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October 1985

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Photoelectron Spectra and Bonding in Cerocene,
Di- π -[8]AnnuleneCerium(IV)

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Photoelectron Spectra and Bonding in Cerocene, Di- π -

[8]Annulene cerium(IV)

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Abstract: The preparation of cerocene (di- π -[8]annulene cerium(IV)) by reaction of cerium(IV) isopropoxide with triethylaluminum in cyclo-octatetraene has been confirmed. The reversible half-wave potential of -1.28 V vs NHE found in THF is the lowest known for a Ce(IV)/Ce(III) couple and suggested the preparation of choice: shaking a THF solution of bis-[8]annulene cerate(III) ion with excess silver iodide gives quantitative conversion to cerocene. The compound reacts slowly with uranium tetrachloride and at a measureable rate with water. The

photoelectron spectra are similar to those of thorocene and give ionization potentials in excellent agreement with $X\alpha$ -SW calculations. The spectroscopic, chemical and theoretical results are consistent with ring-metal bonding having substantial covalency with significant 4f contributions.

Quasirelativistic SCF- $X\alpha$ Scattered-Wave calculations have recently indicated that cerocene (di- π -[8]annulenecerium(IV)) has an electronic structure unexpectedly similar to that of di- π -[8]annuleneuranium(IV) (uranocene) and -thorium(IV) (thorocene).¹ Various theoretical criteria indicate a substantial covalency for the lanthanide sandwich including a degree of f-orbital interaction comparable to uranocene itself.² Such involvement of 4f orbitals in ring-metal bonding in an organolanthanide compound would be unusual and unprecedented but the simple existence of cerocene should alone be considered to be remarkable: the compound combines a strong reducing agent (the [8]annulene dianion rings) with a powerful oxidizing agent, cerium(IV). This combination would imply that the structure could not be that of a simple ionic cluster. We have reproduced the synthesis of cerocene reported by Greco, Cesca and Bertolini;^{3,4} chemical properties and the photoelectron spectrum agree with the theory and suggest the importance of ring-metal covalency in this unusual compound.

The reaction of cerium(IV) isopropoxide with triethylaluminum in cyclooctatetraene gives the reported air-sensitive, brown-black microcrystalline compound. The compound shows a single signal in $^1\text{H-NMR}$ at 5.9 ppm in THF-d_8 or at 5.75 ppm in toluene-d_8 . When the

toluene solution of the complex was exposed to air, the brown solution became pale yellow and the $^1\text{H-NMR}$ contained only one peak at 5.61 ppm, which is the resonance for neutral cyclooctatetraene. The infrared spectrum agrees with that reported. Conversion of bis-[8]annulenece(III)⁵ ion to cerocene can be accomplished electrochemically. The reversible half-wave potential for the Ce(IV)/Ce(III) couple in this system is -1.28 V vs NHE⁶ and is, to our knowledge, the lowest Ce(IV)/Ce(III) couple reported.⁷ This observation suggested that bis-[8]annulenece(III) ion could be chemically converted to cerocene with mild oxidizing agents; indeed, we found that shaking a THF solution with excess silver iodide gives quantitative conversion to cerocene. This simple procedure is clearly the preparation of choice.

Cerocene reacts slowly with UCl_4 to give uranocene; this behavior is similar to that of thorocene and unlike the di- π -[8]annulene lanthanate(III) anions that react rapidly with UCl_4 . Cerocene also hydrolyzes in wet THF more slowly than thorocene to produce a mixture of 80% 1,3,5- and 20% 1,3,6-cyclooctatrienes.⁸ This reactivity pattern does not suggest an ionic cluster.

Electronic absorption bands of thorocene at 2.75 eV and uranocene at 2.01 eV assigned as ligand-metal charge-transfer excitations, $e_{2g}(\pi) \rightarrow e_{3u}(f)$, agree well with the X α orbital energy differences, 3.03 and 1.97 eV, respectively. We now report that cerocene has an intense band ($\epsilon \approx 8000$) at 469 nm (2.63 eV) in THF with a broad shoulder that, on deconvoluting using Gaussian functions,⁹ has λ_{max} 570 nm (2.18 eV, $\epsilon \approx 1000$). The latter band is in good agreement with the

calculated orbital energy difference of 1.92 eV.^{1,2} We note that this band has comparable intensity to the visible band in uranocene ($\epsilon=1800$).

A further test of the theory is the direct comparison of the X α transition state energies with the ionization potentials determined from photoelectron spectra. The spectra were recorded on a Perkin Elmer PS 18 spectrometer modified by the inclusion of a hollow cathode discharge source giving a high output of He-II photons (Helectros Development Corp.). The spectra were run at 140 °C and "multiple scan mode" with the aid of a channeltron electron multiplier and a MOSTEK computer interfaced directly to the spectrometer. The results of ten scans were averaged; the signal-to-noise ratio for the He-I spectrum is greater than 10^3 . The energy scale of consecutive scans was locked to reference values of the Ar $P^2P_{3/2}$ and He($1s^{-1}$) self-ionization lines.

The photoelectron spectra of cerocene (Fig. 1) are similar to those of thorocene. There are two bands (a and b in Fig. 1) in the 6-8 eV region; both show fine structure. A well resolved band (c) is present in the 9-10 eV range (Table 1). Some other rather overlapped structures (d, e, and f) follow in the higher ionization energy region up to 19 eV. The bands present beyond 11 eV are common features of photoelectron spectra of all of the [8]annulene complexes thus far studied.¹⁰⁻¹³ They belong to inner π and σ MO's having major contributions from the ligands. By analogy to the actinide compounds and on the basis of the X α -SW calculations, bands a and b are undoubtedly associated with ionization from the e_{2u} and e_{2g} MOs, respectively. The

fine structure associated with these bands is probably due to vibronic Jahn-Teller effects in the ion states. Band c is taken to represent the ionizations from both the e_{1g} and e_{1u} MO's. This band shows a shoulder in the higher ionization energy side whose separation from the main peak compares well with the computed $X\alpha$ -SW e_{1u} - e_{1g} splitting. The intensity changes in this band on going to He-II radiation are comparable to those observed in the actinide series. The excellent agreement between the experimental and theoretical ionization potential differences (Table 1) gives additional credence to the interpretation of the $X\alpha$ wave functions.^{1,2}

The chemistry of organolanthanide compounds in the +2 and +3 oxidation states is that of essentially ionic systems; however, theory, reaction chemistry and spectroscopy combine in the case of cerocene to show that this higher oxidation state organolanthanide has substantial ring-metal covalency and that metal 4f orbitals are involved in such bonding.

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1. Rösch, N.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* 1983, 105, 7237.
2. Rösch, N. *Inorg. Chim. Acta.* 1984, 94, 297.
3. Greco, A.; Cesca, S.; Bertolini, G. *J. Organometal. Chem.* 1976, 113, 321.
4. We have not been able to reproduce the synthesis of the compound reported with much different properties by Kalsotra, B.L.; Multani, R.K.; Jain, B.D. *Chem. Ind.[London]* 1972, 339.
5. Hodgson, K.; Mares, F.; Starks, D.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* 1973, 95, 8650.
6. In THF with tetrabutylammonium tetrafluoroborate as supporting electrolyte; the peak-to-peak separation by cyclic voltammetry was the same as for the ferrocene reference. We are indebted to K. Moran for technical assistance in this determination.
7. We thank Professor K. Raymond for this observation.
8. Unpublished results of Robert A. Moore.
9. (a) We are indebted to Scott Gronert for this analysis. (b) A definite assignment of both bands is not possible at this time; however, measurements with substituted ferrocenes in several solvents are currently in progress.
10. Clark, J. P.; Green, J. C. *J. Chem. Soc., Dalton Trans.* 1977, 305.
11. Fragala, I.; Condorelli, G.; Zanella, P.; Tondello, E. *J. Organomet. Chem.* 1976, 122, 357.
12. Bruno, G.; Ciliberto, E.; Fischer, R. D.; Fragala, I.; Spiegl, A. *W. Organometallics* 1982, 1, 1060.
13. Green, J. C.; Payne, M. P.; Streitwieser, A., Jr. *Organometallics* 1983, 2, 1707.

Table 1. Ionization energies of cerocene.

Band label	Ionization Energy (I.E.) eV	Δ I.E. ^a eV	X α Transition State Energy eV	X α $\Delta E^{a,b}$ eV
a	6.75	0	6.31 (e_{2u})	0
a'	6.92 ^c			
b	7.68	0.93	7.20 (e_{2g})	0.89
b'	(7.81) ^c			
c	9.98	3.23	9.42 (e_{1u})	3.11
c'	10.32	3.57	9.84 (e_{1g})	3.53

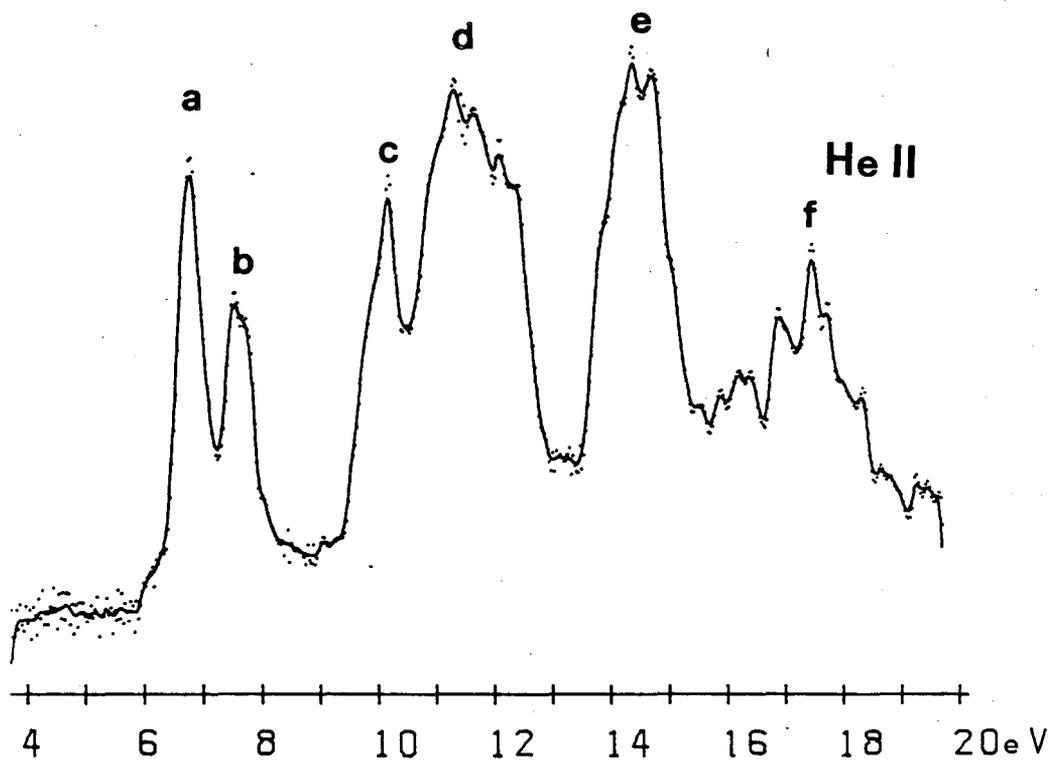
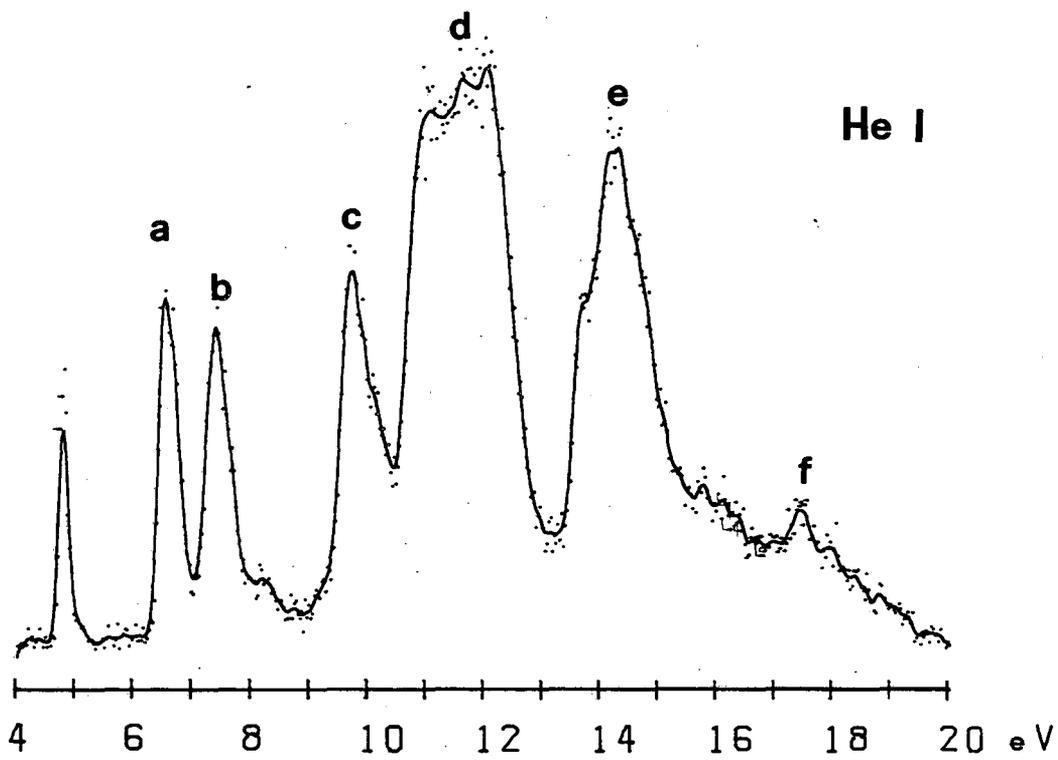
(a) Difference compared to band a.

(b) Ref. 1

(c) Fine structure. Shoulders are in parentheses.

Figure caption:

Fig. 1. Photoelectron spectrum of cerocene.



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