_{17}$ plus *one* extra electron. The C–C distance in the double octahedron is 145 pm and it is 141 pm in the perpendicular C_2 molecules. The smallest C–Gd distance is again 221 pm in the double octahedron and 222 pm in the "perpendicular" single octahedron. Finally, the average Gd–Gd distance is 381 pm with the shortest distances being those of the shared edge of the double octahedron (319 pm), of the edges parallel to it (357 pm), and of the edge shared between the double and the single octahedra (336 pm).[4]

In this paper we analyze the chemical binding by performing molecular-orbital calculations for a single $Gd_{10}C_4Cl_{18}$ cluster "taken out of" the $Gd_{10}C_4Cl_{18}$ compound. The occupancy of metal–metal bonding orbitals and the role of the C_2 molecules in chemical binding are the principal points of discussion here.

Method

$Gd_{10}C_4Cl_{18}$ crystallizes in a monoclinic lattice with two $Gd_{10}C_4Cl_{18}$ clusters per unit cell.[3] Each cluster is fairly well isolated and is connected to the rest of the lattice via a few of the chlorine atoms. In order to avoid performing a band structure calculation for a compound with 64 atoms per unit cell, we merely perform a molecular-orbital calculation for a single cluster. This should give a reasonable description of the binding in the $Gd_{10}C_4$ complex, but the width of the Cl 3p band will, or course, be underestimated. The only symmetry element of the single cluster is the inversion.

Our molecular-orbital method, the linear muffin-tin orbital method in its atomic sphere approximation (LMTO–ASA)[6,7] is a standard tool for self-consistent density-functional calculations in solids. We included the relativistic shifts, but the spin–orbit coupling was neglected. In the present calculation we do not attempt to calculate total energies. The one-electron potential is not self-consistent but is obtained by the standard Mattheiss construction.[8] This involves superposition of neutral-atom charge densities from all atoms in the compound and retaining only the spherically symmetric part inside the (slightly overlapping) atomic muffin-tin spheres. Full Slater exchange is used.

The radii of the atomic muffin-tin spheres are chosen in such a way that the spheres on one hand are so large as to fill space as well as possible and on the other hand are small enough that the spheres do not overlap by more than about 20% ($s_1 + s_2 \leq 1.20$ times the interatomic distance). Furthermore, the sphere sizes are such that the discontinuities of the muffin-tin potential between neighboring spheres are small. The Gd, C, and Cl sphere radii used in our calculations are respectively 3.2, 1.7, and 2.4 Bohr radii, which may be compared with the covalent radii of respectively 3.0, 1.5, and 1.9 units. The cluster is finally enclosed in a Watson sphere[7] of radius 10 Bohr radii. The results of our calculation turn out to be insensitive to small changes in these sphere radii.

For each atom the s, p, and d muffin-tin orbitals are included in the basis set so that the Hamiltonian matrix has the dimension 288 × 288. We use the orthonormal representation[7] so that the electronic eigenstates of the cluster are obtained by a single diagonalization. It should be mentioned that with our orthonormal set of atom-centered orbitals the Mulliken and Löwdin definitions of charge belonging to a particular atom are identical. Moreover, for the orthonormal set of muffin-tin orbitals this charge also equals the charge inside the chosen atomic muffin-tin sphere.[7]

Results and Discussion

The molecular-orbital (MO) scheme calculated for the $Gd_{10}C_4Cl_{18}$ cluster is shown in the central part of Figure 2. We here show projected density-of-states curves as obtained by projection onto the various groups (Gd_{10}, C_4, or Cl_{18}) of orthonormal atomic orbitals. For convenience of display we have broadened the discrete energy levels by a Gaussian of width 5 mRy. In left- and

---

(5) Kettle, S. F. A. *Theor. Chim. Acta* **1965**, *3*, 211.

(6) Andersen, O. K. *Phys. Rev. B: Solid State* **1975**, *12*, 3060. Skriver, H. L. "The LMTO Method"; Springer Verlag: Berlin, 1984. See also: Andersen, O. K.; Wolley, G. *Mol. Phys.* **1973**, *26*, 906.

(7) Andersen, O. K. In "The Electronic Structure of Complex Systems", Temmerman, W., Phariseau, P., Eds.; Plenum Press: New York, 1984.

(8) Mattheiss, L. F. *Phys. Rev.* **1964**, *133*, A1399.

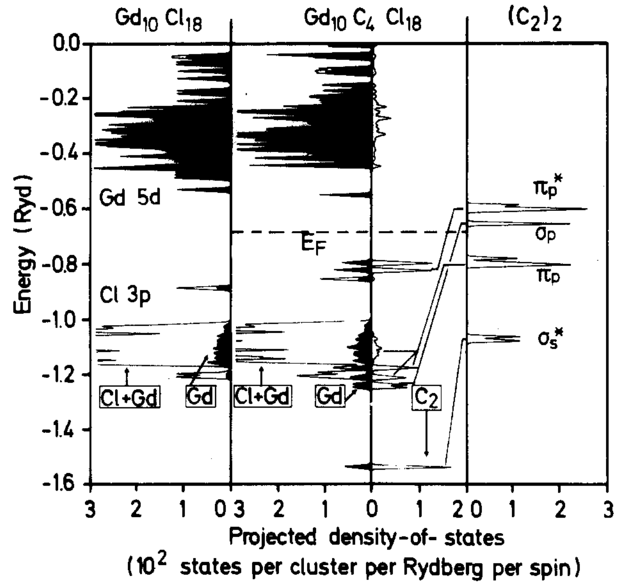

Figure 2. Gd_{10}-, Cl_{18}-, and C_4-projected densities of states for the $Gd_{10}C_4Cl_{18}$ cluster. For clarity, the discrete energy levels have been broadened by a Gaussian of width 5 mRy. The left- and rightmost panels show the levels for noninteracting $Gd_{10}Cl_{18}$ and $(C_2)_2$ systems. These were defined as explained in the text. The σ_s and σ_p^* C_2 levels fall outside the frame of the figure.

rightmost panels we show the result of setting those matrix elements of the Hamiltonian equal to zero which couple C orbitals to Gd or Cl orbitals. This calculation, in which the two C_2 molecules and the $Gd_{10}Cl_{18}$ cage are decoupled from each other but in which the atomic positions, potentials, and orthonormal orbitals are those of the truly coupled system, will be compared with the full calculation in order to describe the bonding.[9]

The ordering of the decoupled $(C_2)_2$ levels in the rightmost panel is the same as for the free C_2 molecule. All levels below π_p and including π_p are occupied while σ_p and the levels above are empty. The weak interaction between the two C_2 molecules gives rise to splittings of the order of 20 mRy.

The decoupled $Gd_{10}Cl_{18}$ levels shown in the leftmost panel are separated into a band extending between −1.20 and −0.88 Ry of predominantly Cl 3p character and a band extending between −0.53 and −0.21 Ry of predominantly Gd 5d character. Above this is the Gd 6s band. The degree of covalent mixing between the Cl and the Gd orbitals may be expressed by the fact that the Gd orbitals contribute 1.0 electron/Gd atom (0.3 Gd s, 0.3 Gd p, and 0.4 Gd d electron) to the Cl 3s- and 3p-like bands. The Fermi level of this hypothetical cluster is placed 12 electrons up in the Gd d-like band. The lowest Gd d-like state at −0.53 Ry split off below the Gd d-band "continuum" is the single metal–metal bond mentioned in the Introduction, to which we shall return later. Apart from this, the Gd d-band shows no pronounced gaps, which indicates that, regardless of the filling of this band, no further strong metal–metal bonds are possible. This is quite distinct from the situation for the *single* M_6X_{12} octahedral cluster where the three-center bonds in the triangular faces give rise to a pronounced gap after 16 electrons.[5,11] Also condensed, corner-sharing M_6X_{12} clusters as found, for instance, in the vacancy structure Nb_3O_3 have more than one metal–metal bond. This is so because the back-lobes of the directed d orbitals, responsible for the three-center bonds in the single cluster, can be used to bind in such condensates where there is (approximate) inversion symmetry around the shared atom.[11] This is *not* the case for an *edge*-sharing cluster based on M_6X_{12}. The $Gd_{10}Cl_{18}$ cluster thus possesses no particular stability.

Table I. Energy and Percent Character of the Occupied C_2-like Molecular Orbitals in the $Gd_{10}C_4Cl_{18}$ Cluster[a]

		atomic characters, %				
			Gd			
MO	energy, Ry	C	s	p	d	Cl
π_p^*	−0.81	64	0	2	29	5
π_p	−1.20	51	11	3	10	24
σ_p	−1.24	68	10	6	10	6
σ_s^*	−1.54	75	6	8	11	0
σ_s	−2.14	88	3	5	4	0

[a] There are more than one MO of a particular symmetry differing from each other only slightly. Here only the average values are given.

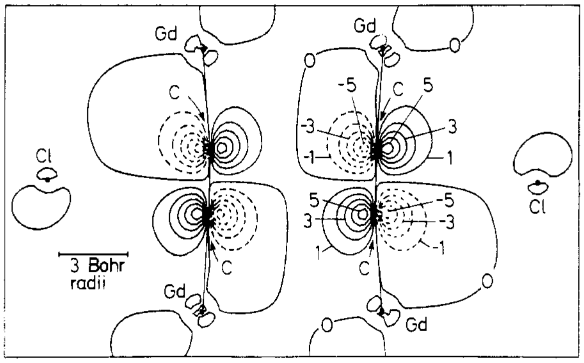

Figure 3. An occupied π_p^*-like molecular orbital plotted in the plane perpendicular to the basal plane of the double octahedron and through the C atoms. The contour values are in units of 0.05(Bohr radius)$^{-3/2}$. Straight lines are drawn, in this and the following figures, between certain atoms to help the eye. These lines correspond to the lines in Figure 1.

As seen in the central panels of Figure 2, when the noninteracting $(C_2)_2$ and $Gd_{10}Cl_{18}$ systems, prepared by having the proper atomic positions and the proper orthogonalized orbitals, are brought into contact, 12 electrons transfer *from* the cluster *to* the carbon molecules and fill the lower lying σ_p and π_p^* orbitals. This gives an ionic contribution to the binding. The covalent interaction, predominantly with the Gd orbitals, furthermore stabilizes the $Gd_{10}C_4Cl_{18}$ cluster by lowering the energies of the π_p^*-, σ_p-, π_p-, σ_s^*-, and σ_s-like levels as seen in the figure. Our calculations thus support the second, basically ionic, model described in the Introduction.

The covalent mixing of the C_2-like states, which may be visualized in Figure 2, is analyzed in Table I. The π_p^*-like states have about 29% Gd d contributions. π_p are the most strongly mixed states, and they have about 11% Gd s, 10% Gd d, and 24% Cl p character. The latter does not contribute to the binding because the Cl p band is occupied. σ_p are the states whose energies are lowered the most by the interactions with the $Gd_{10}Cl_{18}$ cage because they have the strongest overlap with the s, p, and d orbitals of the terminal Gd atoms; the σ_p states have 10% Gd s, 6% Gd p, and 10% Gd d character. The low-lying, more localized σ_s^* and in particular σ_s states mix less with the Gd orbitals and not at all with the Cl orbitals.

The four MOs with predominant contribution from the carbon π_p^* orbitals differ either in the direction of the carbon orbitals (along or perpendicular to the length of the double octahedron) or in the phase of the same orbitals between the two C_2 molecules (bonding or antibonding). The antibonding π_p^* state directed along the length of the double octahedron is shown in Figure 3. The four MOs have a dispersion of about 30 mRy in energy primarily because of the slightly different amount of covalent interaction with the Gd framework.

---

[9] The noninteracting systems could, alternatively, have been defined as those given by the one-electron potentials constructed for respectively C_2 and $Gd_{10}Cl_{18}$. For $Gd_{10}Cl_{18}$ the result is very similar to the one shown in Figure 2. For C_2 one can, however, not solve the corresponding Schrödinger equation with sufficient accuracy using the ASA. Self-consistent LMTO (non-ASA) density-functional calculations for C_2 are reported in ref 10. From these we gather that the unusually small π_p–π_p^* splitting seen in the rightmost panel of our Figure 2 is the result not only of the long C–C distance (single rather double bond) but also of the orthogonalization of our C_2 orbitals to the Gd orbitals.

[10] Harris, J.; Jones, R. O. *Phys. Rev. A* **1978**, *18*, 2159.

[11] Satpathy, S.; Andersen, O. K. In "Basic Properties of Binary Oxides"; Dominguez Rodriguez, A., Castaing, J., Marquez, R., Eds.; Universidad de Sevilla: Sevilla, Spain, 1984.

Table II. Mulliken Electron Population Count and Ionicity for the Cluster $Gd_{10}C_4Cl_{18}$[a]

orbital		Mulliken count			
		from C_2-like MOs	from Cl-like MOs	total	ionicity
C	σ_s	0.8	0	0.8	
	σ_s^*	0.6	0	0.6	
	σ_p	0.8	0	0.8	
	σ_p^*	0.1	0	0.1	
	π_p	1.0	0.5	1.5	
	π_p^*	1.3	0	1.3	
	d	0	0	0	
	total	4.6	0.6	5.2	−1.2
Gd	s	0.2	0.1	0.3	
	p	0.1	0.4	0.5	
	d	0.4	0.5	0.9	
	total	0.7	1.0	1.7	+1.3
Cl	total	0.1	7.4	7.45	−0.45

[a] The Mulliken counts are given in electrons per C, Cl, or Gd atom with spin included.

Although, as previously speculated,[3,4] the π_p^*-like state has the highest Gd d content caused by strong pdπ interactions, the total covalency is not concentrated on this state. Moreover, as evidenced from Figure 2, the C_2 orbitals do not mix with just a few, individual molecular orbitals of the $Gd_{10}Cl_{18}$ cluster but the π_p^* character is, for example, spread over the entire Gd d band so that in $Gd_{10}C_4Cl_{18}$ there are neither metal–metal bonds nor Gd–C bonds.

In Table II we give the electron-population count; that is, we sum over all occupied MOs and give the contribution of individual—or groups of—orbitals to the valence-electron charge density, shown graphically in Figure 4. In this table we have furthermore separated the occupied MOs into the C_2-like MOs listed in Table I and the (remaining) Cl-like MOs. The redistribution of the electrons onto various atoms is summarized by the ionicity formula $(Gd^{1.3+})_{10}(C^{1.2-})_4(Cl^{0.45-})_{18}$ for the single cluster. Of the average 1.7 valence electrons/Gd sphere, 0.7 is contributed by the C_2-like MOs and 1.0 by the Cl-like MOs. The latter contribution from the Cl band has the same size as was found for the decoupled $Gd_{10}Cl_{18}$ cluster. The numbers of electrons on various inequivalent Gd atoms differ from the average by about ±0.1 electron due to the lack of certain mirror symmetries. This difference is apparent in Figure 4. The difference among the charges on (and hence between the covalent binding of) the apex, the shared, and the corner Gd atoms is small: The apex atoms carry 1.61 or 1.87, the shared atoms 1.68, and the corner atoms 1.54 or 1.74 electrons. Of these, 0.74 electron on an apex atom, 0.82 electron on a shared atom, and 0.57 electron on a corner atom are contributed by the C_2-like MOs. These differences are consistent with the fact that, of all the Gd atoms, the ones at the corners have least contact with the C atoms. The view that the apex atoms should have particular strong bonds to the C_2 molecules is, however, not supported.

The shortening of the C_2 single bond from the normal 154 pm to the observed 147 pm is the combined effect (i) of strengthening the bond through mixing more of the high-lying Gd orbitals into the antibonding σ_s^* and π_p^* states than into the bonding σ_s and π_p states and (ii) of weakening the bond through admixture into the bonding σ_p state. As a crude measure of the bond strength we may take from Table II the sum of the occupancies of the C_2 bond orbitals minus those of the C_2 antibond orbitals. For the strength of the σ_s bond this gives 0.2, for the π_p bond 0.2, and for the σ_p bond 0.7, that is, a total strength of 1.1.

The most dubious part of our results shown in Figure 2 is presumably the width of the Cl p band because, by considering a single cluster rather than a solid, we have neglected about half the neighbors of any Cl atom. However, since the bandwidth is roughly proportional to the square root of the number of nearest neighbors (assuming the same distance),[6,7] it seems that in the solid the width of the Cl p band can hardly exceed ours by more than a factor of 2. This means that the Cl p band could, at most, overlap the C_2 π_p^* levels, but there still would remain a gap between the top of the Cl p band and the lowest level of the Gd d band. The compound $Gd_{10}C_4Cl_{18}$ would thus remain ionic although its energy gap might be reduced because the highest occupied orbital might not be the C_2 π_p^* MO but rather the top of the Cl p band. Another way of estimating the limits of the Cl p band is to substitute each C_2 molecule by a Cl atom such that the resulting Cl lattice is face-centered cubic. From the so-called canonical fcc p band (or the Wigner–Seitz rules)[6,7] one then finds that the pure Cl p band extends from −1.28 to −0.99 Ry. From a comparison with Figure 2, this seems to be a realistic estimate.

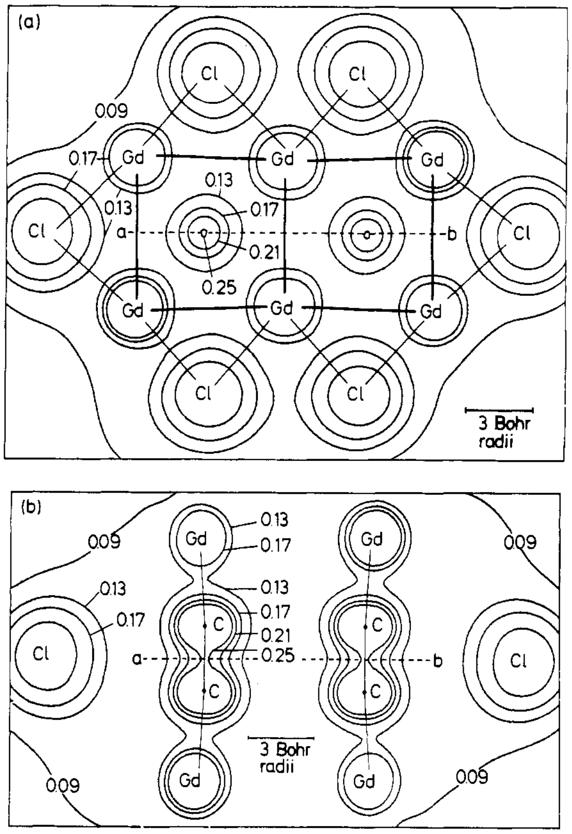

Figure 4. Total valence-electron charge density contour plots for the $Gd_{10}C_4Cl_{18}$ cluster on (a) the basal plane and (b) the plane through the carbon atoms and perpendicular to the basal plane. The dashed line (ab) is the line on which the two planes intersect. Note the relatively low valence charge on the Gd atoms. As discussed in the text, charge is transferred from the Gd atoms to the C and the Cl atoms, resulting in an essentially ionic compound. The contour values are in units of electron per (Bohr radius)^3 per spin.

The lowest unoccupied molecular orbital (LUMO; $E = -0.47$ Ry) of the $Gd_{10}C_4Cl_{18}$ cluster is the only orbital which, if occupied, would give rise to a strong metal–metal bond. It has over 90% Gd d character and shows strong bonding between the metal atoms in the basal plane (Figure 5). The orbitals on the apex atoms contribute very little to this molecular orbital. The metal–metal bond is particularly strong between the two Gd atoms that form the edge shared by the two component octahedra of the double octahedron.

In the compound $Gd_{10}C_4Cl_{17}$, the extra electron would occupy this orbital resulting in a stronger bonding between the Gd atoms on the shared edge. Consequently, the length of the shared edge would decrease. As mentioned in the Introduction such a decrease of 9 pm is indeed experimentally observed, which is thus consistent with our analysis. In $Gd_{10}C_4Cl_{17}$ the clusters are connected with each other as indicated by the dotted and the dash-dotted lines in Figure 5. The broadening of the LUMO into a band can now be estimated simply by evaluating the hopping integral between the two LUMOs placed on the neighboring clusters. First, the energy of the LUMO itself with respect to the center of the d band

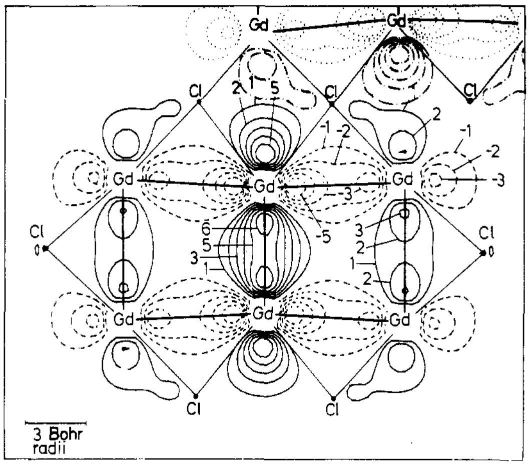

Figure 5. Lowest unoccupied molecular orbital (LUMO) of the $Gd_{10}C_4Cl_{18}$ cluster plotted in the basal plane of the double octahedron. Notice that this metal-metal bond is especially strong between the two atoms on the shared edge. The contour values are in units of 0.02(Bohr radius)$^{-3/2}$. The dash-dotted and the dotted contours indicate the LUMO on the neighboring cluster of the compound $Gd_{10}C_4Cl_{17}$.

is seen to be roughly 2ddσ and, as seen from Figure 2, this is approximately 0.2 Ry. Second, the *inter*cluster hopping integral is seen to be roughly ddσ'/3, where the ratio between the inter and the intra hopping integrals, ddσ' and ddσ, approximately equals the ratio between the intra- and the intercluster Gd-Gd distances to the fifth power. As a result, the LUMO bandwidth 2ddσ'/3 is roughly 20 mRy. This is so small that the LUMO band presumably preserves its identity and does not overlap the rest of the Gd d band. However, due to the exchange coupling with Gd 4f magnetic moments, the LUMO band will be spin split and the one extra electron will thus fill the lower subband.

The compound $Gd_{12}C_6I_{17}$, where the clusters are condensed into infinite zigzag chains,[4] also has one extra electron per double octahedron, and the LUMOs on neighboring double octahedra can be seen to interact only weakly. We believe that also in this compound the extra electron occupies a magnetic subband formed from the LUMO or similar two-center bonds concentrated on (all) the shared edges. This view is supported by the experimental fact that the edge shared in the double octahedron of this compound has the length 0.836 in units of the average Gd-Gd distance. This is very similar to the case $Gd_{10}C_4Cl_{17}$, where the LUMO is also occupied and where the corresponding number is 0.841. In $Gd_{10}C_4Cl_{18}$, where the LUMO is empty, this relative distance is 0.859, that is, considerably larger than the previous two cases. The need for using relative—rather than absolute—distances for this comparison between Cl and I compounds stems from the fact that it is the X-C_2 matrix that mostly determines the size of the metal octahedron.

Summary

In summary, by means of LMTO-ASA calculations we have studied the electronic structure of the cluster $Gd_{10}C_4Cl_{18}$. A principal conclusion was that in the compound $Gd_{10}C_4Cl_{18}$ there are no strong metal-metal bonds. The transfer of metal d electrons into the carbon atoms causes the antibonding π^* states of the C_2 molecules to be occupied, in consistence with the experimentally observed single C-C bond distance. Furthermore, our calculations and the observed differences in the shortest metal-metal distances indicate that whereas $Gd_{10}C_4Cl_{18}$ is an ionic compound with no strong bonds between the metal atoms, the compounds $Gd_{10}C_4Cl_{17}$ and $Gd_{12}C_6I_{17}$ have in contrast one occupied metal-metal bonding molecular orbital split off below the bulk of the metal states.

Acknowledgment. We thank Professor A. Simon and Dr. E. Warkentin for stimulating this research.

Registry No. $Gd_{10}C_4Cl_{18}$, 84989-58-2; $Gd_{10}C_4Cl_{17}$, 85248-21-1; $Gd_{12}C_6I_{17}$, 96826-77-6.

Contribution from the Department of Chemistry,
McMaster University, Hamilton, Ontario, L8S 4M1 Canada

Study of the $OTeF_5$ Donor Properties of $Te(OTeF_5)_4$ by ^{75}As and ^{125}Te NMR Spectroscopy. Preparation and Characterization of the $[TeFe_x(OTeF_5)_{3-x}]^+$ Cations, $TeF_x(OTeF_5)_{4-x}$, $As(OTeF_5)_5$, and $[As(OTeF_5)_6]^-$ [1]

MICHAEL J. COLLINS and GARY J. SCHROBILGEN*

Received July 3, 1984

The $OTeF_5^-$ ion donor properties have been studied for $Te(OTeF_5)_4$ in the presence of the acceptor species AsF_5 and $As(OTeF_5)_5$. The synthesis of the latter compound from $B(OTeF_5)_3$ and AsF_5 is described. The mixed cations $[TeF_x(OTeF_5)_{3-x}]^+$ (x = 0-3) and the neutral species $TeF_x(OTeF_5)_{4-x}$ (x = 0-2) have been characterized in solution by ^{125}Te NMR spectroscopy. The novel anion $As(OTeF_5)_6^-$ has also been identified. Owing to the local octahedral symmetry about the quadrupolar ^{75}As atom in $As(OTeF_5)_6^-$, the ^{75}As NMR line is sufficiently narrow to permit ready observation of the signal as well as the two-bond natural-abundance ^{125}Te-^{75}As coupling (430 Hz). The activation energy barrier to intramolecular exchange in the trigonal-bipyramidal $Te(OTeF_5)_4$ molecule also has been derived from low-temperature ^{19}F and ^{125}Te NMR studies in SO_2ClF solvent (E_a = 31.0 ± 0.4 kJ mol^{-1}). No activation energy for $As(OTeF_5)_5$ was determinable above the freezing point of SO_2ClF (-124 °C). Reduced (K) and relativistically corrected reduced (K_{RC}) coupling constants have been calculated for observed one-bond ^{19}F-^{77}Se and ^{19}F-^{125}Te and two-bond ^{75}As-^{125}Te and ^{125}Te-^{125}Te scalar couplings.

Introduction

A considerable portion of the main-group chemistry of simple binary fluorides is based upon the fluoride ion donor/acceptor properties of the parent compounds. In the present work we have extended the analogy to the $OTeF_5^-$ anion and have studied its donor/acceptor properties in a series of mixed F/$OTeF_5$ compounds of Te(IV), leading to the novel mixed-cation series $[TeF_x(OTeF_5)_{3-x}]^+$ and their counterions $[AsF_y(OTeF_5)_{6-y}]^-$. Examples of $OTeF_5$/F ligand redistributions have been reported for $O_2XeF_x(OTeF_5)_{2-x}$, $XeF_x(OTeF_5)_{4-x}$, and $OXeF_x(OTeF_5)_{4-x}$[2]

---

[1] Presented, in part, at the 10th International Symposium on Fluorine Chemistry, Vancouver, Canada, 1982.

[2] Schumacher, G. A.; Schrobilgen, G. J. *Inorg. Chem.* **1984**, *23*, 2923.

0020-1669/85/1324-2608$01.50/0 © 1985 American Chemical Society