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Some Possible Structures of Lanthanoid Carbonyl Compounds

Y. Q. JIA

Changchun Institute of Applied Chemistry, Academia Sinica Changchun, Jilin, China

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Abstract

The CNDO/2 quantum chemical method was used to determine the most probable configurations for the carbonyl compounds of lanthanoids with different coordination numbers. The most probable structures were linear for RECO and $RE(CO)_2$, trigonal-pyramidal for $RE(CO)_3$, tetragonal-pyramidal for $RE(CO)_3$, tetragonal-pyramidal for $RE(CO)_4$ and $RE(CO)_5$, and trigonal-prismatic for $RE(CO)_6$. The 5d orbitals of the rare earths play a significant role in the formation of chemical bonds in the carbonyl compounds of lanthonoids. There is a linear relationship between the C–O stretching frequencies and the net charges on the central rare earth atoms.

Introduction

The organometallic chemistry of the lanthanoids has become in the last few years a subject of great interest, because the organometallic compounds of lanthanoids display some interesting properties as reagents or catalysts and have some properties that are distinctly different from those of the organometallic compounds of transition metals [1, 2].

Carbonyl compounds of the rare earths are an important type of organometallic compound of lanthanoids. Sheline and Slater [3] synthesized some binary carbonyl compounds of the rare earths and measured the infrared spectra of these compounds. They also predicted some possible structures these carbonyl compounds might possess on the basis of hybridization of the orbitals of the central lanthanoid atoms.

In this paper, we attempt to make some quantum chemical calculations for the molecules of the rare earth carbonyl compounds with different coordination numbers by means of the CNDO/2 and EHMO methods to determine the most probable equilibrium configurations of these molecules, and to discuss the chemical bond in these binary carbonyl compounds of lanthanoids on the basis of calculated results.

Calculations

CNDO/2 is a semi-empirical quantum chemical method and can be used to calculate the equilibrium distances between atoms in a molecule, as well as the equilibrium configuration of the molecule. Therefore, first, the CNDO/2 method was used to determine the equilibrium distances between the central rare earth atoms and the carbon atoms in monocarbonyl compounds of all the rare earths. The equilibrium distances between the rare earth atoms and the carbon atoms calculated in the linear structure of the monocarbonyl compounds of lanthanoids, as well as the bond lengths of the C–O bond are shown in Table I. We chose the neodymium carbonyl compound as an example, and made some quantum chemical calculations on several possible structures of the neodymium carbonyl compounds with different coordination numbers by means of the CNDO/2 method. In the calculations, the distance between the neodymium atom and the carbon atom, given in Table I, was taken as the bond length of the Nd–C bond, but some bond angles in these structures were changed to determine the equilibrium configuration for different neodymium carbonyl compounds. The total energies, E, calculated for some molecules of neodymium carbonyl compounds with different coordination numbers and with dif-

TABLE I. Distances between the Rare Earth Atoms and the Carbon Atom and between the Carbon Atom and the Oxygen Atom in the Linear Monocarbonyl Compounds of Lanthanoids

	r (A)		r (A)
La–C	2.22	Tb–C	2.12
Ce–C	2.19	Dy–C	2.12
Pr–C	2.18	Ho–C	2.10
Nd–C	2.16	Er–C	2.10
Pm–C	2.15	Tm–C	2.10
Sm–C	2.13	Yb–C	2.09
Eu–C	2.13	Lu–C	2.05
Gd–C	2.12	C–O	1.15

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TABLE II. The Most Probable Configuration for the Carbonyl Compounds of Lanthanoids with Different Coordination Numbers[a]

$RE(CO)_n$	Structure	Symmetry	Total energy (ev)	The most probable configuration (structure, symmetry, hybridization)
$Nd(CO)_2$	linear	C_{2v} (180°)	−48.91 (−472.74)	linear C_{2v} (180°) dp
	angular	C_{2v} (150°)	−48.84 (−472.45)	
	angular	C_{2v} (120°)	−48.86 (−472.36)	
	angular	C_{2v} (90°)	−48.76 (−472.18)	
$Nd(CO)_3$	trigonal planar	D_{3h}	−72.58 (−672.79)	
	trigonal pyramidal	C_{3v} (10°)	−72.60 (−672.28)	
	trigonal pyramidal	C_{3v} (30°)	−72.66 (−674.05)	trigonal-pyramidal C_{3v} (30°) d^2p
	trigonal pyramidal	C_{3v} (45°)	−72.61	
$Nd(CO)_4$	tetrahedral	T_d	−96.36 (−874.66)	
	tetragonal planar	D_{4h}	−96.30 (−874.96)	
	tetragonal pyramidal	C_{4v} (10°)	−96.38 (−874.97)	
	tetragonal pyramidal	C_{4v} (35°)	−96.65 (−876.54)	tetragonal-pyramidal C_{4v} (35°) d^4
	trigonal-pyramidal	C_{3v} (0°)	(−875.04)	
	trigonal-pyramidal	C_{3v} (20°)	(−874.69)	
$Nd(CO)_5$	trigonal-bipyramidal	D_{3h}	−120.15(−1076.11)	
	tetragonal-pyramidal	C_{4v} (0°)	−120.07(−1076.09)	
	tetragonal-pyramidal	C_{4v} (15°)	(−1076.14)	
	tetragonal-pyramidal	C_{4v} (35°)	−120.32(−1076.54)	tetragonal-pyramidal C_{4v} (35°) d^4p
$Nd(CO)_6$	octahedral	O_h	−143.70(−1276.66)	
	trigonal-prismatic	D_{3h} (35°)	−144.27(−1277.28)	trigonal-prismatic D_{3h} (35°) d^5p
	trigonal-prismatic	D_{3h} (45°)	−144.06(−1277.24)	
	trigonal-antiprismatic	$S6$ (30°)	−143.89(−1276.76)	

[a] Total energy in parentheses was calculated by the EHMO method. The angle in parentheses is the bond angle of C–Nd–C for $Nd(CO)_2$; and is the angle between the Nd–C bond and the plane composed of the carbon atoms for $Nd(CO)_{3-6}$.

ferent geometrical configurations are shown in Table II.

The valence orbitals used in the CNDO/2 calculations were the 6s, 6p and 5d orbitals for the rare earth atoms; and the 2s and 2p orbitals for the carbon atom and the oxygen atom.

However, to check the effect of the 4f orbitals of the central rare earth atoms on the configurations of the carbonyl compounds of lanthanoids and on the formation of a chemical bond between the rare earth atom and the carbon monoxide, we also made some calculations for the corresponding carbonyl compounds by the EHMO quantum chemical method, including the 4f orbitals of the rare earths.

Results and Discussions

As the calculated results in Table I show, the distances between the rare earth atoms and the carbon atms in the monocarbonyl compounds of lanthanoids decrease monotonically with increasing atomic number from La to Lu. This may reflect the effect of lanthanoid contraction on the bond lengths between the rare earth atoms and the carbon atoms in the carbonyl compounds of lanthanoids.

The calculated results of the EHMO method, including the 4f orbitals of the rare earths, show that in all the carbonyl compounds of lanthanoids, the 4f orbitals do not participate in the formation of chemical bonds. Therefore, this demonstrates that the assumption that the 4f orbitals do not participate in the bonding in the binary carbonyl compounds of lanthanoids, and the interpretation about the remarkable similarity in the infrared spectra of the 'normal' lanthanoid carbonyls presented by Sheline and Slater is reasonable [3]. It also shows that the results we calculated were valid, although the 4f orbitals of the rare earth atoms were ignored in the CNDO/2 calculations.

We want to point out that in Table II, the 'total energy' *E* calculated by the EHMO method is rather different from that calculated by the CNDO/2 method for the same carbonyl compound of neodymium. This is because the electronic interaction is not considered in the EHMO method. However, from Table II, we know that both the results calculated by the CNDO/2 method and the results calculated by the EHMO method give the same conclusion for the equilibrium configurations of all the neodymium carbonyl compounds with different coordination numbers.

The calculated results show that the most probable structure for NdCO and $Nd(CO)_2$ molecules is a linear structure. However, the most probable structure for the $Nd(CO)_3$ molecule is trigonal-pyramidal with a C_{3v} symmetry. For the $Nd(CO)_4$ molecule, the most probable structure is neither tetrahedral nor tetragonal-planar, but tetragonal-pyramidal with a C_{4v} symmetry. In $Nd(CO)_5$ and $Nd(CO)_6$ molecules, if all the carbon monoxide molecules were on the same plane or on the same side of the rare earth atom, they would be too crowded to bond with the central rare earth atom. The calculated results show that for the $Nd(CO)_5$ molecule the most probable structure is tetragonal-pyramidal with a C_{4v} symmetry. In the $Nd(CO)_5$ molecule, four carbon monoxide molecules are on one side of the central rare earth atom, and are coplanar, but one carbon monoxide molecule is on another side of the central rare earth atom, and is axial with the rare earth atom. In the $Nd(CO)_6$ molecule, there are three carbon monoxide molecules on each side of the central rare earth atom, and each of the three carbon monoxide molecules is coplanar. So, the most probable structure for the $Nd(CO)_6$ molecule is trigonal-prismatic with a D_{3h} symmetry.

In this way, we have determined the most probable geometrical configurations for all the neodymium carbonyl compounds with different coordination numbers from the various possible structures Sheline and Slater [3] predicted for the carbonyl compounds of lanthanoids. The predications of Sheline and Slater were based on the hybridization of the atomic orbitals of the central rare earth atom. They presented different hybridization schemes for each possible structure of the carbonyl compounds of lanthanoids. Most, if not all, of the hybridization schemes related to the 5d orbitals of the central rare earth atom. In quantum chemical calculations we found that the 5d orbitals of the central rare earth atom did play a very important role. The 5d orbitals were the main components in some occupied molecular orbitals, especially in the highest occupied molecular orbital and in the lowest unoccupied molecular orbital. It has been shown that the 5d orbitals of the rare earth atoms participate in the formation of chemical bonds in the carbonyl compounds of lanthanoids. So, we considered that the most probable configurations of the rare earth carbonyl compounds we determined on the basis of the quantum chemical calculations would be just those structures that Sheline and Slater assumed on the basis of the orbital hybridization schemes, in which the 5d orbitals were the main components for orbital hybridization.

The calculated results show that the net charge (Q) on the central rare earth atom becomes more and more negative with an increase in the coordination number. For example, $Q = 0.05$ in NdCO; $Q = -0.24$ in $Nd(CO)_2$; $Q = -0.66$ in $Nd(CO)_3$; $Q = -0.90$ in $Nd(CO)_4$; $Q = -1.50$ in $Nd(CO)_5$; and $Q = -2.00$ in $Nd(CO)_6$. This implies that there is a π-back bonding between the central rare earth atom and the carbon monoxide molecule in the carbonyl compounds of lanthanoids. We have also noted that in all the $Fe(CO)_n$ molecules, the net charge on the iron atom is negative, but not positive. However, unlike FeCO, in monocarbonyl compounds of neodymium, the net charge on the neodymium atom is positive, as mentioned above. The neodymium is a 'normal' or a 'typical' lanthanoid. This obvious difference shows that the rare earth atom is a weak acceptor in the formation of π-back bonding in the carbonyl compounds of lanthanoids; perhaps it can be used to explain why some properties of the organometallic compounds of lanthanoids are rather different from those of the organometallic compounds of transition metals, for example why the carbonyl compounds of lanthanoids are less stable than the carbonyl compounds of transition metals.

It is very interesting that we found that there was a linear relationship between the C–O stretching frequencies and the net charges on the central rare earth atom in the carbonyl compounds of lanthanoids. This relationship is shown in Fig. 1. As is well known, the force constant is related to the electron distribution in the molecule. Indeed, there is also a linear relationship between the C–O stretching frequencies and the coordination numbers of the lanthanoids. However, the change of the C–O stretching frequencies in the carbonyl compounds of lanthanoids with different coordination numbers is, practically, due to the change of the net charges on the central rare earth atoms.

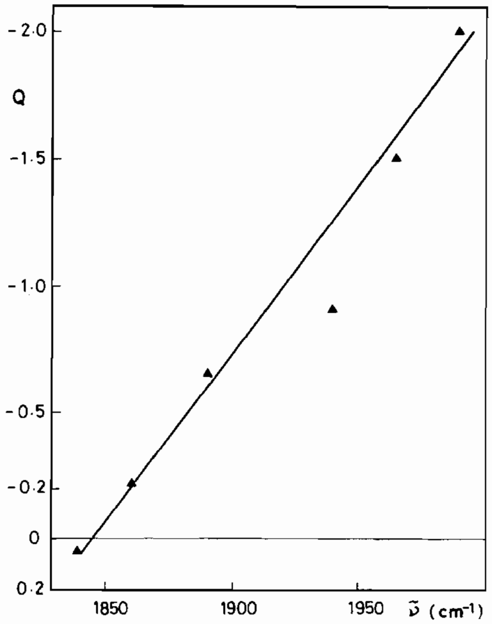

Fig. 1. The relationship between the C–O stretching frequencies ($\tilde{\nu}$) and the net charges (Q) on the central rare earth atoms in the carbonyl compounds of lanthanoids.

Conclusions

CNDO/2 and EHMO methods were used to determine the most probable configurations for the carbonyl compounds of lanthanoids with different coordination numbers. The results show that the most probable structures are linear for RECO and $RE(CO)_2$, trigonal-pyramidal for $RE(CO)_3$, tetragonal-pyramidal for $RE(CO)_4$ and $RE(CO)_5$, and trigonal-prismatic for $RE(CO)_6$.

The 5d orbitals of the rare earth atom participate in formation of chemical bonds in the carbonyl compounds of lanthanoids and play a significant role, but the 4f orbitals of the rare earth atom do not take part in chemical bonding.

In the carbonyl compounds, the rare earth atoms are weaker acceptors in the formation of π-back bonding in comparison with the transition metals.

The results show that there is a linear relationship between the C—O stretching frequencies and the net charges on the central rare earth atoms.

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