Electronic Spectra of Eight-co-ordinate Complexes of some Lanthanoids(III) with *OO′*-Diethyl Dithiophosphate

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A series of *OO′*-diethyl dithiophosphates (ddtp) of the trivalent lanthanoids La, Ce, Pr, Nd, Sm, Eu, Tb, and Ho, general formula $[NEt_4][Ln(ddtp)_4]$, have been prepared. The electronic spectra have been investigated for methyl cyanide solutions in the spectral range 7 000—45 000 cm^{-1} and bands attributed to electronic transitions of *f—f*, charge-transfer, and *f—d* type. With the cerium(III) complex five bands in the spectral range 27 000—37 000 cm^{-1} are attributed to the five $4f \rightarrow 5d$ transitions. With the samarium, europium, and ytterbium compounds, a number of electron-transfer transitions are found and the ligand molecular orbitals involved are discussed.

In a previous paper we have dealt with the electronic spectra of a series of *NN*-diethyldithiocarbamates of lanthanoids(III) having the general formula $Na[Ln(Et_2NCS_2)_4]$ (Ln = La to Yb, except Pm).[1] The occurrence of intense ligand absorptions at frequencies $>26\,000$ cm^{-1} limited the spectral range investigated, particularly with respect to the study of electron-transfer transitions, with Sm, Eu, and Yb, and $f \rightarrow d$ transitions with Ce and Tb. With the aim of further investigating these transitions for the little-studied LnS_8 chromophores we have now used the ligand *OO′*-diethyl dithiophosphate (ddtp) which is almost transparent up to 37 000 cm^{-1} [$\varepsilon < 20$ dm^3 mol^{-1} cm^{-1} with K(ddtp)].

The preparation of two series of lanthanoid(III) diethyl dithiophosphates with the general formula $[AsPh_4][Ln(ddtp)_4]$ (Ln = Ln to Lu, except Pm) and $Na[Ln(ddtp)_4]$ (Ln = La to Er, except Pm) has been described by Pinkerton, but no detailed spectral data have been reported.[2] In order to avoid the u.v. absorption due to the $[AsPh_4]^+$ cation, we have prepared complexes of the general formula $[NEt_4][Ln(ddtp)_4]$ (Ln = La, Ce, Pr, Nd, Sm, Eu, Tb, and Ho). The present compounds of the heavier lanthanoids are strongly hygroscopic and do not crystallize easily.

In this paper the electronic spectra of the $[Ln(ddtp)_4]^-$ species are reported and discussed.

EXPERIMENTAL

Preparation of the Compounds.—Potassium diethyl dithiophosphate (8 mmol) and tetraethylammonium chloride (2 mmol) were added to a solution of the anhydrous metal trichloride (2 mmol) in absolute ethanol. After a few minutes, solvent was removed *in vacuo*, the residue extracted into ethyl acetate (30 ml), and the filtered solution concentrated *in vacuo* to *ca.* 15 ml. Slow addition of n-hexane caused crystals of $[NEt_4][Ln(ddtp)_4]$ to separate which were washed with n-hexane and dried *in vacuo*. All operations were performed under anhydrous conditions. With the heavier lanthanoids (Er—Yb) impure materials resulted which could not be recrystallized satisfactorily. The compound $[AsPh_4][Yb(ddtp)_4]$ was prepared by the above procedure using $[AsPh_4]Cl$. Table 1 reports analytical data and colours of the compounds.

Spectral Measurements.—Reflectance spectra were recorded with a Beckman DK2 spectrophotometer equipped with a standard reflectance attachment and magnesium oxide as the reference. Solution spectra (7 000—45 000 cm^{-1}) were recorded with a Cary 17 spectrophotometer. With the ytterbium complex, Beer's law was not obeyed for concentrations $<10^{-2}$ mol dm^{-3} using pure methyl cyanide as a solvent, probably because of a moderate solvolysis. In this case, the spectrum was recorded using a 2×10^{-2} mol dm^{-3} solution of K(ddpt) in methyl cyanide as a solvent medium. With the other complexes investigated no significant spectral change was found for the two media.

TABLE 1

Analytical data and colours for the compounds

		Analysis Found (Calculated) %		
Compound	Colour	C	H	N
$[NEt_4][La(ddtp)_4]$	White	28.7	6.1	1.3
		(28.56)	(5.99)	(1.39)
$[NEt_4][Ce(ddtp)_4]$	White	28.4	5.8	1.4
		(28.51)	(5.98)	(1.39)
$[NEt_4][Pr(ddtp)_4]$	Pale green	28.1	6.1	1.5
		(28.48)	(5.97)	(1.38)
$[NEt_4][Nd(ddtp)_4]$	Pale lilac	28.4	6.2	1.3
		(28.39)	(5.96)	(1.38)
$[NEt_4][Sm(ddtp)_4]$	Pale yellow	27.9	6.0	1.3
		(28.22)	(5.92)	(1.37)
$[NEt_4][Eu(ddtp)_4]$	Orange	28.0	6.0	1.6
		(28.18)	(5.91)	(1.37)
$[NEt_4][Tb(ddtp)_4]$	White	27.9	6.1	1.4
		(27.98)	(5.87)	(1.36)
$[NEt_4][Ho(ddtp)_4]$	Pale pink	27.1	6.2	1.5
		(27.82)	(5.84)	(1.35)
$[AsPh_4][Yb(ddtp)_4]$	Yellow	37.1	4.8	
		(37.03)	(4.66)	

RESULTS AND DISCUSSION

$4f \rightarrow 4f$ *Transitions.*—The spectral data of the *f—f* transitions of these $[Ln(ddtp)_4]^-$ ions are not reported in detail since they are very similar to those of the corresponding dithiocarbamates.[1] Only in a few cases is the baricentre of intensity for each *J* level, as well as the single peaks, shifted more than ± 50 cm^{-1} in the present complexes with respect to dithiocarbamates. More marked differences are found in the oscillator strengths, which are very often up to 40% lower with $[Ln(ddtp)_4]^-$ than with $[Ln(Et_2NCS_2)_4]^-$. This is mainly a consequence of the sharper nature of the bands with the ddtp complexes since their ε values are usually about the same as those with the Et_2NCS_2 complexes.

Spectrum of the Cerium(III) *Dithiophosphate.*—The electronic spectrum of $[Ce(ddtp)_4]^-$ in methyl cyanide exhibits a sharp and intense band at 27 500 cm^{-1} (δ = 700 cm^{-1}; ε, 700 dm^3 mol^{-1} cm^{-1}) and a group of bands

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[1] M. Ciampolini, N. Nardi, P. Colamarino, and P. L. Orioli, *J.C.S. Dalton*, 1977, 379.

[2] A. A. Pinkerton, *Inorg. Nuclear Chem. Letters*, 1974, **10**, 495.

at higher frequencies with peaks at 31 800, 33 300, and 35 500, and a shoulder at 36 700 cm^{-1} (Table 2 and Figure 1). This group of bands merges with the strong *intra*ligand band which shows a shoulder at *ca.* 42 000 cm^{-1} (ε *ca.* 8 000 dm^3 mol^{-1} cm^{-1}). The band envelope can be resolved by means of four Gaussian curves having δ *ca.* 1 000 cm^{-1} and peaks at 31 500, 33 300, 35 100, and 36 700 cm^{-1} (ε 470, 260, 220, and 170 dm^3 mol^{-1} cm^{-1} respectively).

It is tempting to assign these five transitions in the spectral range 27 500—36 700 cm^{-1} as all the electron transitions from the ground state $4f^1$ to the five $5d$ orbitals, assuming a complete lifting of their degeneracy (except Kramer's degeneracy) in this complex. Actually it is well known that the co-ordination geometry of the eight-co-ordinate complexes with bidentate ligands is very often irregular and intermediate between the square antiprism (D_{4d}) and the dodecahedron (D_{2d}).[3]

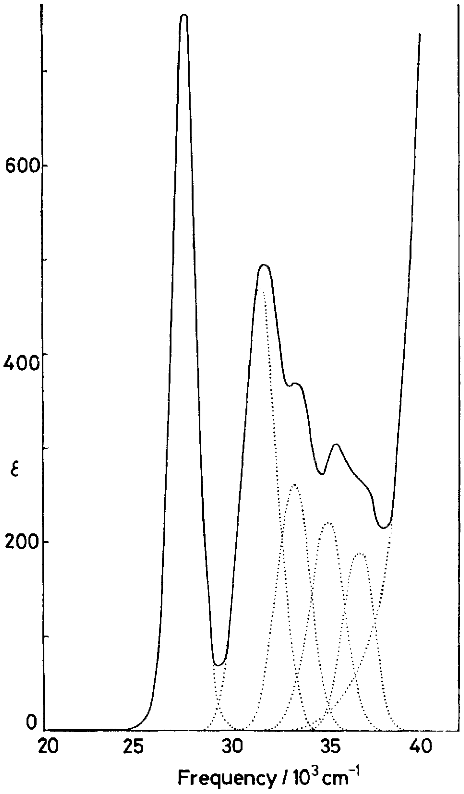

FIGURE 1 Absorption spectrum of [NEt$_4$][Ce^{III}(ddtp)$_4$] in methyl cyanide solution; the dotted lines are Gaussian functions

TABLE 2

Solid and solution electronic spectra for some *OO′*-diethyl dithiophosphate complexes *

Compound	State	Absorption bands/10^3 cm^{-1}
[NEt$_4$][Ce(ddtp)$_4$]	Solid	27.3
	MeCN	27.5 (766), 31.8 (498), 33.3 (299), 35.5 (304), 36.7 (sh)
[NEt$_4$][Sm(ddtp)$_4$]	MeCN	28.3 (sh), 31.0 (sh), 33.4 (700)
[NEt$_4$][Eu(ddtp)$_4$]	Solid	21.3 (sh), 23.9, 27.0 (sh)
	MeCN	21.4 (sh), 24.1 (451), 27.4 (sh), 32.8 (108)
[AsPh$_4$][Yb(ddtp)$_4$]	Solid	23.3
	MeCN	23.8 (sh), 27.8 (155), 27.1 (sh)

* Absorption coefficients (ε/dm^3 mol^{-1} cm^{-1}) are given in parentheses.

Such a distorted dodecahedral structure has just been found, in the solid state, with a complex of the similar ligand [Et$_2$NCS$_2$]$^-$, Na[La(Et$_2$NCS$_2$)$_4$], the true symmetry of this LaS$_8$ chromophore being only C_s. Nevertheless it must be stressed that for the higher symmetries D_{4d} or D_{2d}, the lifting of degeneracy within e-type orbitals can be achieved *via* the Jahn–Teller effect and/or spin-orbit coupling. For instance, in D_{2d} symmetry the e-type orbitals (d_{xz}, d_{yz}) are separated by ξ(Ce^{III},$5d$) = 1 000 cm^{-1} in the strong crystal-field limit, and somewhat more in the present case of intermediate spin-orbit coupling.* Such a splitting is about the same as the band separations found with this cerium(III) spectrum (1 600—1 800 cm^{-1}).

The above assignment of the five transitions as $4f \rightarrow 5d$ is supported by the small band half-widths δ ($\leqslant$1 000 cm^{-1}), a spectral feature that is considered characteristic of f—d transitions in contrast to the larger band half-widths of the electron-transfer transitions (*ca.* 1 500—2 500 cm^{-1}).[4] Furthermore, the frequency pattern of the five transitions is fairly similar to that anticipated for the splitting of d orbitals in eight-co-ordinate chromophores of D_{2d} or D_{4d} symmetry in the absence of strong π interactions. Assuming reasonable values of the geometrical and electronic parameters the energies of d orbitals are, in D_{2d} symmetry, $b_1 \ll a_2 \sim e \sim b_2$, whereas in D_{4d} the levels $a_1 < e_2 < e_3$ are equally spaced.[5]

As further support to the above assignment one may compare the frequency of the baricentre of the five f—d transitions, *i.e.* 32 800 cm^{-1}, with the anticipated mean energy of the $5d$ orbitals relative to the $4f$ orbitals. Indeed, the nephelauxetic effect β(Ce^{III},$5d$), for $5d$ orbitals, may be calculated according to the formula $1 - \beta(\text{Ce}^{III},5d) = h(\text{ddtp}^-) \times k(\text{Ce}^{III},5d)$.[6] Making use

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* For D_{2d} dodecahedral symmetry, a set of the d spin-orbital functions and the relative energy matrices of spin-orbit coupling are as follows. $\varepsilon(i)$ is the ligand-field energy of a d_i orbital.

$$\begin{aligned}\Gamma_6(a_1) &= |z^{2-}> \\ \Gamma_6(e) &= \frac{i}{\sqrt{2}}|xz^+> + \frac{1}{\sqrt{2}}|xz^+>\end{aligned} \qquad \begin{pmatrix} \varepsilon(a_1) & \frac{i\sqrt{3}}{\sqrt{2}}\xi \\ \frac{-i\sqrt{3}}{\sqrt{2}}\xi & \varepsilon(e) - \frac{1}{2}\xi \end{pmatrix}$$

$$\begin{aligned}\Gamma_7(b_1) &= |x^2 - y^{2-}> \\ \Gamma_7(b_2) &= i\,|xy> \\ \Gamma_7(e) &= \frac{i}{\sqrt{2}}|xz^+> - \frac{1}{\sqrt{2}}|xz^+>\end{aligned} \qquad \begin{pmatrix} \varepsilon(b_1) & -\xi & -\frac{i}{\sqrt{2}}\xi \\ -\xi & \varepsilon(b_2) & -\frac{i}{\sqrt{2}}\xi \\ \frac{i}{\sqrt{2}}\xi & \frac{i}{\sqrt{2}}\xi & \varepsilon(e) + \frac{1}{2}\xi \end{pmatrix}$$

[3] S. P. Sinha, *Structure and Bonding*, 1976, **25**, 69, and references therein.

[4] C. K. Jørgensen, *Mol. Phys.*, 1962, **5**, 271.

[5] M. Randic, *Croat. Chem. Acta*, 1960, **32**, 189; *J. Chem. Phys.*, 1962, **36**, 2094; G. Gliemann, *Theor. Chim. Acta*, 1962, **1**, 14; J. R. Perumareddi, A. D. Liehr, and A. W. Adamson, *J. Amer. Chem. Soc.*, 1963, **85**, 249.

[6] C. K. Jørgensen, 'Oxidation Numbers and Oxidation States,' Springer–Verlag, Berlin, 1969, p. 72.

of the values $h(\mathrm{ddtp}^-) = 2.8$,[6] $k(\mathrm{Ce^{III}},5d) = 0.13$,[1] and $E_{\text{free ion}}(\mathrm{Ce^{III}},5d) = 51\,200$ cm^{-1},[7] one obtains $\beta(\mathrm{Ce^{III}},5d) = 0.64$ and $E_{\text{mean}}(\mathrm{Ce^{III}},5d) = (\mathrm{Ce^{III}},5d) \times E_{\text{free ion}}(\mathrm{Ce^{III}},5d) = 0.64 \times 51\,200$ cm^{-1} $= 32\,800$ cm^{-1}, in excellent agreement with the baricentre of the five transitions.

According to this spectral assignment the overall splitting of the $5d$ shell in this $\mathrm{Ce^{III}S_8}$ chromophore is 9 200 cm^{-1}, a value which is to be compared with $\Delta(\text{oct}) = 8\,000$—12 000 cm^{-1} for octahedral $\mathrm{Ce^{III}O_6}$ chromophores in a number of oxide lattices,[8] $\Delta(\text{cube}) =$ 14 000 and 11 000 cm^{-1} for cubic $\mathrm{Ce^{III}O_8}$ chromophores in oxide lattices [8] and glasses,[7] respectively, and $\Delta(\text{cube}) =$ 11 200 cm^{-1} for the cubic $\mathrm{Ce^{III}F_8}$ chromophore in the $\mathrm{CaF_2}$ lattice.[8] In this connection it may be recalled that $\Delta(\text{oct}) : \Delta(\text{cube}) : \Delta(\text{square antiprism}) = 1 : 8/9 : 8/9$ and that $\Delta(\text{square antiprism}) \simeq \Delta(\text{dodecahedron})$. All these Δ-values are rather small with respect to $\Delta(\text{oct})$ for $[\mathrm{CeCl_6}]^{3-}$, which was shown by Jørgensen to be $>15\,000$,[9] since the spectrochemical order is $\mathrm{F^-} > \mathrm{ddtp^-} > \mathrm{Cl^-}$.[6] Perhaps this is a consequence of the increased cerium(III)–ligand distance in eight-co-ordinate complexes.

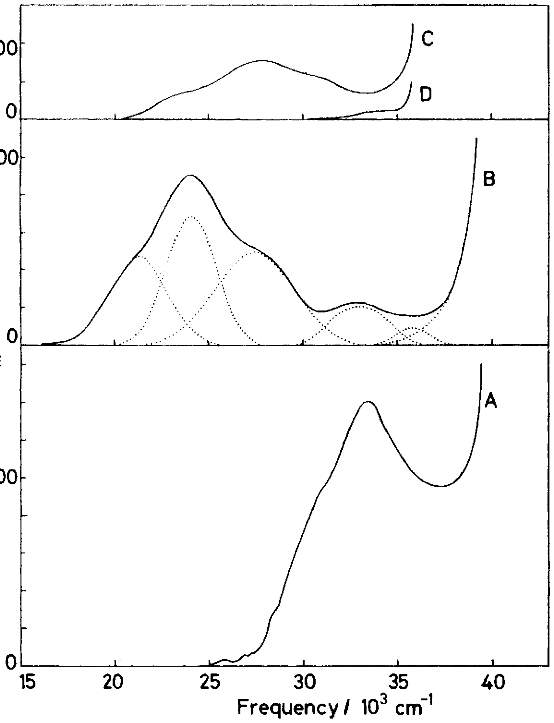

FIGURE 2 Absorption spectra of some lanthanoid dithiophosphates in methyl cyanide solution: A, $[\mathrm{NEt_4}][\mathrm{Sm(ddtp)_4}]$; B, $[\mathrm{NEt_4}][\mathrm{Eu(ddtp)_4}]$; C, $[\mathrm{AsPh_4}][\mathrm{Yb(ddtp)_4}]$; D, $[\mathrm{AsPh_4}]\mathrm{Cl}$. The dotted lines are Gaussian functions

Spectra of the Samarium, Europium, and Ytterbium Dithiophosphates.—The absorption spectra of $[\mathrm{Ln(ddtp)_4}]^-$ (Ln = Sm, Eu, and Yb) in methyl cyanide exhibit a group of bands of moderate intensity at frequencies just below those of the intraligand bands (Table 2 and Figure 2), which may be safely attributed to electron-transfer transitions from the highest-filled molecular orbitals of the ligands to the $4f$ orbitals of the reducible metal ions.

The shape of the band envelope is very similar for these three ions, showing one maximum and a shoulder on both sides; with the samarium compound the high-frequency shoulder appears by subtracting the absorbance of the intraligand band. With the europium complex, where these transitions fall at lower energies, a further band is found at frequencies just below the steeply rising intraligand absorption. A Gaussian analysis, made on the europium complex, shows that the band envelope can be accurately resolved into a minimum number of four functions with peaks at 21 300, 24 100, 27 400, 33 100 cm^{-1} (and possibly a weaker band at *ca.* 36 000 cm^{-1}) and half-widths of 1 500—2 400 cm^{-1}.

In accordance with their nature as electron-transfer transitions, the frequency shifts of corresponding bands for the europium, ytterbium, and samarium complexes strictly parallel the differences in the uncorrected optical electronegativity of the metal ions. Furthermore the frequencies of the more intense band agree fairly well with the frequencies calculated according to the formula $\sigma = [\chi_{\text{opt.}}(\mathrm{ddtp^-}) - \chi_{\text{uncorr.}}(\mathrm{M})] \times 30\,000$ cm^{-1} using the literature values of $\chi_{\text{opt.}}(\mathrm{ddtp^-}) = 2.7$, $\chi_{\text{uncorr.}}(\mathrm{Ce^{III}}) = 1.9$, $\chi_{\text{uncorr.}}(\mathrm{Yb^{III}}) = 1.8$, and $\chi_{\text{uncorr.}}(\mathrm{Sm^{III}}) = 1.6$.[10] The calculated values are 24 000, 27 000, and 33 000 cm^{-1} for the europium, ytterbium, and samarium dithiophosphates respectively.

With europium(III) and ytterbium(III) there is only one low-lying level for the excited electron-transfer configuration, *i.e.* $^8G_{7/2}(4f^7)$ and $^1S_0(4f^{14})$ respectively whereas with samarium there is a group of seven levels $^7F_{0-6}(4f^7)$, closely spaced within a range of *ca.* 4 000 cm^{-1}. Thus, it appears that a number of loosest bound, filled molecular orbitals are present in the complexes in order to account for the electron-transfer bands.

Jørgensen studied the electron-transfer spectra of a number of d-metal diethyl dithiophosphates and assumed that the highest-filled molecular orbitals of the ligand were bonding and antibonding combinations of $3p(\pi)$ orbitals of adjacent S atoms in each $\mathrm{S_2P}$ unit.[11] The remaining $3p$ sulphur orbitals should have much lower energies since they are involved in strong S–M and S–P σ bonds.[11]

Nevertheless, with the present lanthanoid dithiophosphates the energy order of σ(S–M) and π(S) molecular orbitals might also be inverted since σ (as well as π) bonding interactions between sulphur and lanthanoid ions are presumably rather weak. On the other hand, the length of the S–P bond in metal dialkyl dithiophosphates is intermediate between that of a single and

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[7] R. Reisfeld, *Structure and Bonding*, 1973, **13**, 53 and references therein.

[8] G. Blasse, *Structure and Bonding*, 1976, **26**, 43 and references therein.

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

[10] C. K. Jørgensen, ref. 6, p. 141.

[11] C. K. Jørgensen, *Mol. Phys.*, 1962, **5**, 485; *J. Inorg. Nuclear Chem.*, 1962, **24**, 1571; *Inorg. Chim. Acta Rev.*, 1968, **2**, 65.

double bond,[12] indicating strong π interactions between sulphur and phosphorus which stabilize $3p(\pi)$ sulphur orbitals. The order of the energies expected is, therefore, $3s(\mathrm{S}) < \sigma(\mathrm{S{-}P}) < [\pi(\mathrm{PSM}), \sigma(\mathrm{S{-}M})] < 4f(\mathrm{M})$.

Thus, for instance, the four bands found with the europium complex, covering a frequency range of *ca.* 12 000 cm^{-1}, can be assigned as electron transfers to empty $4f$ orbitals from $\sigma(\mathrm{S{-}M})$ and/or $\pi(\mathrm{PSM})$ molecular orbitals which, assuming dodecahedral symmetry (D_{2d}) for the chromophore $\mathrm{LnS_8}$, transform as $\sigma(\mathrm{S{-}M}) = 2a_1 + 2b_2 + 2e$ and $\pi(\mathrm{PSM}) = 2a_2 + 2b_1 + 2e$.[13] The degeneracy of these energy levels is lifted by σ and π interactions with the metal orbital of proper symmetry, which behave as $4f$ $(a_1 + a_2 + b_2 + 2e)$, $5d$ $(a_1 + b_1 + b_2 + e)$, $6s$ (a_1), and $6p$ $(b_2 + e)$.[13] Of course, S–S interactions may also play a role in removing the degeneracy, as was suggested by Jørgensen.[11]

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[12] Q. Fernando and C. D. Green, *J. Inorg. Nuclear Chem.*, 1967, **29**, 647; J. F. McConnell and V. Kastalsky, *Acta Cryst.*, 1967, **22**, 853; S. Ooi and Q. Fernando, *Inorg. Chem.*, 1967, **6**, 1558; S. L. Lawton and G. T. Kokotailo, *ibid.*, 1969, **8**, 2410; S. L. Lawton and G. T. Kokotailo, *Nature*, 1969, **221**, 550; C. Furlani, P. Porta, A. Sgamellotti, and A. A. G. Tomlinson, *Chem. Comm.*, 1969, 1046; D. Furlani, A. A. G. Tomlinson, P. Porta, and A. Sgamellotti, *J. Chem. Soc.* (*A*), 1970, 2929; P. Coggon, J. D. Lebedda, A. T. McPhail, and R. Q. Palmer, *Chem. Comm.*, 1970, 78; J. F. McConnell and A. Schwartz, *Acta Cryst.*, 1972, **B28**, 1546.

[13] J. C. Eisenstein, *J. Chem. Phys.*, 1956, **25**, 142.