The Oxidation State of Ce in the Sandwich Molecule Cerocene

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Sandwich compounds, in which two planar and parallel unsaturated carbocyclic rings are held together by the presence of a metal atom midway between the ring centroids, occupy a central position in organometallic and indeed inorganic chemistry.[1] They have drawn much attention as models for our understanding of both structural chemistry and bonding theory and have provided the impetus to study what has become a fundamental area of stoichiometric and catalytic reactivity. Compounds of the type [M(COT)$_2$],[2] which are confined to M = 4f, 5f elements, have been the subject of extensive electronic structural investigations.[3−14] Among the lanthanides, the sandwich molecule cerocene has been formulated as a complex between the Ce^{4+} ion (Xe core, 4f^0) and two planar cyclooctatetraene dianions (COT)$^{2−}$. This compound is an air-sensitive, brown-black material characterized by two strong absorption bands in the visible region which have been assigned as ligand to metal charge transfer transitions.[15,16] Subsequently the proposed structure was confirmed by an X-ray structural study on the substituted cerocene [Ce(MeCOT)$_2$].[17] Recently two more substituted cerocene analogs have been synthesized, and one of these compounds has been structurally characterized.[18] The synthesis and stability of cerocene has been noted as being quite remarkable because the Ce^{4+} ion is a strong oxidizing agent and the cyclooctatetraene dianion (COT)$^{2−}$ is a strong reducing agent.[16,19] Quasi-relativistic Xα-scattered wave calculations for thorocene [Th(COT)$_2$], uranocene [U(COT)$_2$], and cerocene [Ce(COT)$_2$] showed strong covalent bonding in all three molecules, although cerocene was the most ionic.[7] Later, theoretical calculations by Neumann and Fulde suggested that the Ce ion in cerocene is trivalent and the ground state of cerocene is a [Ce^{3+}\{(C$_8$H$_8$)$_2$\}$^{3−}$] species.[20] The basis for these calculations came from an analogy between the cerocene molecule and the observed Kondo effect in cerium metallic solids. The necessary conditions for the Kondo effect in a cerium alloy are strong correlations between the Ce f orbitals (strong Coulomb repulsion) and a weak hybridization between the 4f orbitals of Ce and the conduction electrons of the alloy. In cerocene, the hybridization should occur with the π electrons of the two (COT)$^{2−}$ ions.[21]

Sophisticated *ab initio* calculations by Dolg *et al.* have supported the earlier idea that cerocene is a trivalent Ce^{3+} compound (Xe core, 4f^1) complexed by two (COT)$^{1.5−}$ ions.[22,23] In this picture, the 4f^1 electron is in a localized Ce^{3+} 4f orbital of e_{2u} symmetry (D$_{8h}$ point group), and there are three electrons in the highest-occupied ligand-based π molecular orbital, also of e_{2u} symmetry, which are delocalized over both eight-membered rings. The unpaired electron on the metal atom is coupled with an unpaired electron in the ligand orbitals to form a 4f$^1_{e_{2u}}$π$_{e_{2u}}^3$ singlet ground state with the triplet excited state approximately 0.5 eV higher in energy. Configuration interaction couples the 4f$^1_{e_{2u}}$π$_{e_{2u}}^3$ singlet state with the higher energy 4f^{0}π$_{e_{2u}}^4$ singlet state so that the final ground configuration consists of approximately 83% of the 4f$^1_{e_{2u}}$π$_{e_{2u}}^3$ and 17% of the 4f^{0}π$_{e_{2u}}^4$ configurations. Because of this singlet ground state, cerocene in this trivalent formulation will be diamagnetic or show weak, temperature-independent paramagnetism.[21] Thus, it is very difficult to distinguish between the tetravalent and the trivalent models on the basis of magnetic measurements.

One method for determining the oxidation state of an atom is X-ray absorption near-edge structure (XANES), where the absorption is measured below and above a characteristic X-ray elemental edge.[24] The energy at which the absorption edge occurs can be correlated with the oxidation state of the metal. The edge energy is also somewhat sensitive to the coordination number and type of atoms surrounding the element of interest.[24] For Ce ions, both the L- and K-edges have been utilized to determine oxidation state. Recent measurements of Ce XANES have determined the Ce oxidation state in a cerium-exchanged Preyssler's heteropolyanion and in a mixed Pr/Ce high-temperature superconductor.[25,26] In the latter work, a shift in the K-edge energy of 7 eV to higher energy was found for the tetravalent standard CeO$_2$ relative to the trivalent standard CeF$_3$. In this paper, we report measurements of the XANES spectra of various substituted cerocenes, related trivalent cerocene salts, and some Ce standard compounds in order to determine the formal oxidation state of the Ce ion in substituted cerocenes.

The samples used in these experiments are numbered and listed in Table 1. The compounds [Ce(COT″)$_2$] and [Ce-(COT‴)$_2$] were prepared following the work of Kilimann *et al.* and Burton *et al.* as was the salt Li[Ce(COT″)$_2$].[18,27] K[Ce-(COT)$_2$] was synthesized following the work of Hodgson *et al.*[28] The Ce compounds used as standards were purchased com-

(1) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley-Interscience: New York, 1988.
(2) In this paper we use the following notation: Me = CH$_3$, TMS = (CH$_3$)$_3$Si, COT = η^8-C$_8$H$_8$, MeCOT = η^8-MeC$_8$H$_7$, COT″ = η^8-1,4-(TMS)$_2$C$_8$H$_6$, and COT‴ = η^8-1,3,6-(TMS)$_3$C$_8$H$_5$.
(3) Amberger, H.-D.; Fischer, R. D.; Kanellakopoulos, B. *Theor. Chim. Acta (Berlin)* **1975**, *37*, 105.
(4) Hayes, R. G.; Edelstein, N. M. *J. Am. Chem. Soc.* **1972**, *94*, 8688.
(5) Pyykkö, P.; Lohr, L. L. *Inorg. Chem.* **1981**, *20*, 1950.
(6) Rösch, N.; Streitwieser, A. *J. Organomet. Chem.* **1978**, *145*, 195.
(7) Rösch, N.; Streitwieser, A. *J. Am. Chem. Soc.* **1983**, *105*, 7237.
(8) Rösch, N. *Inorg. Chim. Acta* **1984**, *94*, 297.
(9) Boerrigter, P. M.; Baerends, E. J.; Snijders, J. G. *Chem. Phys.* **1988**, *122*, 357.
(10) Chang, A. H. H.; Pitzer, R. M. *J. Am. Chem. Soc.* **1989**, *111*, 2500.
(11) Kaltsoyannis, N.; Bursten, B. E. *J. Organomet. Chem.* **1996**. In press.
(12) Streitwieser, A.; Müller-Westerhoff, U.; Sonnichsen, U. G.; Mares, D. G.; Hodgson, K. O.; Harmon, C. A. *J. Am. Chem. Soc.* **1973**, *95*, 8644.
(13) Dallinger, R. F.; Stein, P.; Spiro, T. G. *J. Am. Chem. Soc.* **1978**, *100*, 7865.
(14) Brennan, J. G.; Green, J. C.; Redfern, C. M. *J. Am. Chem. Soc.* **1989**, *111*, 2373.
(15) Greco, A.; Cesca, S.; Bertolini, G. *J. Organomet. Chem.* **1976**, *113*, 321.
(16) Streitwieser, A., Jr.; Kinsley, S. A.; Rigsbee, J. T.; Fragalà, I. L.; Ciliberto, E.; Rösch, N. *J. Am. Chem. Soc.* **1985**, *107*, 7786.
(17) Boussie, T. R.; Eisenberg, D. C.; Rigsbee, J.; Streitwieser, A.; Zalkin, A. *Organometallics* **1991**, *10*, 1922.
(18) Kilimann, U.; Herbst-Irmer, R.; Stalke, D.; Edelmann, F. T. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1618.
(19) Fischer, R. D. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2165.

(20) Neumann, C. S.; Fulde, P. *Z. Phys.* **1989**, *B74*, 277.
(21) Fulde, P. *Electron Correlations in Molecules and Solids*; Springer-Verlag: Berlin, 1991; pp 268−273.
(22) Dolg, M.; Fulde, P.; Küchle, W.; Neumann, C. S.; Stoll, H. *J. Chem. Phys.* **1991**, *94*, 3011.
(23) Dolg, M.; Fulde, P.; Stoll, H.; Preuss, H.; Chang, A.; Pitzer, R. M. *Chem. Phys.* **1995**, *195*, 71.
(24) Prins, R.; Koningsberger, D. E. *X-ray Absorption: Principles, Applications, Techniques for EXAFS, SEXAFS, and XANES*; Wiley-Interscience: New York, 1988.
(25) Antonio, M. R.; Soderholm, L. *Inorg. Chem.* **1994**, *33*, 5988.
(26) Skanthakumar, S.; Soderholm, L. *Phys. Rev. B* **1996**, *53*, 920.
(27) Burton, N. C.; Cloke, F. G. N.; Joseph, S. C. P.; Karamallakis, H.; Sameh, A. A. *J. Organomet. Chem.* **1993**, *462*, 39.
(28) Hodgson, K. O.; Raymond, K. N. *Inorg. Chem.* **1972**, *11*, 3030.

Table 1. Numbering and Characteristics of Ce Samples

no.	compd	type of sample	color	ref
1	CeO_2	solid		
2	$Ce(NH_4)_4(SO_4)_4 \cdot 2H_2O$	solid		
3	$Ce(NH_4)_4(SO_4)_4 \cdot 2H_2O$	1.6 M HNO_3 soln	yellow	
4	$Ce(CH_3C(O)CHC(O)CH_3)_4$	toluene soln	dark red	31
5	$CeCl_3 \cdot 6H_2O$	solid		
6	CeF_3	solid		
7	Ce_2O_2S	solid		
8	$Ce_2(SO_4)_3$	solid		
9	$CeSi_2$	solid		
10	$CeI_3 \cdot (THF)_x$	THF soln	pale yellow	30
11	$[Ce\{(Me_3C)_2C_5H_3\}_3]$	toluene soln	purple	29
12	$Ce_2(SO_4)_3$	1.6 M HNO_3 soln	colorless	
13	$Ce_2(SO_4)_3$	1.2 M HCl soln	colorless	
14	$Ce(NO_3)_3$	1.6 M HNO_3 soln	colorless	
15	$Ce(NO_3)_3$	1.2 M HCl soln	colorless	
16	$[Ce(COT'')_2]$	toluene soln	deep purple	18
17	$[Ce(COT''')_2]$	toluene soln	deep purple	18
18	$Li[Ce(COT'')_2]$	toluene soln	dark green	18
19	$K[Ce(COT)_2]$	toluene soln	light green	28
standard	CeB_6	solid		

Figure 1. Representative K-edge spectra of Ce compounds: thick line, CeO_2; thin line, $[Ce\{(Me_3C)_2C_5H_3\}_3]$; dotted line, $[Ce(COT'')_2]$; dashed line, $Li[Ce(COT'')_2]$.

Figure 2. K-edge shifts of the Ce compounds relative to CeB_6. The numbering of the samples is given in Table 1.

mercially or prepared from literature references.[29–31] Since a number of the Ce organometallic compounds are air-sensitive, the solution samples were prepared on a Schlenk line where appropriate. The solution samples were sealed in thin-walled 10 mm o.d. tubes which were used directly on the beamline. The concentration of Ce in these samples was between 0.05–0.3 M. Stable solid samples were finely ground, diluted with polystyrene beads to an absorption density of approximately 40 mg/cm², and sealed with mylar tape in a 1.5 mm thick Al holder which had a slot of 5 mm × 25 mm.

Cerium K-edge X-ray absorption spectra (at approximately 40.443 keV) were collected at the Stanford Synchrotron Radiation Laboratory (SSRL) on wiggler beamline 4−2 (unfocused) under dedicated ring conditions (3.0 GeV, 50−100 mA) using a Si (400) double-crystal monochromator. All spectra were collected in the transmission geometry using Ar-filled ionization chambers and a vertical slit of 0.8 mm. Edge data were collected from each sample at ambient temperature, and if more than one scan was taken, the data were averaged. Data reduction and XANES analyses were done using the appropriate routines from the EXAFSPAK suite of programs developed by G. George of SSRL. The spectra were energy calibrated by simultaneously measuring the spectrum from a reference sample of solid CeB_6, defining its first inflection point as 40.443 keV. The edge energies for all the remaining samples were determined subsequently by taking the maximum of the first derivative of the absorption edge. XANES spectra of some representative samples are shown in Figure 1.

The convolution of the Ce K-edge natural line width (15.1 eV) and the Si (400) monochromator (17.5 eV) gives an overall energy resolution of ∼23 eV,[26] which broadens the fine structure in the XANES region. However, this broadening does not diminish the precision of the edge energy determinations, which is estimated to be ±0.5 eV for the Ce standards and ±1.0 eV for the cerocene type complexes.

Figure 2 shows the K-edge shifts of the numbered samples (Table 1) relative to the Ce standard, CeB_6. The data fall into two different regions characterized by the two formal oxidation states Ce^{3+} and Ce^{4+}. The separation between these two regions is greater than 7 eV. The compounds $[Ce(COT'')_2]$ and $[Ce(COT''')_2]$ are definitely in the Ce^{3+} region. The spread of the data points in the Ce^{3+} region is of the order of 5 eV with
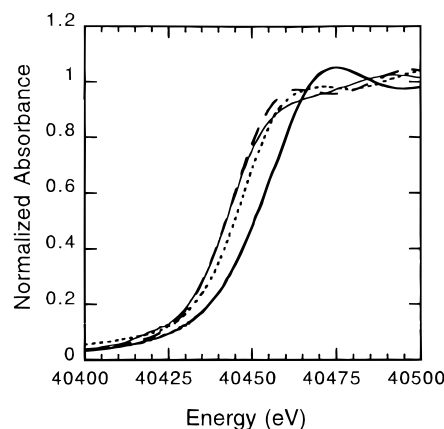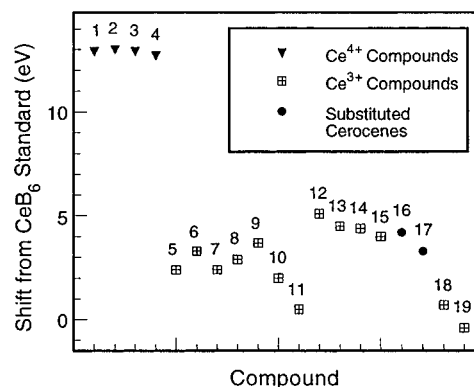
$[Ce\{(Me_3C)_2C_5H_3\}_3]$, $Li[Ce(COT''')_2]$, and $K[Ce(COT)_2]$ at the extreme electron-rich end (close to 0.0 eV in Figure 2) and the aqueous Ce^{3+} ion plus $[Ce(COT'')_2]$ and $[Ce(COT''')_2]$ are in the range of 4.5−5 eV. The difference between the cerocenes and their trivalent salts appears significant. Formally, we may write the configuration of the salts as $4f^1_{e2u}\pi_{e2u}^4$. As stated above, the neutral cerocences are believed to have a ground configuration best regarded as a mixture of $4f^1_{e2u}\pi_{e2u}^3$ and $4f^0\pi_{e2u}^4$. It may well be that the ca. 20% contribution of the formally Ce(IV) latter configuration is responsible for the difference in edge energies between the neutral cerocenes and their Li/K salts.

The XANES spectra in this paper give the assignment of the oxidation state of the Ce ion in substituted cerocene molecules as trivalent. The Ce ion in the substituted cerocenes appears to be less electron-rich than in their akali metal salts, as shown by a 4.5 eV shift toward higher oxidation state of their X-ray K-edges. This argument is supported by structural data which show the Ce ring centroid distance for the substituted cerocenes is ∼1.97 Å as compared to ∼2.07 Å for the $K[Ce(COT)_2]$ diglyme salt.[17,18,28] Our experimental results therefore support the conclusion of the sophisticated *ab initio* calculations that the cerocene ground configuration should be formulated primarily as a $4f^1_{e2u}\pi_{e2u}^3$ singlet.[22,23]

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(29) Sofield, C. D.; Andersen, R. A. *J. Organomet. Chem.* **1995**, *501*, 271.
(30) Hazin, P. N.; Huffman, J. C.; Bruno, J. W. *Organometallics* **1987**, *6*, 23.
(31) Pinnavaia T. J.; Fay, R. C. *Inorg. Synth.* **1970**, *12*, 77.