Emission Spectra of some Lanthanoid Decatungstate and Undecatungstosilicate Ions

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Emission spectra have been recorded of polycrystalline samples of $Na_7Eu^{III}W_{10}O_{35}\cdot xH_2O$ and $K_{13}Eu^{III}(SiW_{11}O_{39})_2\cdot xH_2O$. The fluorescence of the europium ion can be efficiently pumped *via* the internal states of the tungstate groups. The cluster maintains its integrity in neutral aqueous solution, in which the europium ion also luminesces intensely. The symmetry of the crystal field surrounding the lanthanoid ion has been assigned by an analysis of the Stark splittings seen in the $^5D_0 \rightarrow {}^7F_J$ emission lines. The praseodymium(III), neodymium(III), and holmium(III) analogues of $Na_7Eu^{III}W_{10}O_{35}\cdot xH_2O$ do not give enhanced fluorescence under excitation in the polytungstate bands, but emission could be detected by direct laser excitation of the *f–f* states. An analysis of the praseodymium spectrum has been attempted, but overlapping of transitions prevents an unambiguous assignment of the Stark splittings.

THE spectra of lanthanoid ions arising from electronic transitions within *f* electron configurations can be used as probes of the local microsymmetry of the environment of the ion.[1,2] This is possible for the following reason. The large spin–orbit coupling splits the free-ion terms into multiplets of a given *J* value which are separated by several hundred wavenumbers. The Stark splitting of these multiplets due to the local crystal field is much less than this and reflects directly the symmetry of the crystal field. Thus on changing the environment of a lanthanoid ion the separation of the baricentres of the multiplets is virtually unaltered whereas the Stark splitting may be totally changed. Because of the rather weak coupling of the *f* electrons to the field of the surrounding nuclei, the *f–f* transitions are sharp, possessing few vibrational side bands. Hence the details of the Stark-splitting pattern are often readily discernible even in spectra of ions at room temperature in the solution phase. Although the oscillator strengths of *f–f* transitions are exceedingly low, the spectra are readily recorded by observation of the luminescence spectra of the ions.

The most commonly used probe has been the europium(III) ion which has the following special advantages.[3] The intense part of the emission spectrum, which consists of many relatively sharp lines spread throughout the visible region, originates from a non-degenerate excited state, $^5D_0$. Transitions from this to the Stark components of the ^7F_J manifold of the ground state are readily observed and the number of crystal-field components of each ^7F_J level can be counted. Comparison is then made with the number of transitions predicted by group theoretical arguments. Before a firm assignment can be established it is necessary to know the multipole nature of the transition and the selection rule which is operating. This has been established for a number of europium compounds,[4] but should ideally be done for each new system studied by examination of the polarizations of individual transitions. In addition, examination of the relative intensities of the different sets of lines can give a qualitative indication of the site group, which, for example, may indicate the presence or absence of a site of inversion.[1]

In this work we apply these methods to a determin-

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[1] W. C. Nieuwport, G. Blasse, and A. Bril, ' Optical Properties of Ions in Crystals,' eds. H. M. Crosswhite and H. W. Moos, Interscience, New York, 1967, p. 161.

[2] G. H. Dieke, ' Spectra and Energy Levels of Rare Earth Ions in Crystals,' Interscience, New York, 1968.

[3] See, for example, H. Samelson, A. Lempicki, V. A. Brophy, and C. Brecher, *J. Chem. Phys.*, 1964, **40**, 2547.

[4] C. Brecher, H. Samelson, and A. Lempicki, ref. 1, p. 73.

ation of the site symmetries of the lanthanoid ion in the polytungstate-complexes recently prepared by Peacock and Weakley.[5] The novel compounds are $Na_7Eu^{III}W_{10}O_{35}\cdot xH_2O$ and $K_{13}Eu^{III}(SiW_{11}O_{39})_2\cdot xH_2O$. Apparently, the structural integrity of these clusters is retained in neutral aqueous solution and we have been able to probe their symmetries. The monomer was also available containing the ions Pr^{III}, Nd^{III}, and Ho^{III}, respectively, in place of Eu^{III}, and the luminescence of these has also been measured. The intense absorption band of the polytungstate group suggested that the lanthanoid luminescence could be pumped efficiently *via* these levels. Only in the europium complexes did this prove possible with high efficiency.

EXPERIMENTAL

The rare-earth polytungstate chelate complexes were a gift from Drs. T. J. R. Weakley and R. D. Peacock, Dundee University. The europium chelates were: (*i*) $Na_7Eu^{III}W_{10}O_{35}\cdot xH_2O$ referred to as the monomer and (*ii*) $K_{13}Eu^{III}(SiW_{11}O_{39})_2\cdot xH_2O$ referred to as the dimer. The other chelates were all analogues of the former, $Na_7Pr^{III}W_{10}O_{35}\cdot xH_2O$, $Na_7Nd^{III}W_{10}O_{35}\cdot xH_2O$, and $Na_7Ho^{III}W_{10}O_{35}\cdot xH_2O$. The preparation, characterization, and absorption spectra have been fully described.[5] The samples were in microcrystalline form and were used without further purification. Solutions were made up in water and adjusted to pH *ca.* 7.1 with dilute Na[OH]. A saturated solution was filtered and diluted 10 fold before use to reduce the number of scattering particles in the solution.

Emission spectra were recorded on one of two spectrometers. (*i*) A spectrometer based on a Hilger and Watts D331 double monochromator for excitation and a Monospex 600 (D460) single monochromator for analysis with an A.E.I. 500 W high-pressure xenon arc as the source lamp. Detection was with either an E.M.I. 9558 Q (S-20) or 9659 QB (extended S-20 response) photomultiplier, cooled with solid carbon dioxide–ethanol, using a lock-in amplifier (AIM Electronics Ltd., Cambridge) with a reference frequency of either 50 or 420 Hz, the frequency of a chopper placed between the sample and exit slit of the excitation monochromator. (*ii*) A Spex Raman spectrometer based on a Spex 1401 double monochromator, a photomultiplier with extended S-20 characteristics, and a Spectra-Physics model 165 laser using a Kr–Ar gas-filled laser with lines at 476.5 (60) and 488 nm (250 mW) (Spex. Industries, New Jersey, U.S.A.).

Spectra at temperatures between 60 and 5 K were recorded from powdered samples which were cooled by a copper ' cold finger ' from the heat exchanger of a B.O.C. flow cryostat (British Oxygen Co. Ltd., London). The crystalline sample was finely powdered, poured into a depression in a copper cell, and covered with a silica window glued to the copper with Araldite. The sample face was orientated at 45° to both excitation and emission monochromators. Detection of the emission intensity followed front-face excitation. The temperature of the sample was monitored by a gold–0.03 atom% iron–Chromel P thermocouple.

The Monospek 600 and the Hilger and Watts D331 monochromators were calibrated using a Hg–Cd–Zn discharge lamp, observing the mercury lines at 4 358.35 and 5 460.74 Å with a slit width of *ca.* 0.01 mm, corresponding to a band pass of *ca.* 0.3 Å, and using the minimum scan rate. The Spex 1401 monochromator was calibrated by observing the wavenumber (cm^{-1}) of one of the lasing lines. The values calculated were correct within 1.0 cm^{-1} at 15 000 cm^{-1}. The spectra from the Hilger and Watts machine were identical in band position to those recorded on the Spex. Corning filters were used to cut off unwanted light on both excitation and emission sides of the sample. Typically, for europium emission a cut-off below 520 nm was used on the analysis side.

RESULTS AND DISCUSSION

Emission spectra were recorded of the polytungstate monomer complexes of Eu^{3+}, Pr^{3+}, Ho^{3+}, and Nd^{3+} and of the europium complex of the dimer in aqueous solution and as crystalline powders at room temperature. The intensity of the visible emission following excitation into the polytungstate absorption band at 250 nm was $Eu^{III} > Pr^{III} \gg Ho^{III} \ggg Nd^{III}$. This range of intensities encompassed a bright red glow for the europium(III) complex, to the almost undetectable spectrum of Nd^{III}. Spectra were recorded over several sets of transitions with reasonably high resolution (band pass $\leqslant 5.0\ cm^{-1}$) for the complexes of Eu^{3+} and Pr^{3+}. The emission of the neodymium(III) complex was so weak that the low resolution used (50 cm^{-1}) meant that the spectrum recorded was highly slit dependent and not of sufficient quality to be used for analysis. A further series of spectra were recorded using excitation by the Ar–Kr laser directly into the excited states of the rare-earth ion. A similar relation of the emission intensities was observed and again it was not possible to record the spectrum of the complex of Nd^{III}. Spectra recorded following excitation into the polytungstate excited states with the xenon-arc lamp were identical in band position and relative intensities with those measured with excitation directly into the excited states of the rare earth with the Ar–Kr laser, except in the case of the complex of Pr^{3+} in which some photochemical change was observed under laser irradiation.

Europium(III) *Monomer and Dimer.—Polycrystalline samples.* The room-temperature emission spectra of powdered samples are shown in Figure 1 which also indicates assignment of each region of the spectra. The assignments are unambiguously established by comparison with the detailed assignment of Eu^{III} doped in YVO_4.[4] It can be seen that emission lines originating from the $^5D_1$ state overlap those from the lower-energy $^5D_0$ state. Although the energy separation between the $^5D_1$ and $^5D_0$ states is *ca.* 1 750 cm^{-1}, non-radiative relaxation between them is known to be relatively slow, probably due to the operation of an electronic selection rule which forbids radiationless processes such as $J = 1 \rightarrow J = 0$.[6,7] Due to the quenching of stimulated

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[5] R. D. Peacock and T. J. R. Weakley, *J. Chem. Soc.* (*A*), 1971, 1836, 1937.

[6] E. D. Reed, jun., and H. Warren Moos, *Phys. Rev.*, 1973, **B8**, 980.

[7] E. D. Reed, jun., and H. Warren Moos, *Phys. Rev.*, 1973, **B8**, 988.

multiphonon processes at low temperature, the radiative quantum efficiency of the $^5D_1$ state of Eu^{III} in YVO$_4$ is *ca.* 4% at 4.2 K and below, but $\leqslant 1\%$ at 77 K.[6] Thus emission arising from the $^5D_1$ state is a factor of 10^{-2}—10^{-4} times less intense than that from the $^5D_0$ state at 77 K.

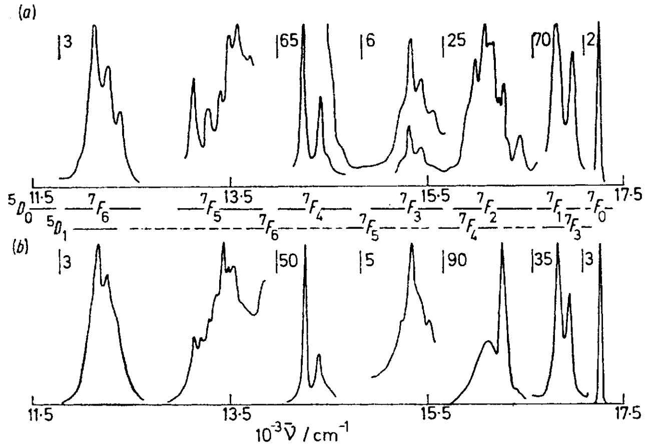

FIGURE 1 Emission spectra at 295 K of Na$_7$Eu^{III}W$_{10}$O$_{35}$·xH$_2$O (*a*) and K$_{13}$Eu^{III}(SiW$_{11}$O$_{39}$)$_2$·xH$_2$O (b) as polycrystalline powders. Energies of the two manifolds $^5D_0 \rightarrow {}^7F_J$ and $^5D_1 \rightarrow {}^7F_J$ are indicated. The numbers at the top of each spectrum indicate the relative intensities of the region to the right

The spectra of monomer and dimer at 12 and 77 K respectively are shown in Figure 2. Some sharpening of lines occurred, but the most noticeable change is in the monomer spectrum in the $^7F_2$ region. This band system simplified considerably. It also underwent a curious sequence of intensity changes as a function of temperature between 6 and 295 K. Reproducible emission intensities were difficult to obtain experimentally, particularly when the emission was recorded from polycrystalline samples. In order to overcome this we recorded the spectrum of the monomer powder at 295, 60, and 6 K with the same sample geometry, monochromator resolution, and amplifier sensitivity using a flow cryostat [Figure (3(*a*)]. The intensities of the bands in these spectra may be compared directly. A more detailed study could now be made by using the intensity of the $^5D_0 \rightarrow {}^7F_1$ transition as an internal standard. The temperature dependences of the integrated intensities of the four major transitions in the spectrum of the monomer powder are compared in Figure 3(*b*) as a ratio with the intensity of the internal standard.

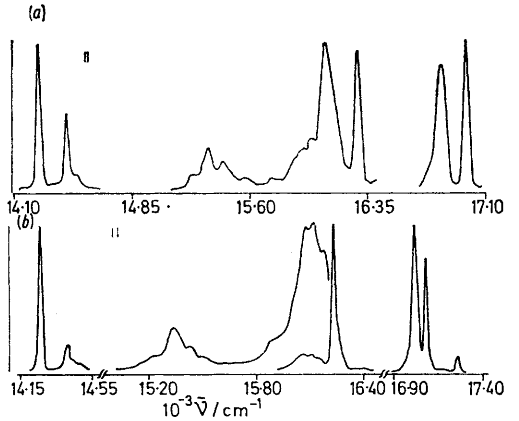

FIGURE 2 Emission spectra of the europium monomer at 12 K (*a*) and the dimer at 77 K (*b*) as powders. The regions terminating at the $^7F_5$ and $^7F_6$ levels are not shown. The spectral band-pass of the monochromator is indicated

Figure 3 shows that the intensities of transitions to $^7F_{1,3,4}$ are little affected by temperature, whereas the transition to $^7F_2$ undergoes first a decrease in intensity and then a steep increase. Since no suitable apparatus was available we were unable to measure lifetimes of emission in order to unravel the cause of this variation, although this would make an interesting study in view of recent work on the temperature dependence of multiphonon radiationless processes of lanthanoid ions in YVO$_4$, YPO$_4$, and YAsO$_4$ lattices.[6] The minimum in the curve at 77 K is difficult to account for unless there is some intensity from an underlying transition, $^5D_1 \rightarrow {}^7F_4$, contributing with a markedly different temperature dependence. Thus, although it is possible that transitions originating in the $^5D_1$ state make a contribution in some of the regions of the monomer and dimer spectra, the major peaks are unlikely to be due to them.

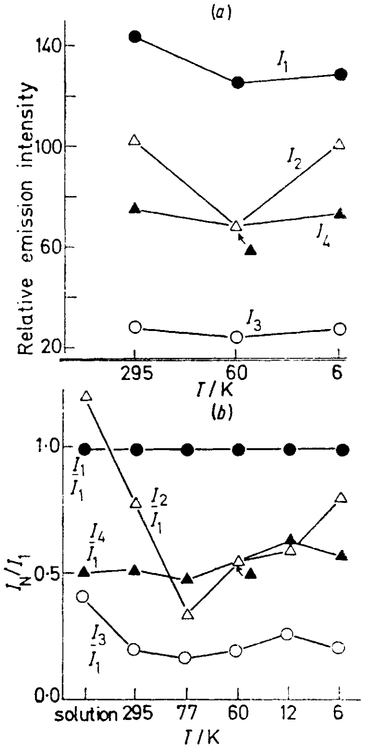

FIGURE 3(*a*) Integrated emission intensities of the four regions of the spectrum of the europium monomer as a function of temperature. I_J indicates the J value of the terminating ^7F_J level. (*b*) Ratios of the integrated intensities using the transition to $^7F_1$, which is a magnetic-dipole transition, as an internal standard

In order to assign the site symmetry of Eu^{III}, it is necessary to assume some selection rules before calculation is possible of the number of Stark components expected. Both electric-dipole and magnetic-dipole transitions have been recognised in the *f–f* spectra of lanthanoids, but there is no experimental evidence that quadrupole transitions contribute significantly to the intensity of any lines. When the lanthanoid ion sits at a centre of inversion, electric-dipole transitions are forbidden by the parity rule and will only pick up intensity through a vibronic mechanism involving *ungerade* modes.[2] An interesting analysis and assignment of vibronic electric-dipole lines of Eu^{III} in a pure O_h site in $Cs_2NaEuCl_6$ has recently appeared.[8] When the site symmetry possesses no centre of inversion then electric-dipole *f–f* transitions can gain intensity through mixing with higher lying states, possibly arising from configurations involving 5*d* electrons. The intensity of the line is controlled by this admixture of opposite parity. The majority of *f–f* transitions observed to date are due to ' forced ' electric-dipole transitions.

Allowed transitions between a $J = 0$ emitting state and the Stark components of the various ground states ($J = 0$—6)

		Terminal state					
Symmetry group	$J = 0$	1 *	2	3	4	5	6
D_{4h} Mag. $E_g + A_{2g}$ Elect. $B_u + A_{2u}$	*f*	A_{2g} E_g (2)	*f*	*f*	*f*	*f*	*f*
D_{4d} Mag. $E_3 + A_2$ Elec. $E_1 + B_1$	*f*	A_2 E_3 (2)	*f*	E_1 (1)	B_2 E_1 (2)	B_2 $2E_1$ (3)	B_2 $2E_1$ (3)
D_4 Mag. $E + A_2$ Elec. $E + A_2$	*f*	A_2 E (2)	E (1)	A_2 $2E$ (3)	A_2 $2E$ (3)	$2A_2$ $3E$ (5)	A_2 $3E$ (4)
C_{4v} Mag. $E + A_2$ Elec. $E + A_1$	A_1 (1)	E A_2 (2)	E A_1 (2)	$2E$ (2)	$2E$ $2A_1$ (4)	$3E$ A_1 (4)	$3E$ $2A_1$ (5)
D_{3d} Mag. $E_g + A_{2g}$ Elec. $E_u + A_{2u}$		A_{2g} E_g (2)	*f*	*f*	*f*	*f*	*f*
D_{3h} Mag. $E'' + A_2'$ Elec. $E' + A_2''$		E'' A_2' (2)	E' (1)	E' A_2'' (2)	$2E'$ A_2'' (3)	$2E'$ A_2'' (3)	$2E'$ A_2'' (3)
D_3 Mag. $E_1 + A_2$ Elec. $E_1 + A_2$	*f*	E A_2 (2)	$2E$ (2)	$2A_2$ $2E$ (4)	A_2 $3E$ (4)	$2A_2$ $4E$ (6)	$2A_2$ $4E$ (6)
C_{3h} Mag. $E'' + A'$ Elec. $E' + A''$	*f*	A' E'' (2)	E' (1)	E' $2A''$ (3)	$2A''$ $2E'$ (4)	$2A''$ $2E'$ (4)	$2A''$ $2E'$ (4)
D_{2d} Mag. $E + A_2$ Elec. $E + B_2$	*f*	E A_2 (2)	E B_2 (2)	$2E$ B_2 (3)	$2E$ B_2 (3)	$3E$ B_2 (4)	$3E$ $2B_2$ (5)

* The selection rules in this column are derived using the transformation properties of the magnetic (mag.) dipole operators on the assumption that the intensity of this transition is pure magnetic dipole. All other columns were derived using the representations of the electric (elec.) dipole operator.

In spectra of Eu^{III} the $^5D_0 \rightarrow {}^7F_1$ transition is magnetic-dipole allowed under all point groups. When a centre of inversion is present its intensity is much greater than that of vibronic electric-dipole transitions. This is nicely illustrated in the spectra of Eu^{III} in $Cs_2NaEuCl_6$ [8] and in Ba_2GdNbO_6,[9] which has the ordered perovskite structure. On lowering the symmetry successively, the intensities of the forced electric-dipole transitions rise. Indeed, it has been suggested that the ratio of the intensities of the $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions can be used as a qualitative indication of an inversion centre.[1] In the monomer spectrum the magnetic-dipole lines, $^5D_0 \rightarrow {}^7F_1$, are the most intense but the forced electric-dipole transitions have comparable intensity suggesting that no centre of inversion is present. In the dimer, on the other hand, the magnetic-dipole transition is appreciably weaker suggesting a lower symmetry. But in both cases the $^7F_1$ state is split into only two components, presumably a doubly degenerate and a non-degenerate state. Thus the site symmetry must contain at least a three-fold axis of symmetry, the axis being either a rotation or alternation axis. The intensity of the $^5D_0 \rightarrow {}^7F_0$ band is also a useful indicator as Blasse and his co-workers have pointed out.[1] It becomes allowed as a forced electric-dipole process only under groups C_s, C_n, and C_{nv}. It is too weak in both the spectra of the monomer and the dimer to allow assignment to any of these point groups.

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[8] R. W. Schwartz, *Mol. Phys.*, 1975, **30**, 81.

[9] G. Blasse, A. Bril, and W. C. Nieuwport, *J. Phys. and Chem. Solids*, 1966, **27**, 1587.

These arguments considerably reduce the number of point groups which must be considered. We can now compare the number of bands observed with those predicted in each region. The Table gives the number of allowed transitions expected for different possible point groups. For the monomer spectrum, point groups D_{2d} and D_3 give reasonable fits. It is necessary to bear in mind that an exact match is not to be expected as accidental degeneracies can occur or some lines may be vibronic side bands. If the four bands in the $^5D_0 \rightarrow {}^7F_3$ region are taken to be four Stark components then D_3 is the only point group to fit the $^7F_{0-3}$ regions. The regions of $^7F_5$ and $^7F_6$ show, at room temperature, six and three bands respectively. Neither of these point groups predicts precisely this number of Stark components although D_3 should give six under $^7F_5$. Thus we are unable to decide positively between D_{2d} and D_3, although D_3 gives the slightly better match to the experimental result.

Since this work was completed a crystal-structure analysis has appeared of the salt $Na_6Ce^{IV}W_{10}O_{35+x}H_{2x}\cdot(31-x)H_2O$ which turns out to contain the ion $[Ce^{IV}W_{10}O_{36}H_2]^{6-}$.[10] It is thought to have a very similar structure to the lanthanoid(III) complexes. The analytical compositions of the complexes are similar and their powder patterns resemble one another. In the structure determined the Ce^{IV} is bound between two W_5O_{18} units so that there are eight oxygen atoms surrounding the Ce^{IV}, defining a square antiprism. There is apparently no room for additional co-ordination of water molecules by the cerium ion. Thus the point group of this ion is D_{4d} in the absence of crystal forces. The point symmetry of the anion in the crystal is only C_2.

Inspection of the Table shows that the selection rules for the point group D_{4d} give a poor fit to the experimental emission spectrum of the europium(III) complex. The transition to the level $J = 2$ is predicted to be forbidden, although reasonably intense bands were observed in this region. Similarly in the $J = 3$ region, only one band is expected if the point group is D_{4d}, but several components were observed. Thus it seems clear that the effective point group of the europium(III) ion is not D_{4d}, neither is it as low as C_2. It is possible that the anion retains the essential features of the cerium(IV) analogue but that crystal packing has reduced the effective point group to D_{2d}.

The striking feature of the dimer spectrum is the intense single line in the $^5D_0 \rightarrow {}^7F_2$ region. This restricts the point groups to D_4 or possibly D_{3h}. It is not possible to decide between them as the other regions of the spectrum are complex. The complexity of the regions of $^7F_{5,6}$ suggests D_4 rather than D_{3h}, as the former predicts a larger number of Stark components. This is the group preferred by Peacock and Weakley.[5] They suggest co-ordination by four oxygen atoms from each of the two tungstosilicate groups, leading to a cubic co-ordination of eight oxygen atoms.

Aqueous solutions. At neutral pH both clusters remained intact in aqueous solution. Even in solution the bright orange-red emission of the europium ion can be pumped efficiently *via* the tungstate absorption bands. On adding a drop of acid to lower the pH the emission faded as the complex is broken up under hydrolysis. The spectra of aqueous solutions of the dimer and monomer are shown in Figure 4(*a*) and (*b*). In both cases the most obvious change is the increase in the intensity of the $^5D_0 \rightarrow {}^7F_0$ transition and its splitting into components under high resolution. In the monomer spectrum at least three components were plainly visible, whereas two were evident for the dimer. Since neither the ground nor excited states can be split to any order by a crystalline field, the source of this splitting must be due either to the development of vibronic side bands or to the presence of a number of distinct species in solution. It is difficult to understand why one or two quanta of a low-frequency vibration should appear in the solution spectra but not in the previously discussed crystal spectra. Therefore we discard the possibility of vibronic structure. Presumably a number of different species arise in solution by solvation. This is supported by the increase in intensity of the $^5D_0 \rightarrow {}^7F_0$ transition which must be due to a lowering of symmetry possibly by solvation. It is curious that if several species are present in solution why all the bands do not appear as multiples. Admittedly the $^5D_0 \rightarrow {}^7F_0$ band is very sharp and the splitting is therefore evident, whereas the other band systems have become rather broad in solution and possibly mask multiplets.

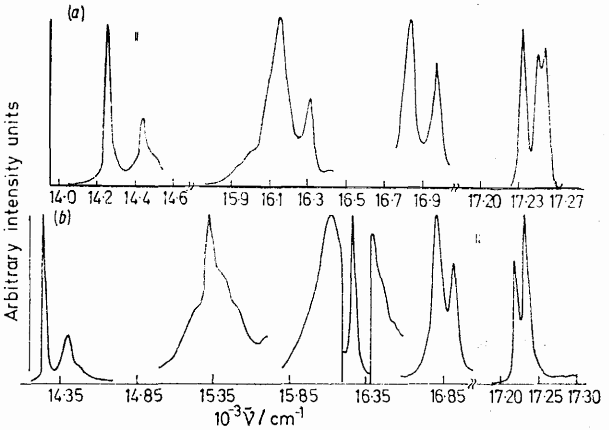

FIGURE 4 Emission spectrum of the europium monomer (*a*) and dimer (*b*) in aqueous solution at room temperature. The $^5D_0 \rightarrow {}^7F_0$ transition is between 17 200 and 17 300 cm^{-1}

Samelson *et al.*[3] also used the appearance of two lines in this region to show the existence of a tris- and a tetrakis-(β-diketone) chelate complex of Eu^{III} in solution. They were able to extract the spectrum due to the pure tetrakis complex, to calculate its dissociation constant, and to assign its symmetry point group.

It is clear from a comparison of Figures 2 and 4 that neither the monomer nor the dimer have changed geometry drastically on dissolution in water.

[10] J. Iball, J. N. Low, and T. J. R. Weakley, *J.C.S. Dalton*, 1974, 2021.

Polytungstate Chelate Monomer Complexes of Praseodymium, Neodymium, and Holmium.—We have seen above how the emission intensity of the europium(III) chelates was enhanced by excitation between 280 and 350 nm, absorption taking place into the polytungstate excited states followed by energy transfer to the rare-earth ion. In order to investigate how general this phenomenon was, we studied the emission from the chelate complexes of Pr^{3+}, Nd^{3+}, and Ho^{3+}(M) as $Na_7MW_{10}O_{35}$. We also attempted to apply the analysis developed for the europium complexes in order to assign the spectrum and to determine the local microsymmetry around these lanthanoid ions. It has been suggested [3] that the symmetry of the rare-earth ion site does not change greatly between each lanthanoid ion and we might expect, therefore, that the symmetry around Eu^{3+}, Pr^{3+}, Nd^{3+}, and Ho^{3+} will be the same.

Optical pumping, with a xenon-arc monochromator combination, between 280 and 350 nm did not produce any emission from these three complexes. In the case of Pr^{3+} the energy-level scheme of Dieke [2] shows no states between $^3P_2$ at *ca.* 22 000 cm^{-1} and the $^1S_0$ state at >40 000 cm^{-1}. Hence energy transfer from the polytungstate levels is not expected. Both Nd^{3+} and Ho^{3+} have a large number of *f* states overlapping the polytungstate spectrum so it is curious that no emission could be detected. Possibly, energy transfer takes place with efficient level by-passing, leading to deactivation of the excited states of the rare-earth ions. The emission was excited directly into the *f* states using the 488-nm line of the Ar–Kr laser in the case of the complexes of Pr^{3+} and Ho^{3+}, but no emission could be detected from the neodymium(III) complex.

Emission from the Praseodymium(III) *Monomer Complex.*—Spectra were recorded for both solution and powder samples using excitation with the 488-nm line of the Ar–Kr laser. It was not possible to record bands in regions other than 15 500—17 000 cm^{-1} with the solution sample as the intensity was too low with a resolution of less than 10 cm^{-1}. The electronic configuration of Pr^{3+} is $4f^2$ giving the ground state $^3H_4$. Three regions of emission were observed following excitation by the laser line, with baricentres of 14 500, 16 610, and 18 800 cm^{-1}. Dieke [2] and Sayre *et al.*[11] established the order and approximate energies of the lowest states. From Peacock's diffuse-reflectance spectrum [12] the energies of the first three excited states can be calculated; these are assigned as $^1D_2$ at 16 700 cm^{-1}, $^3P_0$ at 20 390 cm^{-1}, and $^3P_1$ at *ca.* 21 100 cm^{-1}. The only states that can be populated by 488-nm (20 500-cm^{-1}) excitation are $^3P_0$ and possibly, through radiationless transitions, $^1D_2$. The $^3P_1$ state, which is *ca.* 500 cm^{-1} above $^3P_0$, can also be populated thermally at sufficiently high temperatures.

The room temperature spectrum of the powder is shown in Figure 5. The three regions of the spectrum were originally assigned as: (*a*) (13 500—14 600 cm^{-1}), $^3P_0 \rightarrow {}^3F_4$ and $^3F_3$; (*b*) (15 400—17 100 cm^{-1}), $^3P_0 \rightarrow {}^3F_2$ and $^3H_6$; and (*c*) (17 600—19 000 cm^{-1}), $^3P_0 \rightarrow {}^3H_5$. The highest-energy $^3P_0 \rightarrow {}^3H_4$ transition was not detected. The temperature dependence of the powder emission was measured over the range 100—300 K. Figure 6 shows the results for the (*c*) region of the spectrum. The intense line at 18 830 cm^{-1} disappeared on cooling to 100 K. On warming the line reappeared. This is undoubtedly emission originating in the $^3P_1$ state. It has recently been shown that, in Pr^{3+} (1%) in $LaCl_3$, strong fluorescence from $^3P_1$ is obtained when pumping $^3P_0$ despite the fact that it lies 591 cm^{-1} above $^3P_0$ in this crystal. The intensity quotient, $^3P_1/^3P_0$, decreased with temperature and an Arrhenius plot was obtained which showed that a thermally activated process gives rise to the $^3P_1$ emission.[13] The difference in energy between the temperature-dependent line, at 18 830 cm^{-1}, and the nearest temperature-independent line, at 18 240 cm^{-1},

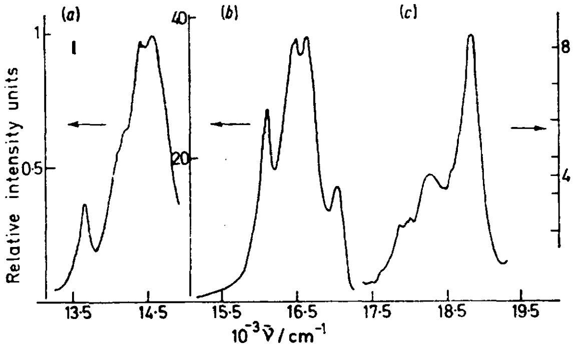

FIGURE 5 Emission spectrum of powdered $Na_7PrW_{10}O_{35} \cdot xH_2O$ at room temperature

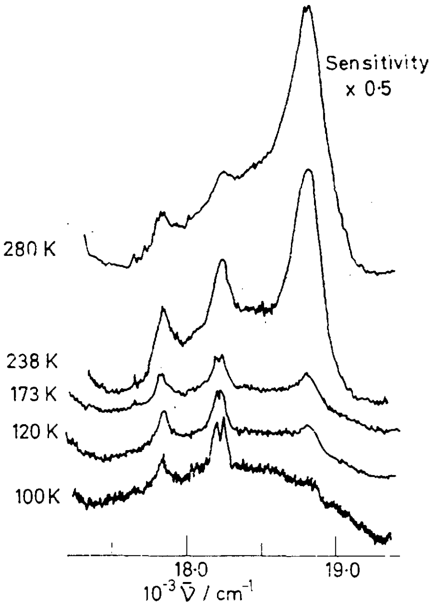

FIGURE 6 Emission spectrum of the (*c*) region of powdered $Na_7PrW_{10}O_{35} \cdot xH_2O$ at 280, 238, 173, 120, and 100 K

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[12] R. D. Peacock, Ph.D. Thesis, University of Dundee, 1970.

[13] K. R. German and A. Kiel, *Phys. Rev.*, 1973, **B8**, 1846.

is 590 cm^{-1}, in excellent agreement with the energy separation of $^3P_1$ and $^3P_0$ in LaCl$_3$.

Curiously, no other regions of the spectrum contain temperature-dependent lines originating from $^3P_1$. Possibly this is because they happen to be masked by more intense transitions from $^3P_0$. Locating the $^3P_1$ origin at 21 066.4 cm^{-1}, then transitions to $^3F_2$ and $^3H_6$ are expected at *ca.* 16 100 and 16 800 cm^{-1}. Both must therefore lie under the intense (*b*) region. One further curiosity was noted in the emission spectrum. Our original spectra contained a sharp line at 15 413 cm^{-1}, but this was present only after laser irradiation at high power of the sample had taken place. The change was not reversible. Clearly some photoinduced change had occurred, possibly the removal of water vapour by laser heating. The line is not present in the solution spectrum of the praseodymium(III) monomer (Figure 7).

As all the lines at 100 K originate from a $J = 0$ state, namely $^3P_0$, the selection rules derived to interpret the spectra of Eu^{III} are applicable to the praseodymium spectrum (Table). Figure 8 shows the (*b*) region at 50 K under high resolution. However, the overlapping of transitions to $^3F_2$ and $^3H_6$ in this region does not allow an unambiguous assignment of a point group. It is certainly consistent with both D_{2d} and D_3, the point groups suggested for the monomer on the basis of the europium(III) spectrum. Without rigorous assignment criteria it is not possible to carry the analysis further.

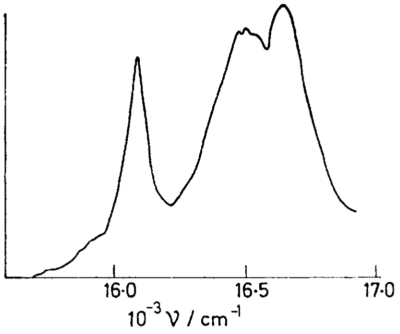

FIGURE 7 Emission spectrum of an aqueous solution of Na$_7$-PrW$_{10}$O$_{35}$·xH$_2$O at room temperature

Conclusions.—Clearly the high-resolution emission spectrum of lanthanoid ions, especially Eu^{III}, are valuable in assigning point groups to a surrounding field of ligands. Most uncertainty arises from the assignment problem and an inability to distinguish pure electronic lines from vibrational side bands. A technique such as magnetic circular-dichroism spectroscopy could be invaluable in this task. In view of the increasing use of lanthanoid ions as probes of geometry, especially in n.m.r. experiments, it would be of great interest to see studies of a wider range of compounds and the assignments of individual lines within a Stark manifold put on a more secure basis.

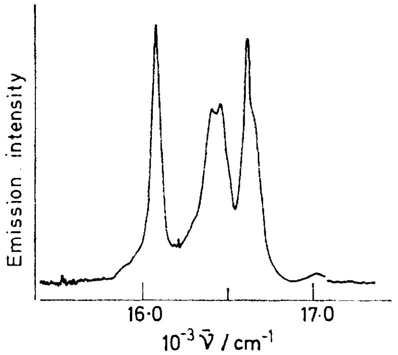

FIGURE 8 The (*b*) region of the emission spectrum of polycrystalline Na$_7$PrW$_{10}$O$_{35}$·xH$_2$O at 100 K

In the case of the present complexes, the most interesting feature was the intense emission obtainable from a solution of the europium complexes on pumping in the polytungstate absorption bands. The potential of these materials as liquid lasers should certainly be investigated, as should the possibility of using them as stains of biological material for fluorescence microscopy.

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