

Lawrence Berkeley National Laboratory

LBL Publications

Title

The Oxidation State of Ce in the Sandwich Molecule Cerocene

Permalink

<https://escholarship.org/uc/item/7dk4b5sr>

Journal

Journal of the American Chemical Society, 118(51)

Author

Edelstein, Norman M.

Publication Date

1996-05-01

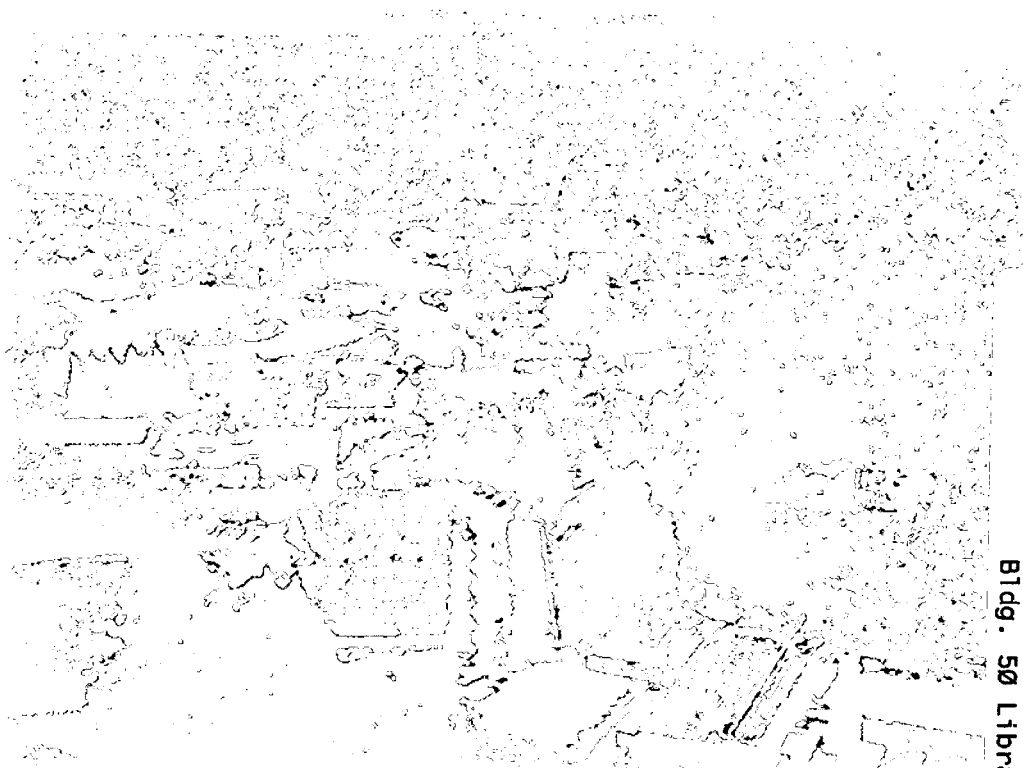


ERNEST ORLANDO LAWRENCE BERKELEY NATIONAL LABORATORY

The Oxidation State of Ce in the Sandwich Molecule Cerocene

N.M. Edelstein, P.G. Allen, J.J. Bucher,
D.K. Shuh, C.D. Sofield, N. Kaltsoyannis,
G.H. Maunder, M.R. Russo, and A. Sella
Chemical Sciences Division

May 1996
Submitted to
*Journal of
the American
Chemical Society*



REFERENCE COPY
Does Not
Circulate

Bldg. 50 Library.

Copy 1

LBL-39311

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

The Oxidation State of Ce in the Sandwich Molecule Cerocene

N.M. Edelstein, P.G. Allen, J.J. Bucher, D.K. Shuh, and C.D. Sofield

Chemical Sciences Division
Ernest Orlando Lawrence Berkeley National Laboratory
University of California
Berkeley, CA 94720

N. Kaltsoyannis, G.H. Maunder, M.R. Russo, and A. Sella

Department of Chemistry
University College London
20 Gordon Street
London WC1H 0AJ, U.K.

May 1996

The Oxidation State of Ce in the Sandwich Molecule Cerocene

N. M. Edelstein, P. G. Allen, J. J. Bucher, D. K. Shuh, and C. D. Sofield
Chemical Sciences Div., Lawrence Berkeley National Laboratory, Berkeley, CA 94720

N. Kaltsoyannis, G. H. Maunder, M. R. Russo, and A. Sella
Department of Chemistry, University College London, 20 Gordon St.,
London WC1H 0AJ, U. K.

The sandwich molecule cerocene has been formulated as a complex between the Ce^{4+} ion (Xe core, $4f^0$) and two planar cyclooctatetraene dianions $[C_8H_8]^{2-}$. 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.^{1,2} Subsequently the proposed structure was confirmed by an X-ray structural study on the substituted cerocene $[Ce(MeC_8H_7)_2]$.³ Recently two more substituted cerocene analogs have been synthesized and one of these compounds has been structurally characterized.⁴ 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 $[C_8H_8]^{2-}$ is a strong reducing agent.^{2,5} Quasi-relativistic $X\alpha$ scattered-wave calculations for thorocene ($Th[C_8H_8]_2$), uranocene ($U[C_8H_8]_2$), and cerocene showed strong covalent bonding in all three molecules, although cerocene was the most ionic.⁶ Later, theoretical calculations by Neumann and Fulde suggested that the Ce ion in cerocene is trivalent and the ground state of cerocene is a $Ce^{3+}[(C_8H_8)_2]^{3-}$ species.⁷ 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 $[C_8H_8]^{2-}$ ions.⁸

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 $[C_8H_8]^{-1.5}$ ions.^{9,10} 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 $4f^1_{e2u}\pi_{e2u}^3$ singlet ground state with the triplet excited state approximately 0.5 eV higher in energy. Configuration interaction couples the $4f^1_{e2u}\pi_{e2u}^3$ singlet state with the higher energy $4f^0\pi_{e2u}^4$ singlet state so that the final ground configuration consists of approximately 83% of the $4f^1_{e2u}\pi_{e2u}^3$ and 17% $4f^0\pi_{e2u}^4$ configurations. Because of this singlet ground state, cerocene in this trivalent formulation will be diamagnetic or show weak, temperature-independent paramagnetism.⁸ 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.¹¹ 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.¹¹ 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.^{12,13} 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 letter 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 of $\text{Ce}[1,4(\text{TMS})_2\text{C}_8\text{H}_6]_2$ and $\text{Ce}[1,3,6(\text{TMS})_3\text{C}_8\text{H}_5]_2$ were prepared following the work of Kilimann *et al.* and Burton *et al.* as was the $\text{Li}\{\text{Ce}[1,3,6(\text{TMS})_3\text{C}_8\text{H}_5]_2\}$ salt.^{4,14} $\text{K}[\text{Ce}(\text{C}_8\text{H}_8)_2]$ was synthesized following the work of Hodgson *et al.*¹⁵ Other Ce compounds used as standards were purchased commercially or prepared from literature references.¹⁶⁻¹⁸ 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 OD tubes which were used directly on the beamline. The concentration of Ce in these samples was between 0.05 M - 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 by 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 (unfocussed) 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 CeB₆, 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 linewidth (15.1 eV) and the Si (400) monochromator (17.5 eV) gives an overall energy resolution of ~ 23 eV,¹³ 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, CeB₆. The data fall into two different regions characterized by the two formal oxidation states, Ce³⁺ and Ce⁴⁺. The separation between these two regions is greater than 7 eV. The compounds Ce[1,4(TMS)₂C₈H₆]₂ and Ce[1,3,6(TMS)₃C₈H₅]₂ are definitely in the Ce³⁺ region. The spread of the data points in the Ce³⁺ region is of the order of 5 eV with Ce[(Me₃C)₂C₅H₃]₃, Li{Ce[1,3,6(TMS)₃C₈H₅]₂}, and K[Ce(C₈H₈)₂] at the extreme electron-rich end (close to 0.0 eV in Figure 2) and the aqueous Ce³⁺ ion plus Ce[1,4(TMS)₂C₈H₆]₂ and Ce[1,3,6(TMS)₃C₈H₅]₂ around 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 4f¹e_{2u}πe_{2u}⁴. As stated above, the neutral cerocenes are believed to have a ground configuration best regarded as a mixture of 4f¹e_{2u}πe_{2u}³ and 4f⁰πe_{2u}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 alkali 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 $\sim 1.97 \text{ \AA}$ as compared to $\sim 2.07 \text{ \AA}$ for the $\text{K}(\text{COT})_2\text{Ce}$ diglyme salt.^{3,4,15} Our experimental results therefore support the conclusion of the sophisticated *ab initio* calculations that the cerocene ground configuration should be formulated primarily as a $4f^1 e_{2u} \pi_{e2u}^3$ singlet.^{9, 10}

Acknowledgments

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098 with the University of California. This work was done in part at SSRL which is operated by the Department of Energy, Division of Chemical Sciences. We thank the EPSRC for a studentship (to GHM) and the ERASMUS program for a scholarship (to MRR).

References

- (1) Greco, A.; Cesca, S.; and G. Bertolini *J. Organomet. Chem.* **1976**, *113*, 321.
- (2) Streitwieser Jr., A.; Kinsley, S. A.; Rigsbee, J. T.; Fragala, I. L.; Ciliberto, E.; Rosch, N. *J. Am. Chem. Soc.* **1985**, *107*, 7786.
- (3) Boussie, T. R.; Eisenberg, D.C.; Rigsbee, J.; Streitwieser, A.; Zalkin, A. *Organometallics* **1991**, *10*, 1922.
- (4) Kilimann, U.; Herbst-Irmer, R.; Stalke, D.; Edelman, F. T. *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1618.
- (5) Fischer, R. D. *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2165.
- (6) Rosch, N.; Streitwieser, Jr., A. *J. Am. Chem. Soc.* **1983**, *105*, 7237.
- (7) Neumann, C. S.; Fulde, P. *Z. Physik* **1989**, *B74*, 277.
- (8) Fulde, P. "Electron Correlations in Molecules and Solids," Springer-Verlag, Berlin, 1991, pp. 268-273.
- (9) Dolg, M.; Fulde, P.; Kuchle, W.; Neumann, C. S.; Stoll, H. *J. Chem. Phys.* **1991**, *94*, 3011.

- (10) Dolg, M.; Fulde, P.; Stoll, H.; Preuss, H.; Chang, A.; Pitzer, R. M. *Chem. Phys.* **1995**, *195*, 71.
- (11) Prins, R.; Koningsberger, D. E. "X-ray Absorption: Principles, Applications, Techniques for EXAFS, SEXAFS, and XANES," Wiley-Interscience, New York, 1988.
- (12) Antonio, M. R.; Soderholm, L. *Inorg. Chem.* **1994**, *33*, 5988.
- (13) Skanthakumar, S.; Soderholm, L. *Phys. Rev. B* **1996**, *53*, 920.
- (14) Burton, N. C.; Cloke, F. G. N.; Joseph, S. C. P.; Karamallakis, H.; Sameh, A. A. *J. Organomet. Chem.* **1993**, *462*, 39.
- (15) Hodgson, K. O.; Raymond, K. N. *Inorg. Chem.* **1972**, *11*, 3030.
- (16) Sofield, C. D.; Andersen, R. A. *J. Organomet. Chem.* **1995**, *501*, 271.
- (17) Hazin, P. N.; Huffman, J. C.; Bruno, J. W. *Organometallics* **1987**, *6*, 23.
- (18) Pinnavaia T. J.; Fay, R. C. *Inorg. Synth.* **1970**, *12*, 77.

Figure captions

Figure 1. Representative K edge spectra of Ce compounds: thick line, CeO₂; thin line, Ce[(Me₃C)₂C₅H₃]₃; dotted line, Ce[1,4(TMS)₂C₈H₆]₂; dashed line, Li{Ce[1,4(TMS)₂C₈H₆]₂}.

Figure 2. K-edge shifts of the Ce compounds relative to CeB₆. The numbering of the samples is given in Table 1.

Table 1. Numbering and characteristics of Ce samples

Number	Compound	Type of sample	Color	Reference
1	CeO ₂	Solid		
2	Ce(NH ₄) ₄ (SO ₄) ₄ ·2H ₂ O	Solid		
3	Ce(NH ₄) ₄ (SO ₄) ₄ ·2H ₂ O	1.6 M HNO ₃ solution	Yellow	
4	Ce(CH ₃ C(O)CHC(O)CH ₃) ₄	Toluene solution	Dark red	17
5	CeCl ₃ ·6H ₂ O	Solid		
6	CeF ₃	Solid		
7	Ce ₂ O ₂ S	Solid		
8	Ce ₂ (SO ₄) ₃	Solid		
9	CeSi ₂	Solid		
10	CeI ₃ ·(THF) _x	THF solution	Pale yellow	16
11	Ce[(Me ₃ C) ₂ C ₅ H ₃] ₃	Toluene solution	Purple	15
12	Ce ₂ (SO ₄) ₃	1.6 M HNO ₃ solution	Colorless	
13	Ce ₂ (SO ₄) ₃	1.2 M HCl solution	Colorless	
14	Ce(NO ₃) ₃	1.6 M HNO ₃ solution	Colorless	
15	Ce(NO ₃) ₃	1.2 M HCl solution	Colorless	
16	Ce[1,4(TMS) ₂ C ₈ H ₆] ₂	Toluene solution	Deep purple	4
17	Ce[1,3,6(TMS) ₃ C ₈ H ₅] ₂	Toluene solution	Deep purple	4
18	Li{Ce[1,4(TMS) ₂ C ₈ H ₆] ₂ }	Toluene solution	Dark green	4
19	K{Ce(C ₈ H ₈) ₂ }	Toluene solution	Light green	14
Standard	CeB ₆	Solid		

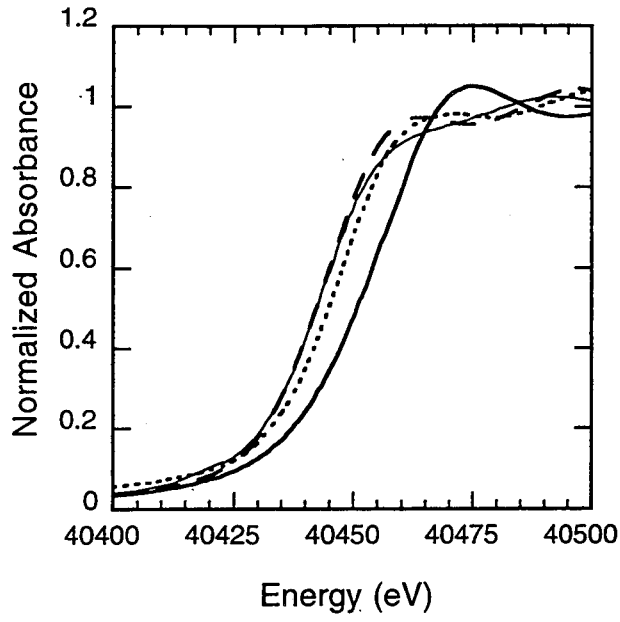


Figure 1 Edelstein, *et al.*

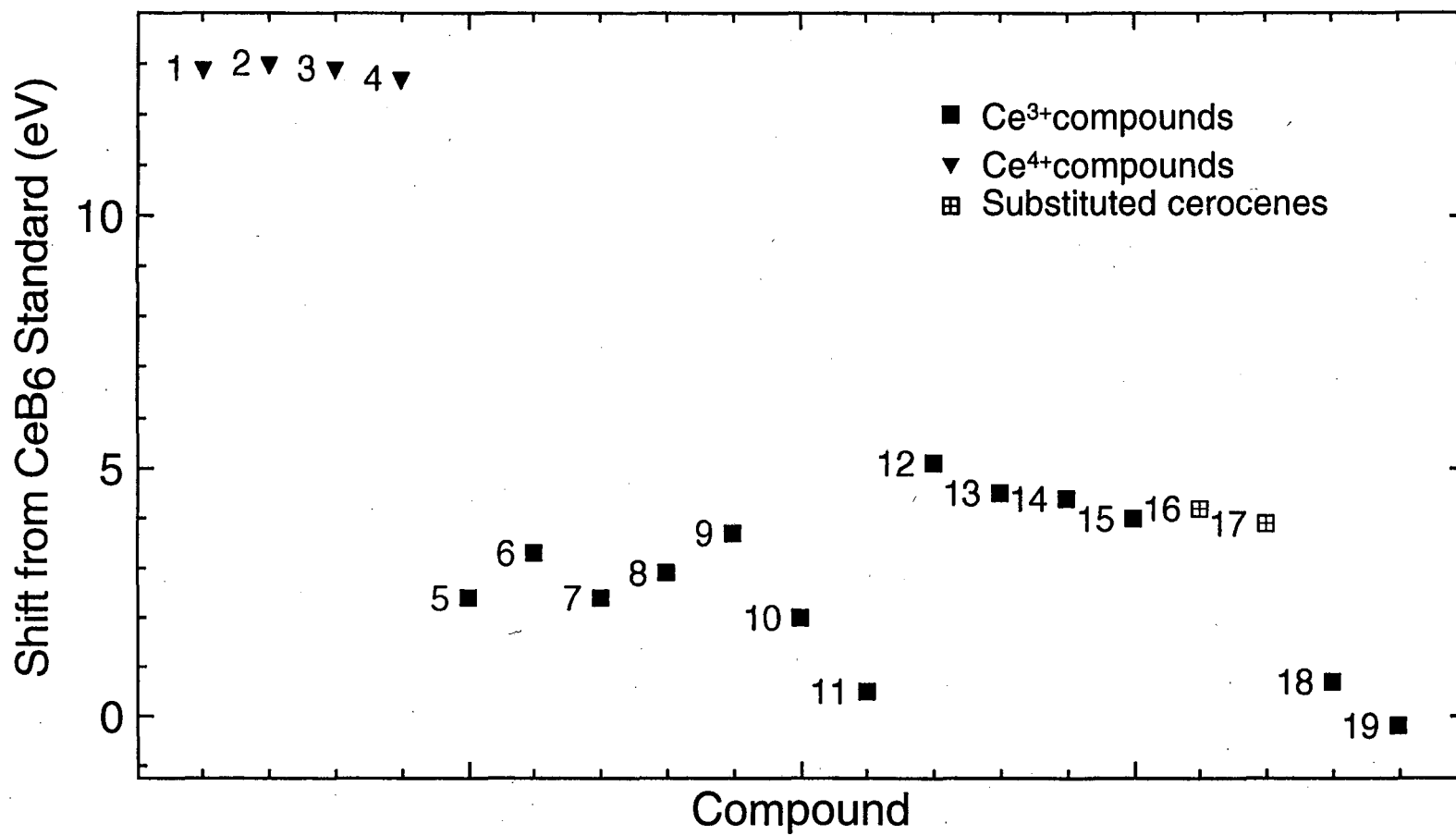


Figure 2 Edelstein, *et al.*

**ERNEST ORLANDO LAWRENCE BERKELEY NATIONAL LABORATORY
ONE CYCLOTRON ROAD | BERKELEY, CALIFORNIA 94720**