

Ligand reduction in variously substituted cerium (IV) tetrakis acetylacetonate complexes by electrochemistry technique

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Abstract:

In this work, substantial evidence was obtained for ligand reduction in cerium tetrakis acac complexes. Also, this ligand reduction of a negatively charged ligand proved to depend far less on the nature central metal than neutral ligands does. It is supposed that in $M^Z(acac)_z$ complexes the charge is distributed evenly over the whole molecule. In this work these complexes were prepared and characterized by IR and CHN analysis to indicate the purities of these complexes. The electrochemistry techniques were shown as obtained for ligand reduction.

This research was carried out at School of Chemistry and Molecular Science, Sussex University, U.K.

Introduction :

This research arose from the notion that there might be ligand- based reduction in cerium tetrakis acetyl acetone complexes. For- valence cerium cannot itself be reduced and any reductions that might be observable can be attributed to ligand reductions. The fact that acac reductions can take place in the first place was proposed by Leslie and Heath [1], who studied ligand reductions on pd, pt and Ni Bis(acac) complexes, in which the metal is not reduced. The experiments involved variously substituted complexes of which measurement of first and second reduction potentials were done. Afterwards these were plotted against slightly modified Taft parameter[1] (Electrochemical Inductive parameters). The findings were that (a) the two lines obtained, were close to parallel, indicating similar acceptor orbital for both reductions (b) the slopes were apparently not influenced by the metal involved in these complexes and (c) the slope of the plot was similar to the slope of the same plot for other complexes (which were widely accepted to exhibit ligand reductions). All this evidence was in favour of the

reductions being ligand- base. Further more, for the non-thio $pd(O_2C_3RHR'')_2$ series, an apparently analogous process was detected in all cases and attributed to diketonate ligand reduction.

It is known that reduction of a neutral ligand is facilitated by about 0.3V by unit charge on the metal [2]. We therefore expected a similar effect for $M^Z(acac)_z$ making $acac^-$ on Ce^{4+} easy to reduce.

The major thing that can be noted from the mentioned [2,3] is the dependence of the reduction potential on the metal (Ni vs. pt vs. pd) is negligible.

We might therefore derive that a similar slope must be obtained for all four successive ligand reductions in the cerium complexes. We can appreciate this by assuming that the charge of -4 , which is the total charge of the ligands, is completely delocalized and because of the valency of 4 for the metal, renders the central ion effectively neutral. The same would apply for n negatively charged ligands attached to a metal of valency n. In all cases, therefore, the ligand is in

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approximately the same state, and large differences in reduction potentials that are ligand-base, are not expected.

Cyclic voltammetry (CV) is a very useful modern electroanalytical technique; its principles and theories have been discussed by Kissinger and Heineman [4]. CV has been used to study electro active species and extensively used in the fields of inorganic chemistry, organic chemistry and biochemistry [5,6]

Taft parameter (TP): R.W. Taft introduced the so-called Taft Parameter (TP) in 1950. He studied acid-catalyzed hydrolysis of substituted benzoate and aliphatic esters and infrared that the rates of these reactions are not dependent on the electronic nature of substituents. He suggested that the observed dependence be due, rather to steric effects, on the other hand, some base-catalyzed hydrolysis reactions do have a dependence on the electronic nature of substituent as well as feels its steric influence. He derived inductive parameters, which are functions of rate constants for both the acid and base catalyzed hydrolysis reactions.

These are Taft parameters (TP).

$$TP = [\log(K/K_0)_B - \log(K/K_0)_A] / 2.48$$

where K and K_0 refer to the substituted and unsubstituted complex respectively. A and B denote acid and base catalyzed reactions, respectively [7-10]. Derived in this way, TP values should reflect the electronic influence of each substituent, free of steric factors.

Experimental

I Synthesis of tetrakis (β -diketonato)Ce(IV) complexes

2-3 grams of ceric oxide (CeO_2) are dissolved in 10 ml of concentrated (36%) hydrochloric acid with 10 ml of absolute ethanol, and added 3-4 drops of hydrogen peroxide, then added 2.5 grams of potassium iodate, the solution was heated between 60-70 $^{\circ}C$ with stirring for 10 minutes, and solution allowed to cool at

room temperature with stirring. β -diketonate (the weight depend up on the molecular weight of β -diketone) was dissolved in absolute ethanol (15 ml) and added to the solution at room temperature, with immediately turn to color. Aqueous sodium hydroxide solution (0.5M) was slowly added until precipitation of the colored solid was complete. The solids were then collected by filtration, washed with deionized water (10 ml x 3), dried in vacuum for three hours, and then for complexes ($Ce(MeHCF_3)_4$, $Ce(CF_3HTh)_4$, $Ce(CF_3HPh)_4$) purified by sublimation and the others complexes ($Ce(MeHMe)_3$, $Ce(PhHPh)_3$) were recrystallized from 50% toluene and 50% petroleum ether mixture. The solid was collected by filtration and transferred it to schlenck tube, heated at 100 $^{\circ}C$ in silicon oil bath under vacuum for four hours [11].

B-Electrochemical

The major experimental set-up is illustrated in figure-1-, which shows the electrochemical cell. This cell is operated under an inert atmosphere to protect air-sensitive compounds and eliminate currents due to the reduction of oxygen, and is fitted with a gas purge inlet. Cells can also be designed for use on a high vacuum line. The reference electrode should provide a stable potential. The reference electrode formed by immersing a silver wire in an acetonitrile of the electrolyte, the potential of this electrode is not as highly reproducible as other electrodes and it is usual to check the potential of a standard couple such as Cp_2Fe/Cp_2Fe^+ during the experiment. A more reliable Ag/Ag^+ reference electrode is prepared by immersing the silver wire in a solution of electrolyte that is also 0.001-0.002M in $AgCl$. The ungreased ground-glass tap is closed but wetted with a film of electrolyte solution. Together with the fine frit in the reference electrode, this helps reduce the diffusion of Ag^+ into the

cell, which could cause problems at the working electrode.

The electrochemical experiments were carried out in a cell of typically 10 ml. Content. The solvent was dichloromethane, dried over potassium hydroxide for two weeks and freshly distilled with phosphorous pentoxide, so as to achieve an exhaustive dehydration. Oxygen in the solution was removed by bubbling dichloromethane saturated dry nitrogen gas through the solution for about 5 minutes.

The supporting electrolyte was tetrabutylammonium tetrafluoro borate $[(tBu)_4N^+BF_4^-]$ abbreviated as TBABF₄. This electrolyte was chosen because of its solubility in dichloromethane. It was synthesized in from $(tBu)_4NOH$ and HF_4 , which should be purified by recrystallization from ethylacetate/pentane mixture [12].

The electrochemical measurements were performed with a Princeton Applied Research Model 170 Electrochemistry system. All SMDE (stationary Mercury Drop Electrode) experiments (ACV, DCV) were sampled. Experiments involving the SMDE or HMDE (Hanging Mercury Drop Electrode) were done on a Metrohm 663 VA Electrode stand, connected to the PAR with an interface. The reference electrode was a Ag/AgCl reference electrode in reference to which ferrocene invariably was oxidized at + 0.52V. The cyclic, AC and DC Voltammograms were recorded for scan rates of 100, 20 and 10mv/s, respectively

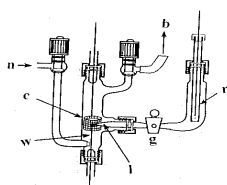


Fig-1- Electrochemical cell for cyclic voltammetry
r: reference electrode; w: working electrode, pt bead with large surface; n: nitrogen inlet; l: luggin capillary; c: counter electrode, pt gauze; g: ungreased tap; b: to manifold or bubbler

Results and discussion:

IR Spectra

The IR spectra of these complexes recorded on a Perkin Elmer 598 machine and Perkin-Elmer 1720 infrared spectrophotometer. Spectrum was calibrated, using a thin film of polystyrene. Sample was prepared as mulls in Nujol (ex. BDH spectroscopic grade), on cesium iodide (ex. BDH spectroscopic) disc.

The IR assignment of these complexes for principal bands are 2852-2970 cm^{-1} correspond to $\nu(C-H)$., 1590-1598 cm^{-1} $\nu(C=O)$ and 1515-1530 cm^{-1} $\nu(C=C)$. The IR assignment spectra for $\nu(Ce-----O)$ of these complexes are showed in table 1.

Tabl-1- The IR assignment spectra for $\nu(Ce-----O)$ for the cerium complexes.

Complex	ν / cm^{-1}
$Ce(O_2C_3MeHPh)_4$	240
$Ce(O_2C_3PhHPh)_4$	236
$Ce(O_2C_3MeHCF_3)_4$	236
$Ce(O_2C_3CF_3HTh)_4$	233
$Ce(O_2C_3CF_3HPh)_4$	240

B-Microanalysis of complexes

The microanalysis of these complexes are showed in table 2

Table-2- The microanalysis (CHN) for the complexes

Complex	Found		Theoretical	
	C%	H%	C%	H%
$Ce(O_2C_3MeHPh)_4$	61.00	4.64	61.20	4.59
$Ce(O_2C_3PhHPh)_4$	70.00	4.31	69.76	4.26
$Ce(O_2C_3MeHCF_3)_4$	31.90	2.13	31.91	2.12
$Ce(O_2C_3ThHCF_3)_4$	37.37	1.58	37.50	1.56
$Ce(O_2C_3CF_3HPh)_4$	48.00	2.40	48.00	2.40

C-Electrochemistry

For our experiments we had access to 5 differently substituted cerium complexes where for the general formula of $Ce(O_2C_3RR'R'')_4$, the sequence $RR'R''$ was:

$Ce(MeHPh)_4$, $Ce(PhHPh)_4$, $Ce(MeHCF_3)_4$, $Ce(CF_3HTh)_4$, $Ce(CF_3HPh)_4$

We measured the cyclic and AC Voltammograms and some of the more satisfactory results are shown in figures 2 to 5. Remarkable are the very negative potentials necessary to reduce the successive ligands. This makes electrochemistry quite hard, because of the large background interference. Not surprising are therefore the many unsatisfactory and disappointing results. It can also be noted that in addition to this difficult electrochemistry, many unexpected hamper investigation things, which do not occur systematically. The splitting of the first reduction wave occurs in only two complexes; some times small wave are observed low potentials; some times the wave are very reversible and at other times seem very irreversible. In spite of all these drawbacks, it was possible to arrive at a nice solution. Having stripped the results of all unsystematic features, the general pattern of an ACV experiment is four roughly equidistant gradually decreasing waves.

In table 3 the reduction potentials (1st, 2nd, 3rd and 4th) are given for each of the five complexes.

A plot of first through fourth reduction potentials versus the modified TP (Taft parameter) of Leslie and Heath (electrochemical inductive parameter) gives the graph of figure (6). We use the

Table-3- The reduction potentials of cerium complexes

Complex	1 st E	2 nd E	3 rd E	4 th E
Ce(O ₂ C ₃ MeHPh) ₄	-1.60	-1.85	-2.06	-----
Ce(O ₂ C ₃ PhHPh) ₄	-1.36	-1.60	-1.94	-2.26
Ce(O ₂ C ₃ MeHCF ₃) ₄	-1.18	-1.44	-1.70	-1.98
Ce(O ₂ C ₃ ThHCF ₃) ₄	-0.93	-1.26	-1.57	-1.72
Ce(O ₂ C ₃ CF ₃ HPh) ₄	-0.95	-1.13	-1.39	-1.72

Modification of TP to enable us to compare with the work on the pd complexes, and indeed, because this gives a better plot. Striking is that all four lines are rather parallel, indicating that all four acceptor orbitals are similar, in agreement

with supposed ligand-base reductions. Also, remembering the two parallel plots of first and second reduction potential of the pd, pt and Ni(acac)₂ system, this is very promising. A possibly still more remarkable feature is that the gradients of the four lines, averaging about 210 mv is about equal to the gradient found for the pd Bis(acac) complex (208 mv).

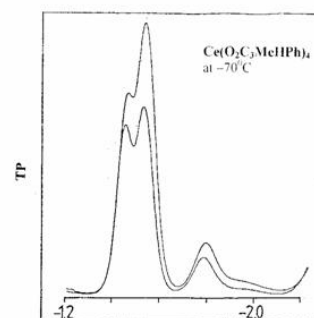


Fig-2- AC Voltammogram for reduction of Ce(O₂C₃MeHPh)₄

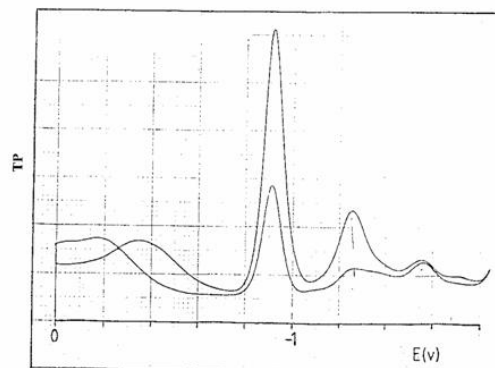


Fig-3- AC Voltammogram for reduction of Ce(O₂C₃ThHCF₃)₄

Conclusions:

Taking all together, firstly, good evidence is obtained for ligand reductions taking place in Ce(acac)₄ complexes. Secondly, things point in the direction that we can indeed think of the negative charge of the ligands as being completely delocalized, rendering all M(acac)_n system neutral and with uniform charge distribution. This is also the explanation for the fact that our prediction of easy ligand reduction proved wrong; in fact reduction is rather difficult. The charge of +4 on cerium that we envisaged, and which would facilitate the reduction substantially, proved to be much less.

The most notable feature of the first reduction plots of Ce and Pd is the intercept on the (TP=0) axis. For the Pd system, this is about -1.5v , whereas this amounts to about -1.8v for the Ce system. The energy of the ligand acceptor orbital must therefore in the Ce systems is slightly higher than those in the Pd systems. But the energy difference between the four orbitals in which the successive electrons are added, must be the same. For neutral ligands (e.g. bipyridyl ligands [2]), the reduction of the ligand becomes easier by approximately 0.4v for every unit valence increase; here clearly this change in reduction potentials is far less dramatic. The reduction of the ligand becomes about 0.1v more difficult per unit valence increase.

Any unsystematic behaviour of the Ce complexes may be due to impurities in the compounds. Another four Ce complexes were electrochemically investigated. These were Ce tris acetylacetonate complexes, $\text{Ce}(\text{MeHMe})_3$, $\text{Ce}(\text{PhHPh})_3$ and $\text{Ce}(\text{MeHCF}_3)_3$, respectively hydrated by H_2O , H_2O , nil and $\text{C}_2\text{H}_5\text{OH}$ (these complexes form complexes with water, ammonia, pyridine, ethanol and other donor molecules, so that the cerium tends to display a coordination number higher than six. Evidence for this has been obtained by x-ray crystallographic studies). Impurities may be playing an even greater role here, because the electrochemistry was so unsatisfactory that it forbids it to say much more about it. However, a slight indication was obtained of the general pattern of the four reduction waves in the $\text{Ce}(\text{MeHMe})_4$ complexes returning here, where, of course, one would expect only two. This can mean a new obsolete interpretation of the data above, or it can simply mean that some $\text{Ce}(\text{MeHMe})_4$ is present in the Ce(III) compounds, or that some Ce(III) compound contributes to the tetrakis MeHMe complex.

Very surprising results were obtained when we added free ligand to a solution of the cerium complexes of that ligand. This was done because it seemed feasible that some side reaction or complication might arise during the successive reductions. Addition of the free ligand in electrochemical measurement might throw some light on the matter. A huge reduction peak was observed some examples are to be found in figures 7 and 8. In some experiments the potential of the reduction wave of the free ligand corresponded to the first reduction peak attributed to the Ce complexes containing that ligand. See table 4 for the results.

Table-4- The reduction potentials of the free ligands

Free ligand	Reduction potential
$\text{O}_2\text{C}_3\text{MeHPh}$	-1.60
$\text{O}_2\text{C}_3\text{PhHPh}$	-1.37
$\text{O}_2\text{C}_3\text{MeHCF}_3$	-1.21
$\text{O}_2\text{C}_3\text{ThHCF}_3$	-1.04
$\text{O}_2\text{C}_3\text{CF}_3\text{HPh}$	-1.14

This coincidence implies that we must carefully re-examine that status of the first peak in cerium complexes systems.

$\text{Ce}(\text{acac})_4$ complexes have been investigated before [13]. There, the reduction of the parent complex is discussed. They did not discuss any substituted cerium complexes. On the basis of their findings lies the reduction of Ce^{IV} to Ce^{III} because we had access to five differently substituted complexes, our study is more versatile, and the interpretation the way we presented of the reductive of $\text{Ce}(\text{MeHMe})_4$ complexes in the region from zero to -2v is probably more reliable.

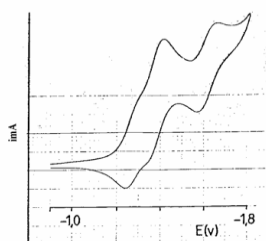


Fig.-4 Cyclic Voltammogram for reduction of Ce(O₂C₃PHHPb);

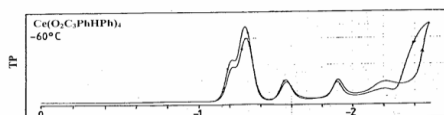


Fig.-5 AC Voltammogram for reduction of Ce(O₂C₃PHHPb);

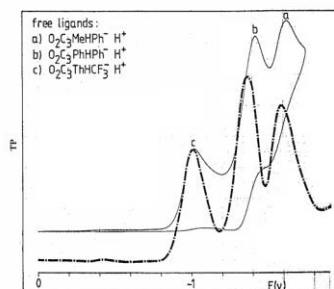


Fig.-8 AC and ACV of a mixture of three free ligands (pi electrode)

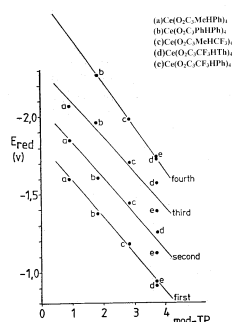


Fig.-6 The four reduction potentials of variously substituted Cerium complexes plotted versus the mod-TP

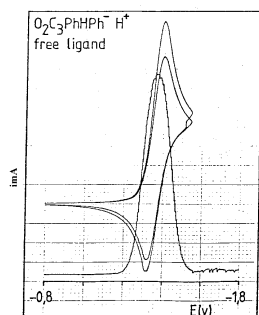


Fig.-7- AC and ACV of the reduction of the free O₂C₃PHHPb ligand; ACV: SMDE, CV: HMDE

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اختزال الليغاند في مختلف تعويض لمعقدات السيريوم بتقنية الكيمياء الكهربائية

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الخلاصة:

تم في هذا البحث دراسة جوهريّة لجهود اختزال الليكند لمعقد رباعي اسيتايل أسيتون سيريوم وبعض مشتقات الاسيتايل أسيتون الداخلة في تكوين معقدات مع السيريوم. كذلك اثبت بان جهد اختزال هذا الليكند المرتبط بالفلز المركزي في المعقد اقل من جهد اختزال اليكند في حالته الحرة. أفترض أن توزيع الشحنة يكون بالتساوي على الجزيئة لمعقدات رباعي الأستايل أسيتون سيريوم ومشتقاته. تم في هذا البحث تحضير خمسة معقدات للسيريوم (IV) ودراسة مواصفاتها بتقنية الأشعة تحت الحمراء والتحليل (CHN) لبيان نقاوة هذه المعقدات ثم دراسة الكيمياء الكهربائية لها. تم إجراء هذا البحث في مدرسة الكيمياء والعلوم الجزيئية-جامعة سسكس-أنكلترا.