Visible and Ultraviolet Spectra of Tetraethylammonium Tetrakis(β-diketonato)cerate(III) and Tetrakis(β-diketonato)cerium(IV) Complexes

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A number of β-diketonates of cerium(III), $[NEt_4][Ce^{III}L_4]$, and cerium(IV), $[Ce^{IV}L_4]$, have been prepared and their spectra have been recorded in the visible and u.v. regions. The spectra of the cerium(III) complexes show a group of two or three bands of moderate intensity at frequencies just below those of the strong intraligand transitions. Such bands are assigned as cerium(III)-to-ligand electron transitions or as $4f\rightarrow5d$ transitions. For the cerium(IV) complexes a very broad absorption is found on the red side of the intraligand transitions, and is attributed to ligand-to-metal electron transfers.

THERE has been much interest in the spectral properties of the β-diketonates of the lanthanoids with a special regard to their hypersensitive, *J–J*, and fluorescence transitions. No detailed spectral study, however, has been carried out on the β-diketonates of cerium(III) and cerium(IV) for which one could anticipate electron-transfer transitions and/or $4f\rightarrow5d$ intershell transitions in the visible or near-u.v. regions.

Thus we report a systematic study on the electronic spectra of cerium(III) and cerium(IV) complexes with a variety of β-diketones, HL. For comparison, cerium(III) complexes have been prepared of the general formula $[NEt_4][Ce^{III}L_4]$ in which the metal is eight-co-ordinate just as in the corresponding cerium(IV) complexes, $[Ce^{IV}L_4]$. Some of the cerium(III) β-diketonates are easily oxidized by atmospheric oxygen, and so their preparation and spectral measurements were carried out under pure nitrogen.

EXPERIMENTAL

Preparation of the Complexes.—The cerium(III) complexes were prepared under pure nitrogen using deoxygenated solvents according to the following general method. A solution of cerium(III) chloride heptahydrate (2 mmol) and 2,2-dimethoxypropane (10 cm^3) in absolute ethanol (15 cm^3) was added to a mixture of the appropriate diketone (8 mmol), sodium hydroxide (8 mmol), and tetraethylammonium chloride (2 mmol) in absolute ethanol (25 cm^3). The solvent was removed *in vacuo*, the residue extracted with ethyl acetate (30 cm^3), and the suspended solid was removed by filtration. The solution was concentrated *in vacuo* to *ca.* 10 cm^3. By slow addition of n-hexane, crystals of $[NEt_4][Ce^{III}L_4]$ separated, which were washed with n-hexane and dried *in vacuo*. All the cerium(III) complexes with the present fluoro-substituted β-diketonates are very stable toward aerial oxidation. At room temperature their solutions in methyl cyanide are not appreciably oxidized by air over several hours.

The cerium(IV) β-diketonates were prepared according to the literature methods.[1-5] Analytical data are reported in the Table. All the present $[NEt_4][Ce^{III}L_4]$ complexes are new.

Spectral Measurements.—Solution spectra were recorded with a Cary 17 spectrophotometer using 1-cm silica cells. Methyl cyanide was distilled from phosphorus pentaoxide. The diffuse-reflectance spectra were obtained with a Beckman DK2 spectrophotometer using the standard Beckman reflectance attachment and magnesium oxide as the reference.

RESULTS AND DISCUSSION

Intraligand Transitions.—The present tetrakis(β-diketonato)-cerate(III) and -cerium(IV) species exhibit some intense absorption bands and shoulders in the range 29 000—48 000 cm^{-1} (ε 1.1 × 10^4—9.4 × 10^4 dm^3 mol^{-1} cm^{-1}) (Table). Many papers have dealt with the spectra of metal diketonates [2,6-12] and there is general agreement that bands having the above characteristics are to be attributed to intraligand transitions between π levels essentially localized in the β-diketonate anions.[7-12] It was also shown that, for a given β-diketone, the frequencies and intensities (per mol of ligand) of these intraligand transitions are practically the same for all the tervalent lanthanoid ions in the complexes $[Ln^{III}L_3]\cdot nH_2O$ ($n = 0$ or 2) [2,6,10] and $[Ce^{IV}L_4]$.[2] Only a small blue shift was found on going from $[Eu(tfpbd)_3]\cdot 2H_2O$ to $[Eu(tfpbd)_4]^-$ (tfpbd = 1,1,1-trifluoro-4-phenylbutane-2,4-dionate).[13] From the data in the Table it is seen that this holds true also with those $[NEt_4][Ce^{III}L_4]$ complexes which are not spontaneously oxidized by air. No attempt was made to measure the absorption spectra of the strongly oxidizable cerium(III) complexes in 10^{-5} mol dm^{-3} solutions.

For the subsequent discussions of the electron transitions of non-intraligand type exhibited by the cerium(III) and cerium(IV) complexes, it is useful to consider in detail the first of the intraligand bands, which for the present complexes falls in the range 29 600—36 400 cm^{-1} for the various β-diketonates (Table). Such a band is to

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[2] D. Purushotham, V. Ramachandra Rao, and Bh. S. V. Raghava Rao, *Analyt. Chim. Acta*, 1965, **33**, 182.

[3] T. J. Pinnavaia and R. C. Fay, *Inorg. Synth.*, 1970, **12**, 77.

[4] E. Uhlemann and F. Dietze, *Z. anorg. Chem.*, 1971, **386**, 329.

[5] J. Selbin, N. Ahmad, and N. Bhacca, *Inorg. Chem.*, 1971, **10**, 1383.

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[8] D. W. Barnum, *J. Inorg. Nuclear Chem.*, 1961, **21**, 221; **22**, 183.

[9] K. DeArmond and L. S. Forster, *Spectrochim. Acta*, 1963, **19**, 1393.

[10] S. P. Tandon and R. C. Govil, *J. Chem. Phys.*, 1972, **57**, 4097.

[11] R. L. Lintvedt and L. K. Kernitsky, *Inorg. Chem.*, 1970, **9**, 491.

[12] A. M. Fatta and R. L. Lintvedt, *Inorg. Chem.*, 1971, **10**, 478.

[13] R. G. Charles and E. P. Riedel, *J. Inorg. Nuclear Chem.*, 1966, **28**, 3005.

be attributed to electron transitions from the highest-filled to the lowest-empty π levels of the β-diketonate anions [$\pi_3 \rightarrow \pi_4$ for the pentane-2,4-dionate (pd) anion in Barnum's treatment].[8] The other bands found at higher frequencies (6 000—10 000 cm^{-1} higher for the second band of the present complexes) involve different π levels.

It is noteworthy that the first intraligand band is not appreciably split in the present β-diketonates of all the lanthanoids (Table, Figure 2, and refs. 2, 6, 10, and 13) whereas it appears to be split into two or three components for the β-diketonates of the 3*d* metal ions.[7-9,11,12] For example, $[Cr(pd)_3]$ has components of the first intraligand band at 33 600, 36 800, and 39 200 cm^{-1}.[12] The lifting of the degeneracy of the corresponding π-molecular orbitals of the ligands in the latter $[ML_3]$ complexes was attributed to their coupling *via* 3*d* orbitals of the central ion.[8]

Assuming an idealized dodecahedral stereochemistry with D_{2d} symmetry for $[Ln^{III}L_4]^-$ and $[Ce^{IV}L_4]$,[14] each group of the corresponding π levels of the four ligands should split into ($a_2 + b_1 + e$) levels. The occurrence of one unsplit band with lanthanoid β-diketonates suggests weaker coupling amongst the corresponding π levels of the four ligands than with 3*d*-metal β-diketonates. This is probably a consequence both of the larger ionic radii of the lanthanoids relative to those of the 3*d* elements, which weakens direct ligand–ligand interactions, and of the low ability of 4*f* and 5*d* orbitals to interact with the π systems of the β-diketones.

Analytical and electronic-spectral data for some cerium(III) and cerium(IV) β-diketonates [a]

Complex	Colour	Analysis (%) [b] C	H	N	Electronic spectra (10^3 cm^{-1}) [c] State	Bands
$[NEt_4][Ce^{III}(pd)_4]$	Yellow	50.1 (50.45)	7.4 (7.25)	2.4 (2.1)	Solid MeCN	24.9, 26.9 25.6 (144), 27.5 (sh)
$[NEt_4][Ce^{III}(tmhd)_4]$	Yellow	62.2 (62.25)	9.6 (9.65)	1.4 (1.4)	MeCN	25.0 (214), 27.1 (224)
$[NEt_4][Ce^{III}(tfpd)_4]$	Yellow	37.6 (38.1)	3.9 (4.1)	1.7 (1.6)	Solid MeCN	23.6 (sh), 25.8 (sh), 27.9 (sh) 23.9 (sh), 25.5 (136), 28.2 (sh), 35.3 (49 500)
$[NEt_4][Ce^{III}(hfpd)_4]$	Yellow	30.8 (30.6)	2.2 (2.2)	1.3 (1.25)	Solid MeCN	22.3 (sh), 24.6 (sh), 27.0 (sh) 22.2 (64), 24.3 (95), 26.9 (sh), 33.0 (55 000)
$[NEt_4][Ce^{III}(pbd)_4]$	Brick	63.3 (63.2)	6.0 (6.15)	1.5 (1.5)	MeCN	23.0 (sh)
$[NEt_4][Ce^{III}(tfpbd)_4]$	Orange	51.0 (50.95)	4.0 (3.9)	1.4 (1.25)	Solid MeCN	22.2 (sh), 24.2 (sh) 22.0 (186), 23.8 (204), 31.6 (62 500), 39.7 (31 000)
$[NEt_4][Ce^{III}(dppd)_4]$	Red-brown	70.2 (70.2)	5.7 (5.5)	1.2 (1.2)	Solid MeCN	19.9, 22.1 20.8 (264), 22.3 (sh)
$[NEt_4][Ce^{III}(tftbd)_4]$	Red-orange	41.4 (41.6)	3.3 (3.15)	1.3 (1.2)	Solid MeCN	21.3 (sh), 22.8 (sh) 21.3 (sh), 22.7 (sh), 29.6 (65 000), 37.4 (26 000)
$[Ce^{IV}(pd)_4]$ [3]	Red-brown	44.9 (44.75)	5.5 (5.25)		MeCN	36.4 (31 000), 46.9 (11 000)
$[Ce^{IV}(tmhd)_4]$ [4,5]	Red-brown	60.8 (60.5)	8.8 (8.75)		MeCN	26.9 (7 100), 36.4 (41 000), 47.6 (23 000)
$[Ce^{IV}(tfpd)_4]$ [3]	Red-brown	31.2 (31.9)	2.0 (2.15)		MeCN	21.3 (sh), 26.5 (4 400), 35.5 (29 100)
$[Ce^{IV}(pbd)_4]$ [1]	Red-brown	60.9 (61.2)	4.5 (4.6)		MeCN	32.5 (76 700), 40.4 (35 700)
$[Ce^{IV}(dppd)_4]$ [1]	Red-brown	69.1 (69.75)	4.2 (4.3)		MeCN	22.7 (sh), 30.5 (94 000), 39.0 (50 500), 46.5 (sh)
$[Ce^{IV}(tftbd)_4]$ [2]	Red-brown	37.5 (37.5)	1.7 (1.55)		MeCN	22.5 (sh), 29.9 (73 200), 36.0 (27 000), 47.0 (sh)

[a] Abbreviations used: pd = pentane-2,4-dionate; tmhd = 2,2,6,6-tetramethylheptane-3,5-dionate; tfpd = 1,1,1-trifluoropentane-2,4-dionate; hfpd = 1,1,1,5,5,5-hexafluoropentane-2,4-dionate; pbd = 1-phenylbutane-1,3-dionate; tfpbd = 1,1,1-trifluoro-4-phenylbutane-2,4-dionate; dppd = 1,3-diphenylpropane-1,3-dionate; tftbd = 1,1,1-trifluoro-4-(2-thienyl)butane-2,4-dionate. [b] Calculated values are given in parentheses. [c] Absorption coefficients (ε/dm^3 mol^{-1} cm^{-1}) are given in parentheses.

Cerium(III) *Spectra*.—The spectra of the cerium(III) β-diketonates $[NEt_4][Ce^{III}L_4]$ in methyl cyanide as well as in the solid state show a group of two or three absorption bands of moderate intensity (ε 64—264 dm^3 mol^{-1} cm^{-1}) (Table). The frequency difference between two different peaks is *ca.* 2 000 cm^{-1} and the group merges into the red tail of the strong intraligand transitions (Figure 1 and Table). The frequency ratio between the peak of the first of these transitions and that of the first intraligand transition is fairly constant, being 0.69 ± 0.02 : 1.

For cerium(III) complexes, absorption bands of moderate intensity in this spectral region may be attributed to: (*i*) ligand-to-metal electron transfers;[15] (*ii*) metal (4*f*)-to-ligand (' inverted ') electron transfers;[15] and (*iii*) intershell electron transitions $4f \rightarrow 5d$. The intensity and width of the bands in the group are so similar that the same mechanism should be responsible for all of them.

Hypothesis (*i*) must be ruled out since such bands would be expected to occur at lower frequencies with the more reducible europium(III) analogues. Europium diketonates, on the contrary, exhibit no absorption band below the intraligand transitions. In this connection, the lower limit of 28 000 cm^{-1} for such charge transfers with $[Eu(pd)_4]^-$ gives an optical-electro-

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[14] B. Allard, *J. Inorg. Nuclear Chem.*, 1976, **38**, 2109.

[15] C. K. Jørgensen, *Acta Chem. Scand.*, 1962, **16**, 2406.

negativity value $\kappa_{\text{opt.}} > 2.8$ for pd$^-$ in lanthanoid tetrakis(pentane-2,4-dionates), if $\kappa_{\text{uncorr.}}(\text{Eu}) = 1.9$.[16]

Assignment (*ii*), *i.e.* inverted electron transfer $4f \rightarrow \pi^*$, requires the occurrence of two or three empty low-lying π levels for the cerium(III) β-diketonates, having energies *ca.* 2 000 cm^{-1} apart. Actually, the shape of the first intraligand band of the complexes does not show any definite splitting of the first group of π^* levels $(a_2 + b_1 + e)$ Nevertheless, it cannot be ruled out that the apparently single intraligand band originates from a number of such closely spaced components. Such an assignment is consistent with the previously noted constancy of the ratio between the peak position of the first of these bands and that of the first intraligand band of different diketonates.

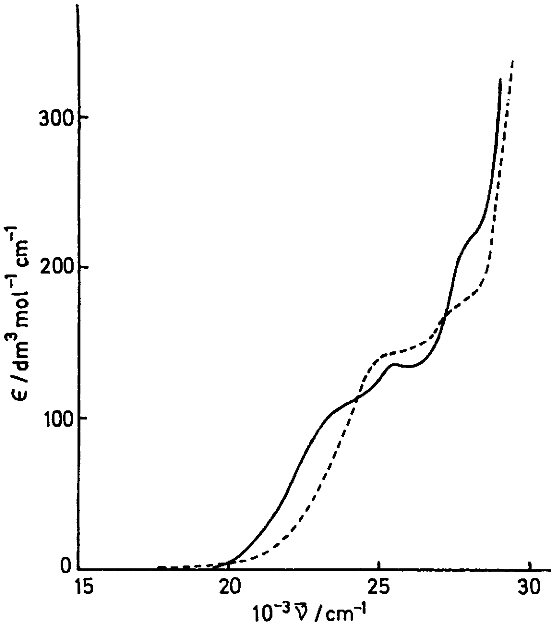

FIGURE 1 Absorption spectra of [NEt$_4$][Ce(pd)$_4$] (— — —) and [NEt$_4$][Ce(tfpd)$_4$] (——) in methyl cyanide (tfpd = 1,1,1-trifluoropentane-2,4-dionate)

Assignment (*iii*), *i.e.* intershell transitions $4f \rightarrow 5d$, is also plausible, since in D_{2d} symmetry the $5d$ orbitals are split by σ and π interactions into four levels $(a_1 + b_2 + b_1 + e)$.[17] Thus several electronic transitions may be expected from the ground-state configuration $4f^1$, which is split by σ and π interactions into the levels $a_1 + a_2 + b_2 + 2e$.[17]

It is noteworthy that β-diketonate anions exhibit both large orbital splittings and large nephelauxetic effects. In the spectrochemical series of ligands they exhibit a slightly larger effect than water, the f factor in Jørgensen's[18] relation $\Delta = f(\text{ligand})g(\text{metal})$ being 1.03—1.05 for many β-diketones (f is 1.00 for H_2O and 0.7 for Br$^-$).[11] On the other hand, the nephelauxetic effects are similar to that of bromide, with pd$^-$, and are even greater with many of the present β-diketonates. In terms of the relation[19] $(1 - \beta_{35}) = h(\text{ligand})k(\text{metal})$, h values of 2.3, 3.1, and 3.4 are found[12] for pd$^-$, pbd$^-$, and dppd$^-$, respectively, which are to be compared with the h values of 1.0, 2.3, and 2.7 for H_2O, Br$^-$, and I$^-$, respectively.[19] Therefore, on the basis of the relative positions of pd$^-$ and Br$^-$ in the nephelauxetic and spectrochemical series, the assignment of the transitions at 25 600 and 27 500 cm^{-1} for [Ce$^{\text{III}}$(pd)$_4$]$^-$ as $4f \rightarrow 5d$. transitions appears to be quite plausible when compared with the frequency of 29 150 cm^{-1} for the similar transition of [CeBr$_6$]$^{3-}$.[20]

On the other hand, such an assignment does not disagree with the constancy of the ratio between the peak position of the first of these bands and that of the first intraligand band, since low-frequency values of the latter bands are usually associated with high h values for the various β-diketonates.[12] Hence a strong nephelauxetic effect and a low energy for $f \rightarrow d$ bands should be expected with β-diketonates having a first intraligand band at low frequency.

Cerium(IV) *Spectra.*—The spectra of tetrakis(β-diketonato)cerium(IV) complexes exhibit a very broad intense absorption close to the red tail of the intraligand band (Figure 2 and Table). This sometimes appears as a shoulder on the more intense intraligand band; in a few cases it looks like a steadily rising absorption merging into the intraligand band. It appears that several mutually overlapping transitions are present under a broad envelope covering at least 10 000 cm^{-1}. These transitions are safely assigned as electron-transfer transitions from the ligand molecular orbitals to the metal $4f$ orbitals.[15] Assuming values of the optical electronegativity of $\kappa_{\text{uncorr.}}(\text{Ce}^{\text{IV}}) = 2.1$ (ref. 16) and $\kappa_{\text{opt.}}(\text{pd}^-) \geqslant 2.8$, one expects $\tilde{\nu} \geqslant 21\,000$ cm^{-1} in good agreement with the intense absorption found in the range 20 000—27 000 cm^{-1} for [Ce$^{\text{IV}}$(pd)$_4$] (Figure 2).

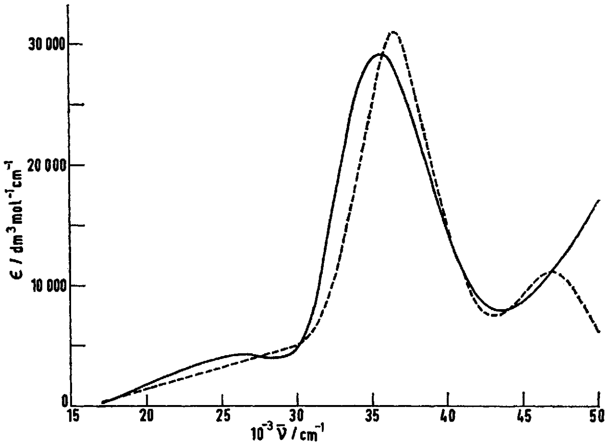

FIGURE 2 Absorption spectra of [Ce(pd)$_4$] (— — —) and [Ce(tfpd)$_4$] (——) in methyl cyanide

The broadness of these absorptions is due in part to the

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[16] C. K. Jørgensen, ' Oxidation Numbers and Oxidation States,' Springer–Verlag, Berlin, 1969, p. 148.

[17] J. C. Eiseinstein, *J. Chem. Phys.*, 1956, **25**, 142.

[18] Ref. 16, p. 84.

[19] Ref. 16, p. 106.

[20] J. L. Ryan and C. K. Jørgensen, *J. Phys. Chem.*, 1966, **70**, 2845.

large half-widths, usually 2 000—3 000 cm^{-1}, which are characteristic of the ligand-to-metal electron transfers.[20] Furthermore, five excited levels, corresponding to the $4f^1$ configuration of cerium, are expected for these transitions in D_{2d} symmetry.[17] These levels are spread over a range of *ca.* 3 000 cm^{-1} because of the combined effect of σ- and π-antibonding interactions and spin–orbit coupling.[21] In addition, the filled molecular orbitals of the ligands involved in these transitions could also be of the σ(oxygen) type, besides those of the π type (π_3 for pd$^-$).

As far as the oxidation behaviour of the cerium(III) complexes is concerned, no relation holds between their aerial-oxidation capability and the spectral properties of the cerium(III) and cerium(IV) diketonates. The known ready oxidizability of the cerium(III) complexes with β-diketones having high pK_a values [4] has been confirmed.

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[21] C. K. Jørgensen, R. Pappalardo, and H.-H. Schmidtke, *J. Chem. Phys.*, 1963, **39**, 1422; M. Gerloch and D. J. Mackey, *J. Chem. Soc.* (*A*), 1970, 3040.