

Europium complexes with organic ligands containing oxygen as donor atom. Calculation of crystal-field and scalar strength parameters for C_{3v} , D_3 and D_{3d} symmetries

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ABBREVIATIONS

MeCN	acetonitrile
BCO ₆	bicapped octahedral
BCTP	bicapped trigonal prism
dmp	2,2-dimethoxypropane
DMA	<i>N,N</i> -dimethylacetamide
DDPA	<i>N,N</i> -dimethyl-diphenylphosphinamide
DMSO	dimethylsulphoxide
DPPA	diphenylphosphinamide
DTMSO	1,4-dithiane monosulphoxide
HMPA	hexamethylphosphoramide

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IR	infrared
MCO _h	monocapped octahedral
MCTP	monocapped trigonal prism
PhNO ₂	nitrobenzene
MeNO ₂	nitromethane
O _h	octahedral
2-picNO	2-picoline- <i>N</i> -oxide
3-picNO	3-picoline- <i>N</i> -oxide
4-picNO	4-picoline- <i>N</i> -oxide
pyzNO	pyrazine- <i>N</i> -oxide
pyO	pyridine- <i>N</i> -oxide
TeCTP	tetracapped trigonal prism
TMSO	tetramethylene sulphoxide
TMU	tetramethylurea
TSO	thioxane oxide
TCTP	tricapped trigonal prism
teof	triethyl orthoformate
TAP	trigonal antiprism
TP	trigonal prism

A. INTRODUCTION

Lanthanide coordination compounds containing oxygen donor organic ligands have been studied for about 30 years in our laboratories at the University of São Paulo. A large number of ligands has been used in reactions with salts containing different inorganic and organic counter anions, with low coordination ability and with coordinating properties. The scope of the study is to contribute to the coordination chemistry of this series of elements, taking into account the synthesis, characterization and properties of the complexes in order to detect the nature and mode of bonding of the ligands, coordination or not of the anions and mode of coordination when pertinent and the most frequent coordination numbers. Spectroscopic properties and parameters, thermoanalytical behaviour and structural aspects have also been explored.

Only europium(III) complexes in the trigonal symmetries (C_{3v} , D_3 , D_{3d}) synthesized in our laboratories are included. In all cases, the study is based on the emission spectrum at 77 K of the complexes in the visible region, using solid samples. The $^5D_0 \rightarrow ^7F_{0,1,2}$ transitions were explored to suggest symmetries and to determine the energies of the different levels in order to calculate the crystal-field and scalar strength parameters and to try to correlate energies and parameters. Crystal-field calculations using the tensor operator technique [1], operator equivalent [2–6] and Wigner coefficients [7] methods were made. The scalar parameters, N , [8] and S [9–13] were determined. The calculations involved 47 compounds.

Before starting the spectroscopic studies, a few items devoted to the description of the synthesis, conductance data, and IR spectra of the complexes will be included. The two latter items, together with the europium spectral study, are important for the conclusions concerning attribution of symmetry of the species.

B. SYNTHESIS, CONDUCTANCE DATA, IR SPECTRA, SYMMETRIES AND GEOMETRIES OF THE COMPLEXES

Table 1 contains a summary of data concerning the synthesis and properties of the europium complexes. It is organized in alphabetical order of the ligands and in chronological date of publication in each ligand. Preparation procedures were performed using the respective hydrated salts, except for some methanesulphonates where the anhydrous salt was used. In the case of recently prepared hexafluorophosphates, a concentrated aqueous solution was employed. In the remaining cases organic solvents (indicated in Table 1) or the ligand were employed as reaction medium. Triethyl orthoformate and 2,2-dimethoxypropane were used as dehydrating agents and/or as precipitating agents.

Conductance measurements were performed at 25°C, generally using millimolar solutions in the solvents nitromethane and acetonitrile, but in some cases methanol or nitrobenzene were employed. The existence of ion pairs was detected in some cases.

IR spectra, using Nujol mulls between KBr plates for the complexes or films of the liquid ligands, were recorded in order to detect the coordination modes of the ligands and/or anions. Shifts of the $\nu_X \rightarrow 0$ ($X = C, N, P, S$) to lower frequencies in relation to the free ligand were found, indicating coordination through the oxygen. Table 1 contains only the frequencies attributed to the anions.

The apparent coordination numbers, symmetries and geometries were attributed on the basis of all the data obtained, but also considering the emission spectra of the compounds.

The microcrystalline nature and the hygroscopy of the majority of the complexes prepared are responsible for the lack of structural studies and for the necessity of using indirect methods for the attributions made.

Considerations about the essentially ionic nature of the bonds between Ln^{3+} and ligands were obtained from the neodymium absorption spectra (not included in this review), based on the parameters: nephelauxetic (β), covalent factors ($b^{1/2}$) [14] and Sinha's parameter (δ) [15].

C. CRYSTAL-FIELD CALCULATIONS

An important characteristic of the lanthanide elements is the small spatial extension of the 4f shell. Thus, even in the compounds, the 4f electrons, which belong to inner orbitals, are shielded from ligand interactions by the closed 5s 5p external

TABLE 1

Synthesis and properties of the europium complexes

Complex	Solvent	Conductance	IR (anion) (cm ⁻¹)	CN (app.)	Sym.	Geom.	Ref.
1 Eu(ClO ₄) ₃ · 7DMA	DMA	—	$\nu_3 = 1100$, $\nu_4 = 740$	7	C_{3v}	MCTP	16,23
2 Eu(NO ₃) ₃ · 3DMA	DMA	Non-electrolyte (MeNO ₂)	$\nu_4 = 1455$, $\nu_1 = 1300$, $\nu_2 = 1032$, $\nu_6 = 817$, $\nu_3 = 737$	9	C_{3v}	MCTP	17,23
3 Eu(CH ₃ COO) ₃ · DMA	DMA	—	—	7	D_3	TP	18,23
4 EuCl ₃ · 3.5DMA	DMA	Non-electrolyte (MeNO ₂)	—	7	D_3 (dimeric)	TP	19,23
5 Eu(NCS) ₃ · 4DMA	DMA	Non-electrolyte	$\nu_{C\equiv N} = 2070$, $\nu_{CS} = 750$	7	C_{3v}	MCTP	20,23
6 Eu(PF ₆) ₃ · 7DMA	H ₂ O, teof	1:3 (MeNO ₂ , MeCN)	$\nu_3 = 835$, $\nu_4 = 558$	7	C_{3v}	MCTP	21,23
7 EuI ₃ · 6DMA · 4H ₂ O	Acetone, teof of dmp	1:3 (MeCN)	—	10	C_{3v}	TP	22,23
8 Eu(F ₃ C-SO ₃) ₃ · 7.5DMSO	teof	1:2 (ion pairs) (MeCN, MeNO ₂) (Methanol)	$\nu_{as}SO_3 = 1260$, $\nu_sSO_3 = 1025$	8	D_{3d}	—	24
9 Eu(NCS) ₃ · 4DDPA	Ethanol	Non-electrolyte (MeNO ₂ , MeCN)	$\nu_{C\equiv N} = 2065$, 2058 $\delta_{NCS} = 495$	7	C_{3v}	MCTP or MCO _h	25,26
10 EuCl ₃ · 4DPPA	Ethanol	—	—	7	C_{3v}	MCO _h	27,29,30
11 EuBr ₃ · 5DPPA	teof	1:1 (MeCN, MeNO ₂) 1:2 (Methanol)	—	8	C_{3v}	BCTP	28,29,30
12 Eu(F ₃ C-SO ₃) ₃ · 5DPPA	Acetone, teof, dmp	1:1 (MeNO ₂) 1:2 (MeCN)	$\nu_{as}SO_3 =$ several bands $\nu_sSO_3 = 1032$, 1020	6	C_{3v} (distorted)	TAP	31
13 EuCl ₃ · 3DPPM	Ethanol, dmp	Non-electrolyte (MeNO ₂)	—	6	C_{3v}	O _h	32,33

14	$\text{EuBr}_3 \cdot 3\text{DPPM}$	teof	Non-electrolyte (MeNO_2 , MeCN)	–	6	C_{3v}	TP or O_h	32,33
15	$\text{Eu}(\text{PF}_6)_3 \cdot 7.5\text{DTMSO}$	Ethanol	1:3 (MeNO_2 , MeCN)	$\nu_3 = 832$, $\nu_4 = 506$	8	D_{3d}	BCO_h (dimeric)	34
16	$\text{Eu}(\text{H}_3\text{C}-\text{SO}_3)_3 \cdot 2\text{HMPA}$	dmp	Non-electrolyte (methanol)	$\nu_{\text{as}} \text{SO}_3 = 1265, 1245, 1230$ $\nu_s \text{SO}_3 = 1160, 1120, 1110$	8	C_{3v}	BCTP	35
17	$\text{Eu}(\text{ClO}_4)_3 \cdot 7(2\text{-picNO}) \cdot 3\text{H}_2\text{O}$	<i>n</i> -Butanol	1:3 (MeNO_2 , MeCN)	$\nu_3 = 1093$, $\nu_4 = 625$	7	C_{3v}	MCTP	36,39
18	$\text{EuCl}_3 \cdot 3(2\text{-picNO}) \cdot 2\text{H}_2\text{O}$	Ethanol, teof	1:1 (methanol)	–	8	C_{3v}	BCTP	37,39
19	$\text{Eu}(\text{NCS})_3 \cdot 3(2\text{-picNO})$	<i>n</i> -Butanol	Non-electrolyte (MeCN)	$\nu \text{C}\equiv\text{N} = 2040$, $\delta \text{NCS} = 470$	6	C_{3v}	TP	38,39
20	$\text{Eu}(\text{NCS})_3 \cdot 4(2\text{-picNO})$	<i>n</i> -Butanol	Non-electrolyte (MeCN)	$\nu \text{C}\equiv\text{N} = 2040$, $\delta \text{NCS} = 470$	7	C_{3v}	MCTP	38,39
21	$\text{Eu}(\text{ReO}_4)_3 \cdot 5(2\text{-picNO})$	<i>n</i> -Butanol	–	$\nu_3 = 910, 870$, $\nu_4 = 290$	8	C_{3v}	BCTP	40
22	$\text{Eu}(\text{ReO}_4)_3 \cdot 3(2\text{-picNO})$	MeCN	–	$\nu_3 = 897, 860$, $\nu_4 = 290$	6	C_{3v}	TP	40
23	$\text{Eu}(\text{H}_3\text{C}-\text{SO}_3)_3 \cdot 2(3\text{-picNO})$	Acetone, teof or dmp	Non-electrolyte (Methanol)	$\nu_{\text{as}} \text{SO}_3 = \text{several bands}$ $\nu_s \text{SO}_3 = \text{several bands}$	8	C_{3v}	BCTP	41
24	$\text{Eu}(\text{NCS})_3 \cdot 3.5(3\text{-picNO})$	teof	Non-electrolyte (MeNO_2 , MeCN)	$\nu \text{CN} = 2040$, $\nu \text{CS} = 798$, $\delta \text{NCS} = 480$	–	C_{3v}	–	42
25	$\text{Eu}(\text{NCS})_3 \cdot 3.5(4\text{-picNO})$	teof	Non-electrolyte (MeNO_2)	$\nu \text{C}\equiv\text{N} = 2060$, $\delta \text{NCS} = 470$	–	C_{3v}	–	43
26	$\text{Eu}(\text{H}_3\text{C}-\text{SO}_3)_3 \cdot 2(4\text{-picNO})$	Methanol, teof	Non-electrolyte (methanol)	$\nu_{\text{as}} = \text{several bands}$ $\nu_s = 1052$	8	C_{3v}	–	44
27	$\text{Eu}(\text{ClO}_4)_3 \cdot 8\text{pyzNO}$	Ethanol, dmp	1:3 (MeCN) 1:2 (MeNO_2) (ion pairs)	$\nu_3 = 1088$, $\nu_4 = 618$	8	D_{3d}	BCO_h	45,48
28	$\text{Eu}(\text{PF}_6)_3 \cdot 8\text{pyzNO}$	Water, ethanol, teof	1:3 (MeCN) (MeNO_2)	$\nu_3 = 825$, $\nu_4 = 560$	8	D_{3d}	BCO_h	46,48

TABLE I (continued)

Complex	Solvent	Conductance	IR (anion) (cm ⁻¹)	CN (app.)	Sym.	Geom.	Ref.
29 Eu(NCS) ₃ · 4pyzNO	teof	Non-electrolyte (MeCN)	$\nu_{\text{C}\equiv\text{N}} = 2035$, $\delta_{\text{NCS}} = 475$	7	C _{3v}	MCIP	47,48
30 Eu(F ₃ C-SO ₃) ₃ · 6pyzNO · 3H ₂ O	teof	1:2 (MeCN) {ion pairs}	$\nu_{\text{as}}\text{SO}_3 = 1259$ $\nu_{\text{s}}\text{SO}_3 = 1033$	9	C _{3v}	TCTP	49
31 Eu(H ₃ C-SO ₃) ₃ · 2pyO	Methanol, teof	Non-electrolyte {methanol}	$\nu_{\text{as}}\text{SO}_3$ = several bands $\nu_{\text{s}}\text{SO}_3 = 1066, 1059$	8	C _{3v}	-	50
32 Eu(ClO ₄) ₃ · 8TMSO	Ethanol	1:3 (MeNO ₂)	$\nu_3 = 1083$, $\nu_4 = 621$	8	D _{3d}	BCO _h	51,59
33 Eu(NCS) ₃ · 4TMSO	n-Butanol	Non-electrolyte (MeNO ₂)	$\nu_{\text{C}\equiv\text{N}} = 2041$, $\delta_{\text{NCS}} = 481, 475$	7	C _{3v}	MCIP	52,59
34 EuCl ₃ · 3TMSO	Ethanol, teof	Non-electrolyte (MeCN)	-	6	C _{3v}	TP	53,59
35 Eu(PF ₆) ₃ · 7.5TMSO	Water, teof	1:3 (MeNO ₂ , MeCN)	$\nu_3 = 983$, $\nu_4 = 560$	8	D _{3d}	BCO _h (dimeric)	54,59
36 EuBr ₃ · 7TMSO	dmp	1:1 (MeNO ₂) 1:2 (methanol)	-	8	D _{3d}	BCO _h	55,59
37 Eu(ReO ₄) ₃ · 7.5TMSO	Methanol	1:1 (MeNO ₂ , MeCN) {ion pairs}	$\nu_3 = 980$	8	D _{3d}	BCO _h (dimeric)	56
38 EuI ₃ · 7.5TMSO	Acetone	1:3 (MeNO ₂ , MeCN)	-	8	D _{3d}	BCO _h (dimeric)	57
39 Eu(F ₃ C-SO ₃) ₃ · 7.5TMSO	teof	1:2 (MeNO ₂ , MeCN) {ion pairs}	$\nu_{\text{as}}\text{SO}_3 = 1275$, $\nu_{\text{s}}\text{SO}_3 = 1030$	8	D _{3d}	BCO _h (dimeric)	58
40 EuCl ₃ · 3TMU	TMU	Non-electrolyte (MeNO ₂)	-	6	D ₃	-	60,62

41	$\text{Eu}(\text{NCS})_3 \cdot 3.5\text{TMU}$	TMU	Non-electrolyte (MeNO_2 , PhNO_2) $\delta\text{NCS} = 482$	$\nu\text{C}\equiv\text{N} = 2070$, 2040	-	C_{3v}	-	61,62
42	$\text{EuCl}_3 \cdot 4.5\text{TSO}$	Ethanol	1:1 (methanol)	-	8	C_{3v}	BCTP	63,68
43	$\text{Eu}(\text{NCS})_3 \cdot 5\text{TSO}$	Ethanol	Non-electrolyte (MeNO_2)	$\nu\text{C}\equiv\text{N} = 2060$, 2030 $\nu\text{CS} = 764$, $\delta\text{NCS} = 469$	8	C_{3v}	BCTP	64,68
44	$\text{Eu}(\text{ClO}_4)_3 \cdot 7.5\text{TSO}$	Ethanol	1:2 (MeNO_2) (ion pairs)	$\nu_3 = 1087$, $\nu_4 = 619$	8	D_{3d}	BCO_h (dimeric)	65,68
45	$\text{Eu}(\text{PF}_6)_3 \cdot 7.5\text{TSO}$	Ethanol	1:3 (MeNO_2 , MeCN)	$\nu_3 = 836$, $\nu_4 = 558$	8	D_{3d}	BCO_h (dimeric)	66,68
46	$\text{EuI}_3 \cdot 7.5\text{TSO}$	Acetone	1:2 (MeCN , methanol) 1:1 (MeNO_2) (ion pairs)	-	8	D_{3d}	BCO_h (dimeric)	67,68
47	$\text{Eu}(\text{F}_3\text{C-SO}_3)_3 \cdot 7.5\text{TSO}$	teof	1:1 (MeNO_2) (ion pairs)	$\nu_{\text{as}} \text{SO}_3 = 1240$, $\nu_{\text{s}} \text{SO}_3 = 1028$	8	D_{3d}	BCO_h (dimeric)	69

orbitals. In particular, the spectra of the compound containing 4f electrons in the solid state retain similar atomic-like properties, which is of great help in the interpretation of their level structure. On the other hand, the small crystal-field perturbation can be used to investigate the surroundings of the ion, which then acts as a local probe.

The free ions present a field-free spherical symmetry, which is perturbed by the inhomogeneous field generated by the electrical charge distribution due to the ligands in the crystals. The crystal-field interaction partially removes the degeneracy of the free ion J states into a number of M_J levels that are dependent on the site symmetry occupied by the ion.

Knowledge of the crystal-field symmetry is very important in the interpretation of optical spectra. The crystal-field levels are, according to group theory, associated with irreducible representation (γ_{Γ_n}) belonging to the symmetry group under consideration [1,70–76].

To determine the crystal-field parameters, three methods were utilized: the tensor operator technique [77], the operator equivalent method [3] and the Wigner coefficients method [7].

(i) The tensor operator technique

A general approach considers the potential energy, $V(r)$, of an electron of a central ion, where r is the radius associated with an f electron. The environment is represented by a classical charge distribution $\rho(R)$, where R is the radius associated with a general point in that environment, then

$$V(r) = - \int \frac{e\rho(R)}{|R-r|} dr \quad (1)$$

According to the parametric approach, it is convenient to write this potential in terms of B_q^k parameters with the Wybourne formalism [1].

The sum over the i electrons may be written as

$$V_{CF} = \sum_{k,q,i} B_q^k C_q^k(\theta_i, \phi_i) \quad (2)$$

where B_q^k (s) are the crystal-field parameters (radial integrals)

$$B_q^k = -e \int (-1)^q \rho(R) C_{-q}^k(\theta, \phi) \frac{r_{<}^k}{r_{>}^{k+1}} dr \quad (3)$$

and C_q^k are tensor operators of rank k for the angular part of the crystal-field interaction [1].

The matrix elements of this crystalline potential among coupled states having

the same J values (to retain eigenvalues) are obtained using the Racah's techniques [71,74–77].

$$\begin{aligned} & \langle f^N WUSLJM_J | H_{ij} | f^N W'U'SL'J'M'_J \rangle \\ & = \sum B_q^k \langle f^N WUSLJM_J | U_q^k | f^N W'U'SL'J'M'_J \rangle \langle l \| C^k \| l' \rangle \end{aligned} \quad (4)$$

where

$$\begin{aligned} & \langle l \| C^k \| l' \rangle = (-1)^l [(2l+1)(2l'+1)]^{1/2} \begin{pmatrix} l & k & l' \\ 0 & 0 & 0 \end{pmatrix} \\ & \langle f^N WUSLJM_J | U_q^k | f^N W'U'SL'J'M'_J \rangle \\ & = (-1)^{J-M_J} \begin{pmatrix} J & k & J' \\ -M_J & q & M'_J \end{pmatrix} \cdot \langle f^N WUSLJ | U^k | f^N W'U'SL'J' \rangle \\ & \langle f^N WUSLJ | U^k | f^N W'U'SL'J' \rangle \\ & = (-1)^{S+L'+J+k} \cdot [(2J+1)(2J'+1)]^{1/2} \cdot \begin{pmatrix} J & J' & k \\ L & L & S \end{pmatrix} \\ & \cdot \langle f^N WUSL \| U^k \| f^N W'U'SL' \rangle \end{aligned} \quad (5)$$

Doubly reduced matrix elements $\langle f^N WUSL \| U^k \| f^N W'U'SL' \rangle$ can be calculated and have been tabulated by Nielson and Koster [78]. WU denotes the remaining quantum numbers required to specify the states [79–81].

$\begin{pmatrix} J & k & J' \\ -M_J & q & M'_J \end{pmatrix}$ are the 3- j symbols which have been tabulated by Rotemberg and Bivig and Landolt-Börnstein [82,83].

Table 2 lists, for each of the thirty-two point groups, the non vanishing B_q^k values.

The point groups are listed in sets, each of them having the same non-vanishing B_q^k . The groups within a set are indistinguishable insofar as the symmetry properties of H_{cf} are concerned. To distinguish groups within a set, the odd-parity part of the crystal-field interaction must be examined. Equally, the point groups within a set can be distinguished by their different electric-dipole selection rules [2] (see also ref. 91).

(ii) The operator-equivalent method

In the operator-equivalent method [2–5], the coupling of different free-ion levels by the crystal-field interaction is ignored and the crystal-field splitting of each $2S+1L_J$ level is treated separately. Traditionally, in this method, the Hamiltonian of

TABLE 2

Non-zero B_q^k parameters for the 32 point groups

Point group	Parameters B_q^k		
	$K = 2$	$K = 4$	$K = 6$
C_1 C_i	All (B_1^2 real)	All	All
C_2 C_s (C_{1h}) C_{2h}	B_0^2 , Re B_2^2	B_0^4 , B_2^4 , B_4^4	B_0^6 , B_2^6 , B_4^6 , B_6^6
D_2 C_{2v} D_{2h}	B_0^2 , Re B_4^4	B_0^4 , Re($B_2^4 B_4^4$)	B_0^6 , Re B_2^6 , Re B_4^6 , Re B_6^6
C_4 S_4 C_{4h}	B_0^2	B_0^4 , Re B_4^4	B_0^6 , B_4^6
D_4 C_{4v} D_{2d} D_{4h}	B_0^2	B_0^4 , Re B_4^4	B_0^6 , Re B_4^6
C_3 S_6 (C_{3i})	B_0^2	B_0^4 , Re B_3^4	B_0^6 , B_3^6 , B_6^6
D_3 C_{3v} D_{3d}	B_0^2	B_0^4 , Re B_3^4	B_0^6 , Re B_3^6 , Re B_6^6
C_6 , C_{3h} , C_{6h} , D_6 , C_{6v} , D_{3h} , D_{6h}	B_0^2	B_0^4	B_0^6 , Re B_6^6
T , T_d , T_h , O , O_h	—	B_0^4 , Re B_4^4	B_0^6 , Re B_4^6

the crystalline field is written as

$$H_{CF} = \sum_{k,q} A_k^q \sum_i V_k^q(r_i) \quad (6)$$

Where A_k^q are crystal-field components, and the $V_k^q(r_i)$ are polynomials in the x , y and z coordinates of the i th electron. These polynomials are tabulated for $2 \leq k \leq 6$ and $|q| \leq k$ in refs. 3 and 84.

In the operator-equivalent method, one is concerned with matrix elements of eqn. (6) within a given free-ion state denoted by $^{2S+1}L_J$. The V_k^q polynomials may

be replaced

$$\sum V_k^q(r_i) \rightarrow \theta_j^k \langle r^k \rangle O_k^q \quad (7)$$

Where θ_j^k ($=\alpha_j$ for $k=2$, β_j for $k=4$ and γ_j for $k=6$) are the operator-equivalent factors and the O_k^q are the Hermitian operator equivalents [84].

The point charge model used in this work is based on

$$B_k^q = A_k^q \langle r^k \rangle \quad (8)$$

The exact forms of the A_k^q parameters are given in ref. 85.

(iii) The Wigner coefficient method

In the Wigner coefficient method, the potential of the crystal-field is written as

$$H_{CF} = \sum_{k,q} \langle A^{2S+1} L_J \| U^k \| A^{2S+1} L_J \rangle C_{M_J q}^{J k J'} Y_k^q \langle r^k \rangle \quad (9)$$

where $\langle A^{2S+1} L_J \| U^k \| A^{2S+1} L_J \rangle$ are the reduced matrix elements of U^k , $Y_k^q \langle r^k \rangle$ are phenomenological parameters, and $C_{M_J q}^{J k J'}$ are the Wigner coefficients [7].

The crystal-field calculations for the three methods are performed by diagonalizing small matrices containing matrix elements of H_{CF} within a given $^{2S+1}L_J$ state.

The dimensions of these matrices are given by $(2J+1) \times (2J+1)$.

D. THE CRYSTAL-FIELD SCALAR STRENGTH PARAMETERS

To compare the magnitude of different crystal-field strengths, it is convenient to use a scalar crystal-field parameter [8] which is expressed as

$$N_v = \left[\sum \frac{4\pi}{(2k+1)} (B_q^k)^2 \right]^{1/2} \quad (10)$$

where N_v is a number which characterizes the crystal-field strength.

The parameter S was also used, as introduced by Leavitt et al. [9–13], and is invariant with the rotation axis.

$$S = \left\{ \frac{1}{3} \sum_k \frac{1}{(2k+1)} \left[(B_0^k)^2 + 2 \sum_{q>0} [(Re B_q^k)^2 + (Im B_q^k)^2] \right] \right\}^{1/2} \quad (11)$$

E. EUROPIUM(III) COMPLEXES WITH TRIGONAL SYMMETRIES (C_{3v} , D_3 , D_{3d})

(i) Analysis of the spectra

Strong electric dipole (ED) transitions to the 7F_2 crystal-field sublevels can be observed around 610 nm, due to the absence of an inversion centre symmetry in the europium sites (C_{3v} , D_3). The $^5D_0 \rightarrow ^7F_1$ transitions induced by magnetic dipole

(MD) interactions at ca. 595 nm have strengths equal to or even higher than those of the ED transitions of D_{3d} symmetry. The intensity of the ${}^5D_0 \rightarrow {}^7F_0$ transition is significant in all compounds with C_{3v} symmetry whereas in others it is much weaker. The transition strength depends on the contributions from the other 7F_M wavefunctions to 7F_0 . An intense ${}^5D_0 \rightarrow {}^7F_0$ transition usually indicates the presence of a strong crystal-field.

The weak ${}^5D_0 \rightarrow {}^7F_3$ transition is difficult to record. The very low intensity of this transition has recently been reported and is related to a small J -mixing effect (mixture of ${}^7F_{1,2,4}$ wavefunctions with 7F_3 leading to a mixed MD-ED character [70,86–89]. Our available spectroscopic equipment does not allow us to record this transition. For these reasons, the parameters with $k=6$ were not calculated.

Following calculations, it was realised that the diagrams used for all the compounds could be summarized in two models, which are presented in Fig. 1.

Mülliken's notation was used in the diagrams to designate the J sublevels. In

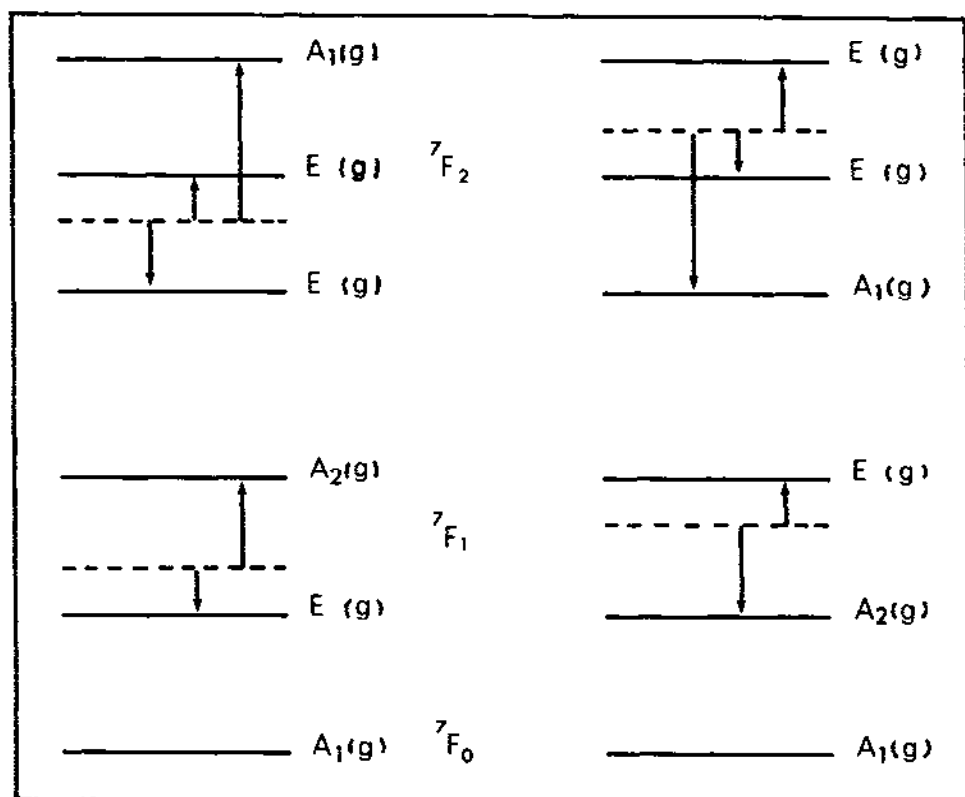


Fig. 1. Qualitative energy levels for C_{3v} , D_3 and D_{3d} symmetries.

TABLE 3

Splitting of the $^{25+1}L_J$ ($J=0-6$) levels in C_{3v} , D_3 and D_{3d} symmetries (for D_{3d} symmetry the character g has to be included in the irreducible representation) [90]

D_J	J						
	0	1	2	3	4	5	6
A_1	1	—	1	1	2	1	3
A_2	—	1	—	2	1	2	2
E	—	1	2	2	3	4	4

the case of the D_{3d} symmetry, the subscript g was used due to the existence of an inversion centre (Table 3).

(ii) Crystal-field parameter calculation for C_{3v} , D_3 and D_{3d} symmetries

The first term in the methods employed has $k=q=0$ and is spherically symmetric. This term is by far the largest and is due to the Coulombic energy of a positive ion surrounded by negative charges. It corresponds to the lattice energy. It shifts all energy levels equally and does not contribute to the crystal-field splitting [86,91]. Since we are concerned only with equivalent f electrons, $k \leq 2l \leq 6$, k has to be even, therefore $k=2, 4, 6$. The values of q are determined by the point symmetry of the $4f^N$ ion site, since the Hamiltonian must be invariant under the operations of the point symmetry group. Only the levels $^7F_{1,2}$ of europium ion were analysed, which led us to the values $k=0, 2, 4$ and $q=0, \pm 3$. Figures 2–7 present the energy diagrams and emission spectra of three europium compounds with C_{3v} , D_3 and D_{3d} symmetries.

The operator equivalent and tensorial method matrix elements can be found elsewhere [92,93]. For the Wigner coefficient method, the following is shown.

$$\begin{aligned} \text{For } J=1 \quad \langle \pm 1 | V_2^0 | \pm 1 \rangle &= -0.06308 Y_2^0 \langle r^2 \rangle \\ \langle 0 | V_2^0 | 0 \rangle &= 0.1262 Y_2^0 \langle r^2 \rangle \end{aligned} \quad (12)$$

The position of the crystalline field component for the 7F_1 manifold level of the Eu^{3+} ion is determined for second-order terms. These energy levels (eigenvalues) are obtained from the diagonalization of the 3×3 matrix (Fig. 8).

$$\begin{aligned} \text{For } J=2 \quad a &= \langle \pm 2 | V_4^0 | \pm 2 \rangle = -0.06608 Y_4^0 \langle r^2 \rangle - 0.01343 Y_4^0 \langle r^4 \rangle \\ b &= \langle \pm 1 | V_4^0 | \pm 1 \rangle = 0.03304 Y_4^0 \langle r^2 \rangle + 0.05373 Y_4^0 \langle r^4 \rangle \\ c &= \langle 0 | V_4^0 | 0 \rangle = 0.06608 Y_4^0 \langle r^2 \rangle - 0.08059 Y_4^0 \langle r^4 \rangle \\ d &= \langle \pm 2 | V_4^{\pm 3} | \mp 1 \rangle = -0.07947 Y_4^{\pm 3} \langle r^4 \rangle \end{aligned} \quad (13)$$

The fourth-order terms are obtained from analysis of the $J=2$ level splittings

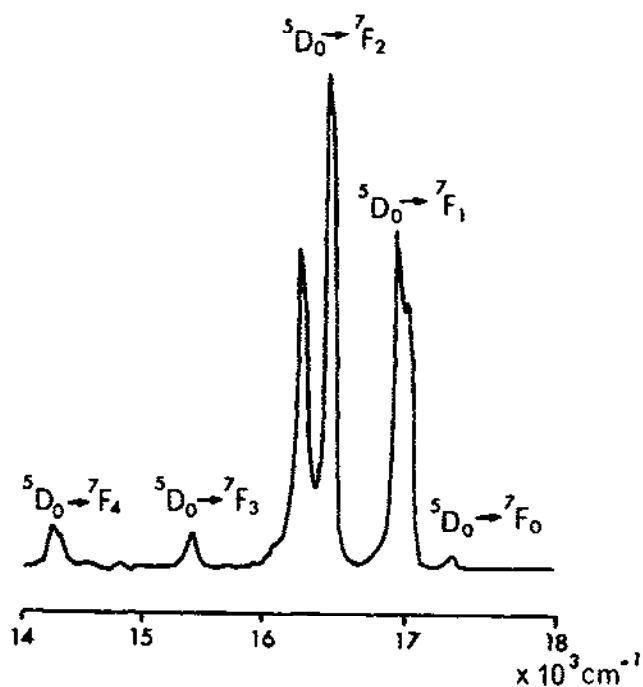


Fig. 2. Emission spectrum of the compound of formula $\text{EuCl}_3 \cdot 3\text{TMU}$ (77 K).

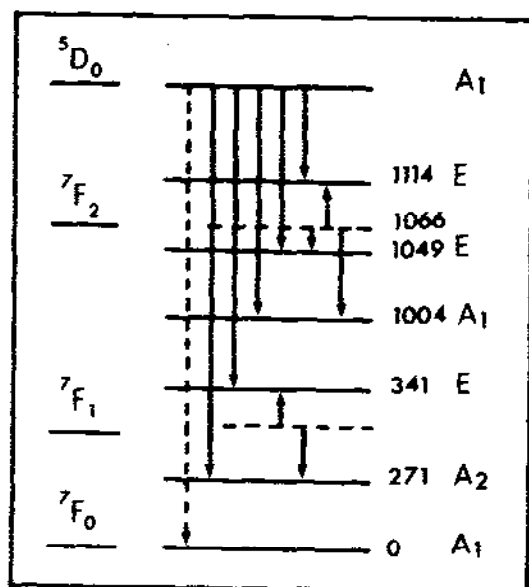


Fig. 3. Energy diagram for the compound of formula $\text{EuCl}_3 \cdot 3\text{TMU}$ (D_3 symmetry).

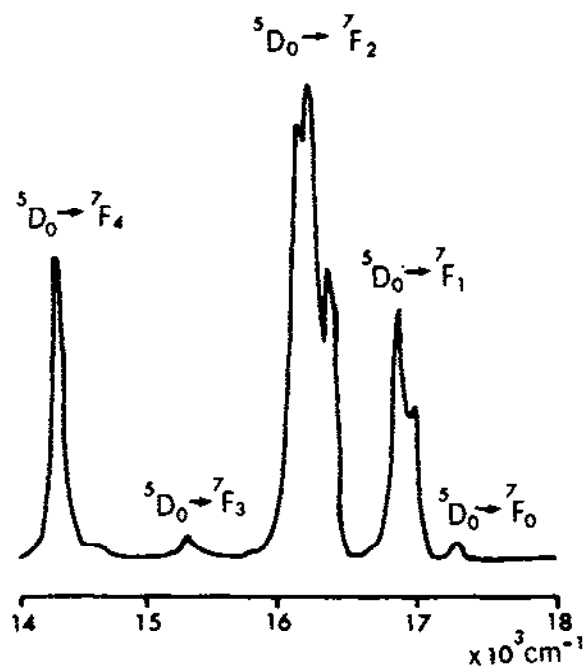


Fig. 4. Emission spectrum of the compound of formula $\text{Eu}(\text{NCS})_3 \cdot 5\text{TMU}$ (77 K).

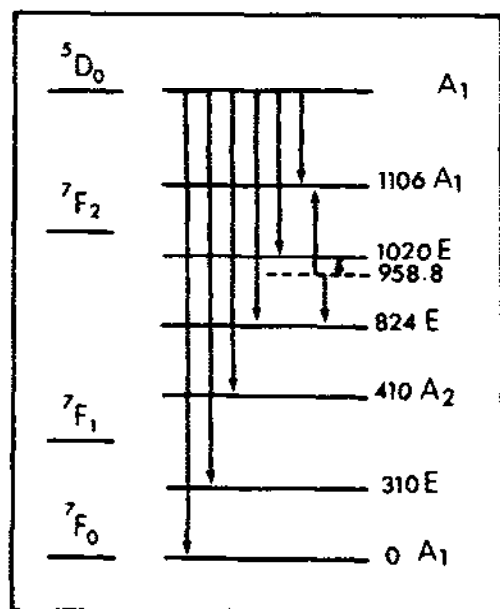


Fig. 5. Energy diagram for the compound of formula $\text{Eu}(\text{NCS})_3 \cdot 3.5\text{TMU}$ (C_{3v} symmetry).

M' \ M	1	-1	0
1	$H_{11}-E$		
-1		$H_{11}-E$	
0			$H_{00}-E$

= 0

Fig. 8. Secular determinant for the 7F_1 manifold in C_{3v} , D_3 and D_{3d} symmetries for Eu^{3+} .

M' \ M	2	-1	-2	0	1
2	$a-E$	$-d$			
-1	$-d$	$b-E$			
-2			$a-E$	0	d
0			0	$c-E$	0
1			d	0	$b-E$

= 0

Fig. 9. Secular determinant for the 7F_2 manifold in C_{3v} , D_3 and D_{3d} symmetries for Eu^{3+} .

and the eigenvalues are obtained through the diagonalization of a (5×5) matrix (Fig. 9).

After resolving the determinants and making adequate substitutions, the parameter values presented in Table 4 were found.

It is possible to obtain the parameters in the equivalent operator formalism (B_k^q) employing the correlation tables found in ref. 1 and the corrections made by Kassman [94].

TABLE 4

Crystal-field parameters for trivalent europium complexes with C_{3v} , D_3 and D_{3d} symmetries

Complex	Methods					
	Tensorial operator			Wigner coefficient		
	B_0^2	B_0^4	B_3^4	$Y_2^0 \langle r^2 \rangle$	$Y_4^0 \langle r^4 \rangle$	$Y_4^3 \langle r^4 \rangle$
<i>C_{3v} symmetry</i>						
Eu(ClO ₄) ₃ · 7DMA	-250	1229	-546	-396	1452	-646
Eu(NO ₃) ₃ · 3DMA	380	-519	-409	602	-613	-483
Eu(NCS) ₃ · 4DMA	250	-1174	-740	396	-1387	-874
Eu(PF ₆) ₃ · 7DMA	217	-1013	-703	343	-1197	-831
EuI ₃ · 6DMA · 4H ₂ O	443	-1171	-697	703	-1384	-824
Eu(NCS) ₃ · 4DDPA	233	-1373	-638	370	-1622	-754
EuCl ₃ · 4DPPA	-620	217	-369	-983	256	-436
EuBr ₃ · 5DPPA	-313	1188	-767	-497	1404	-907
Eu(F ₃ C-SO ₃) ₃ · 5DPPA	143	-1619	-833	227	-1913	-985
EuCl ₃ · 3DPPM	217	-1408	-970	343	-1664	-1146
EuBr ₃ · 3DPPM	-390	823	-948	-618	972	-1120
Eu(H ₃ C-SO ₃) ₃ · 2HMPA	-320	1042	-703	-507	1232	-831
Eu(ClO ₄) ₃ · 7(2-picNO) · 3H ₂ O	250	-880	-501	396	-1040	-592
EuCl ₃ · 3(2-picNO) · 2H ₂ O	313	-1180	-447	497	-1394	-528
Eu(NCS) ₃ · 3(2-picNO)	243	-1341	-453	386	-1584	-535
Eu(NCS) ₃ · 4(2-picNO)	227	-1481	-422	359	-1750	-499
Eu(ReO ₄) ₃ · 5(2-picNO)	-433	783	-862	-687	926	-1019
Eu(ReO ₄) ₃ · 3(2-picNO)	-417	957	-791	-661	1131	-935
<i>D_{3d} symmetry</i>						
Eu(F ₃ C-SO ₃) ₃ · 7.5DMSO	223	-772	-739	370	-913	-873
Eu(PF ₆) ₃ · 7.5DTMSO	227	-1069	-811	423	-1264	-958
Eu(ClO ₄) ₃ · 8pyzNO	143	-834	-584	227	-985	-690
Eu(PF ₆) ₃ · 8pyzNO	143	-779	-518	227	-920	-613
Eu(ClO ₄) ₃ · 7.5TMSO	287	-1558	-898	454	-1841	-1061
Eu(PF ₆) ₃ · 7.5TMSO	297	-1118	-575	470	-1322	-680
EuBr ₃ · 7TMSO	287	-1545	-702	454	-1826	-830
Eu(ReO ₄) ₃ · 7.5TMSO	237	-1193	-536	375	-1410	-634
EuI ₃ · 7.5TMSO	313	-1314	-918	497	-1553	-1085
Eu(F ₃ C-SO ₃) ₃ · 7.5TMSO	373	-1412	-475	592	-1669	-561
Eu(ClO ₄) ₃ · 7.5TSO	-327	-1296	-1007	-518	1531	-1190
Eu(PF ₆) ₃ · 7.5TSO	360	-762	-900	571	-901	-1063
EuI ₃ · 7.5TSO	407	-1316	-879	645	-1556	-1039
Eu(F ₃ C-SO ₃) ₃ · 7.5TSO	200	-1040	-458	317	-1229	541
Eu(H ₃ C-SO ₃) ₃ · 2(3-picNO)	333	-847	-402	528	-1001	-475
Eu(NCS) ₃ · 3.5(3-picNO)	143	-888	-807	227	-1049	-954
Eu(NCS) ₃ · 3.5(4-picNO)	327	-1082	-706	518	-1278	-834
Eu(H ₃ C-SO ₃) ₃ · 2(4-picNO)	363	806	-592	576	-952	-699
Eu(NCS) ₃ · 4pyzNO	-357	1019	-505	-565	1204	-596

TABLE 4 (continued)

Complex	Methods					
	Tensorial operator			Wigner coefficient		
	B_6^2	B_6^4	B_3^4	$Y_2^0 \langle r^2 \rangle$	$Y_4^0 \langle r^4 \rangle$	$Y_4^3 \langle r^4 \rangle$
$\text{Eu}(\text{F}_3\text{C}-\text{SO}_3)_3 \cdot 6\text{pyzNO} \cdot 3\text{H}_2\text{O}$	-420	827	-389	-666	978	-459
$\text{Eu}(\text{CH}_3-\text{SO}_3)_3 \cdot 2\text{pyO}$	433	-720	-588	-690	-851	-695
$\text{Eu}(\text{NCS})_3 \cdot 4\text{TMSO}$	240	-1097	-401	380	-1296	-474
$\text{EuCl}_3 \cdot 3\text{TMSO}$	213	-1093	-318	338	-1291	-376
$\text{Eu}(\text{NCS})_3 \cdot 3.5\text{TMU}$	334	-1166	-1023	529	-1377	-1208
$\text{EuCl}_3 \cdot 4.5\text{TSO}$	287	-1671	-904	454	-1068	-537
$\text{Eu}(\text{NCS})_3 \cdot 5\text{TSO}$	400	-946	-753	634	-1118	-890
<i>D₃ symmetry</i>						
$\text{Eu}(\text{H}_3\text{C}-\text{COO})_3 \cdot \text{DMA}$	-324	984	-52	-514	1163	-62
$\text{EuCl}_3 \cdot 3.5\text{DMA}$	-460	1048	-260	-729	1238	-307
$\text{EuCl}_3 \cdot 3\text{TMU}$	-233	395	-345	-369	466	-408

Using the energy equations in the determinant, one may calculate

$$E(2, -1): E^3 \underbrace{-(a+b)}_m E + \underbrace{ab-d^2}_n = 0$$

$$E(-2, 0, 1) = E^3 + \underbrace{[-(a+b+c)]}_p E^2 + \underbrace{(ab+bc+ac-d^2)}_q E + \underbrace{d^2c-abc}_r = 0 \quad (14)$$

where

$$m = -(a+b) = -(E_1 + E_2)$$

$$n = ab - d^2 = E_1 E_2$$

$$p = [-(a+b+c)] = -(E_1 + E_2 + E_3)$$

$$q = (ab+bc+ac-d^2) = E_1 E_2 + E_2 E_3 + E_1 E_3 \quad (15)$$

$$r = d^2 c - abc = -(E_1 E_2 E_3)$$

The values of m , n , p , q , r and the roots of the equations for all the compounds are given in Table 5.

The relative strengths of the crystal-field, N_v and S , were calculated. The N_v strengths were calculated from eqn. (10) and by eqn. (15) in ref. 8. Table 6 lists the parameters for the compounds on the $^7F_{1,2}$ manifolds.

Very good correlation coefficients were obtained for the three symmetries under investigation when the scalar parameters N_v and S were plotted versus ΔE for the magnetic dipole allowed transitions $^5D_0 \rightarrow ^7F_1$.

TABLE 5

Energy levels of 7F_1 and 7F_2 manifolds and cubic quadratic coefficients of the Eu^{3+} compounds

Compound	Level									
	7F_1		7F_2							
	E_1	E_2	E_1	E_2	E_3	m	n	p	$q \times 10^{-1}$	$r \times 10^{-3}$
<i>C_{3v} symmetry</i>										
$\text{Eu}(\text{ClO}_4)_3 \cdot 7\text{DMA}$	-50.0	25.0	94.8	-23.2	-143.2	-71.6	-2199	71.6	-1245	-314.9
$\text{Eu}(\text{NO}_3)_3 \cdot 3\text{DMA}$	76.0	-38.0	17.2	-61.8	89.2	44.6	-1063	-44.6	-504.1	94.8
$\text{Eu}(\text{NCS})_3 \cdot 4\text{DMA}$	50.0	-25.0	40.0	-109.0	138.0	69.0	-4360	-69.0	-1338	601.7
$\text{Eu}(\text{PF}_6)_3 \cdot 7\text{DMA}$	43.4	-21.6	40.2	-99.8	119.2	59.6	-4012	-59.6	-1112	478.2
$\text{EuI}_3 \cdot 6\text{DMA} \cdot 4\text{H}_2\text{O}$	88.6	-44.4	27.0	-106.0	158.0	79.0	-2862	-79.0	-1534	452.2
$\text{Eu}(\text{NCS})_3 \cdot 4\text{DDPA}$	46.6	-23.4	31.2	-108.8	155.2	77.6	-3395	-77.6	-1544	526.8
$\text{EuCl}_3 \cdot 4\text{DPPA}$	-124.0	62.0	74.4	-31.6	-85.6	-42.8	-2351	42.8	-601.4	-201.2
$\text{EuBr}_3 \cdot 5\text{DPPA}$	-62.6	31.4	112.0	-39.0	-146.0	-73.0	-4368	73.0	-1503	-637.7
$\text{Eu}(\text{F}_3\text{C}-\text{SO}_3)_3 \cdot 5\text{DPPA}$	28.6	-14.4	52.2	-136.8	169.2	84.6	-7141	-84.6	-2146	1208
$\text{EuCl}_3 \cdot 3\text{DPPM}$	43.3	-21.7	59.8	-138.2	156.8	78.4	-8264	-78.4	-2056	1295
$\text{EuBr}_3 \cdot 3\text{DPPM}$	-78.0	39.0	118.8	-59.2	-119.2	-59.6	-7033	59.6	-1414	-838.3
$\text{Eu}(\text{H}_3\text{C}-\text{SO}_3)_3 \cdot 2\text{HMPA}$	-64.0	32.0	101.2	-34.8	-132.8	-66.4	-3522	66.4	-1234	-467.7
$\text{Eu}(\text{ClO}_4)_3 \cdot 7(2\text{-picNO}) \cdot 3\text{H}_2\text{O}$	-50.0	-25.0	22.0	-77.0	110.0	55.0	-1694	-55.0	-774.4	186.3
$\text{EuCl}_3 \cdot 3(2\text{-picNO}) \cdot 2\text{H}_2\text{O}$	62.7	-31.3	11.2	-83.8	145.2	72.6	-938	-72.6	-1148	136.3
$\text{Eu}(\text{NCS})_3 \cdot 3(2\text{-picNO})$	48.7	-24.3	16.2	-92.8	153.2	76.6	-1503	-76.6	-1324	230.3
$\text{Eu}(\text{NCS})_3 \cdot 4(2\text{-picNO})$	45.3	-22.7	15.8	-98.2	164.8	82.4	-1552	-82.4	-1513	255.7
$\text{Eu}(\text{ReO}_4)_3 \cdot 5(2\text{-picNO})$	-86.7	43.3	111.0	-51.0	-120.0	-60.0	-5661	60.0	-1286	-679.3
$\text{Eu}(\text{ReO}_4)_3 \cdot 3(2\text{-picNO})$	83.4	-41.6	108.2	-40.8	-134.8	-67.4	-4415	67.4	-1350	-595.1
$\text{Eu}(\text{H}_3\text{C}-\text{SO}_3)_3 \cdot 2(3\text{-picNO})$	66.7	-33.3	9.6	-67.4	115.6	57.8	-647	-57.8	-732.9	74.8
$\text{Eu}(\text{NCS})_3 \cdot 3.5(3\text{-picNO})$	28.7	-14.3	-104.4	54.6	-99.6	49.8	-5700	-49.8	-1066	-567.7
$\text{Eu}(\text{NCS})_3 \cdot 3.5(4\text{-picNO})$	65.3	-32.7	34.2	-102.8	137.2	68.6	-3516	-68.6	1293	482.4
$\text{Eu}(\text{H}_3\text{C}-\text{SO}_3)_3 \cdot 2(4\text{-picNO})$	72.7	-36.3	26.8	-84.2	114.8	57.4	-2257	-57.4	-577.8	259.1
$\text{Eu}(\text{NCS})_3 \cdot 4\text{pyzNO}$	-71.3	35.7	82.6	-15.4	-134.4	-67.2	-1272	67.2	-1110	-171.0

$\text{Eu}(\text{F}_3\text{C}-\text{SO}_3)_3 \cdot 6\text{pyzNO} \cdot 3\text{H}_2\text{O}$	-84.0	42.0	67.2	-5.8	-122.8	-61.4	-389.8	61.4	-793.0	-47.9
$\text{Eu}(\text{H}_3\text{C}-\text{SO}_3)_3 \cdot 2\text{pyO}$	86.7	-43.3	27.0	-84.0	114.0	57.0	-2268	-57.0	-876.6	258.6
$\text{Eu}(\text{NCS})_3 \cdot 4\text{TMSO}$	48.0	-24.0	12.6	-77.4	129.6	64.8	-975.2	-64.8	-937.3	126.4
$\text{EuCl}_3 \cdot 3\text{TMSO}$	42.6	-21.4	8.4	-71.6	126.4	63.2	-601.4	-63.2	-859.0	76.0
$\text{Eu}(\text{NCS})_3 \cdot 3.5\text{TMSU}$	-66.6	33.4	61.0	-135.0	147.0	73.0	-8235	-73.0	-1911	121.1
$\text{EuCl}_3 \cdot 4.5\text{TSO}$	57.4	-28.6	48.2	-142.8	189.2	94.6	-6883	-94.6	-2478	130.2
$\text{Eu}(\text{NCS})_3 \cdot 5\text{TSO}$	-80.0	40.0	38.0	-104.0	132.0	66.0	-3952	-66.0	-1266	521.7
<i>D₃ symmetry</i>										
$\text{Eu}(\text{H}_3\text{C}-\text{COO})_3 \cdot \text{DMA}$	-64.6	32.4	46.4	17.4	-127.6	-63.8	807.4	63.8	-733.4	1030
$\text{EuCl}_3 \cdot 3.5\text{DMA}$	-92.0	46.0	62.0	12.0	-148.0	-74.0	744	74.0	-1021	110.1
$\text{EuCl}_3 \cdot 5\text{TMSU}$	-46.6	23.4	48.0	-17.0	-62.0	-31.0	-816	31.0	-273.8	-50.6
<i>D_{3d} symmetry</i>										
$\text{Eu}(\text{F}_3\text{C}-\text{SO}_3)_3 \cdot 7.5\text{DMSO}$	46.6	-23.4	46.0	-95.0	98.0	49.0	-4370	-49.0	-907.7	428.3
$\text{Eu}(\text{PF}_6)_3 \cdot 7.5\text{DTMSO}$	45.4	-22.6	48.6	-111.4	125.6	62.8	-5414	-62.8	-1330	680.0
$\text{Eu}(\text{ClO}_4)_3 \cdot 8\text{pyzNO}$	28.7	-14.3	35.4	-82.6	94.4	47.2	-2924	-47.2	-737.9	276.0
$\text{Eu}(\text{PF}_6)_3 \cdot 8\text{pyzNO}$	28.7	-14.3	30.2	-74.8	89.2	44.6	-2259	-44.6	-623.7	201.5
$\text{Eu}(\text{ClO}_4)_3 \cdot 7.5\text{TMSO}$	57.4	-28.6	48.4	-137.6	178.4	89.2	-6660	-89.2	-2257	1188
$\text{Eu}(\text{PF}_6)_3 \cdot 7.5\text{TMSO}$	59.4	-29.6	23.6	-92.4	137.6	68.8	-2180	-68.8	-1165	300.1
$\text{EuBr}_3 \cdot 7\text{TMSO}$	57.4	-28.6	32.2	-120.8	177.2	88.6	-3890	-88.6	-1959	689.3
$\text{Eu}(\text{ReO}_4)_3 \cdot 7.5\text{TMSO}$	47.4	-23.6	23.4	-92.6	138.4	69.2	-2167	-69.2	-1174	299.9
$\text{EuI}_3 \cdot 7.5\text{TMSO}$	62.6	-31.4	51.0	-130.0	158.0	79.0	-6630	-79.0	-1911	1048
$\text{Eu}(\text{F}_3\text{C}-\text{SO}_3)_3 \cdot 7.5\text{TMSO}$	74.6	-37.4	8.6	-95.4	173.6	86.8	-820.4	-86.8	-1589	142.4
$\text{Eu}(\text{ClO}_4)_3 \cdot 7.5\text{TSO}$	-65.4	32.6	137.4	-58.6	-157.6	-78.8	-8052	78.8	-2047	-1269
$\text{Eu}(\text{PF}_6)_3 \cdot 7.5\text{TSO}$	76.0	-38.0	56.4	-112.6	112.4	56.2	-6351	-56.2	-1267	113.8
$\text{EuI}_3 \cdot 7.5\text{TSO}$	81.3	-40.7	43.0	-127.0	168.0	84.0	-5461	-84.0	-1957	917.4
$\text{Eu}(\text{CF}_3-\text{SO}_3)_3 \cdot 7.5\text{TSO}$	40.0	-20.0	20.0	-80.0	120.0	60.0	-1600	-60.0	-880	192.0

TABLE 6

Scalar strength parameters

Complex	7F_1			7F_2		
	ΔE	N_v	S	ΔE	N_v	S
<i>C_{3v} symmetry</i>						
Eu(ClO ₄) ₃ · 7DMA	75	396	65	238	1638	287
Eu(NO ₃) ₃ · 3DMA	114	602	98	151	986	179
Eu(NCS) ₃ · 4DMA	75	396	65	247	1687	319
Eu(PF ₆) ₃ · 7DMA	65	343	56	219	1479	272
EuI ₃ · 6DMA · 4H ₂ O	133	703	114	264	1757	316
Eu(NCS) ₃ · 4DDPA	70	370	60	264	1827	322
EuCl ₃ · 4DPPA	186	983	160	160	1105	194
EuBr ₃ · 5DPPA	94	497	81	258	1744	320
Eu(F ₃ C–SO ₃) ₃ · 5DPPA	43	227	37	306	2164	387
EuCl ₃ · 3DPPM	65	343	56	295	2049	382
EuBr ₃ · 3DPPM	117	618	101	238	1606	319
Eu(H ₃ C–SO ₃) ₃ · 2HMPA	96	507	83	234	1570	289
Eu(ClO ₄) ₃ · 7(2-picNO) · 3H ₂ O	75	396	65	187	1261	227
EuCl ₃ · 3(2-picNO) · 2H ₂ O	94	497	81	229	1572	270
Eu(NCS) ₃ · 3(2-picNO)	73	386	63	246	1716	293
Eu(NCS) ₃ · 4(2-picNO)	68	359	59	263	1855	313
Eu(ReO ₄) ₃ · 5(2-picNO)	130	687	112	231	1538	300
Eu(ReO ₄) ₃ · 3(2-picNO)	125	661	108	243	1609	303
Eu(H ₃ C–SO ₃) ₃ · 2(3-picNO)	100	528	86	183	1228	241
Eu(NCS) ₃ · 3.5(3-picNO)	43	227	37	204	1436	281
Eu(NCS) ₃ · 3.5(4-picNO)	98	518	85	240	1612	296
Eu(H ₃ C–SO ₃) ₃ · 2(4-picNO)	109	576	94	199	1314	242
Eu(NCS) ₃ · 4pyzNO	107	565	92	217	1458	257
Eu(F ₃ C–SO ₃) ₃ · 6pyzNO · 3H ₂ O	126	666	108	190	1269	240
Eu(H ₃ C–SO ₃) ₃ · 2pyO	130	690	112	198	1296	240
Eu(NCS) ₃ · 4TMSO	72	380	62	207	1431	246
EuCl ₃ · 3TMSO	64	338	55	198	1387	234
Eu(NCS) ₃ · 3.5TMU	100	529	86	282	1907	368
EuCl ₃ · 4.5TSO	86	454	74	332	2291	412
Eu(NCS) ₃ · 5TSO	120	634	103	236	1563	293
<i>D₃ symmetry</i>						
Eu(H ₃ C–COO) ₃ · DMA	97	514	84	174	1272	208
EuCl ₃ · 3.5DMA	138	729	119	210	1470	245
EuCl ₃ · 3TMU	70	369	60	108	721	135
<i>D_{3d} symmetry</i>						
Eu(F ₃ C–SO ₃) ₃ · 7.5DMSO	70	370	60	193	1316	257
Eu(PF ₆) ₃ · 7.5DTMSO	68	359	59	237	1626	307
Eu(ClO ₄) ₃ · 8pyzNO	43	227	37	177	1224	229
Eu(PF ₆) ₃ · 8pyzNO	43	227	37	164	1129	209

TABLE 6 (continued)

Complex	7F_1			7F_2		
	ΔE	N_v	S	ΔE	N_v	S
Eu(ClO ₄) ₃ · 7.5TMSO	86	454	74	316	2173	394
Eu(PF ₆) ₃ · 7.5TMSO	89	470	77	230	1559	277
EuBr ₃ · 7TMSO	86	454	74	298	2056	361
Eu(ReO ₄) ₃ · 7.5TMSO	71	375	61	231	1590	279
EuI ₃ · 7.5TMSO	94	497	81	288	1958	365
Eu(F ₃ C–SO ₃) ₃ · 7.5TMSO	112	592	96	269	1857	316
Eu(ClO ₄) ₃ · 7.5TSO	98	518	84	295	2007	380
Eu(PF ₆) ₃ · 7.5TSO	114	602	98	225	1518	302
EuI ₃ · 7.5TSO	122	645	105	295	1979	364
Eu(F ₃ C–SO ₃) ₃ · 7.5TSO	60	317	52	200	1380	241

The following relations were obtained.

$$\Delta E = 0.189N_v, \quad \Delta E = 1.161S \quad (C_{3v} \text{ symmetry})$$

$$\Delta E = 0.186N_v, \quad \Delta E = 1.159S \quad (D_3 \text{ symmetry})$$

and

$$\Delta E = 0.146N_v, \quad \Delta E = 1.162S \quad (D_{3d} \text{ symmetry})$$

Figures 10–12 contain the N_v and S values plotted versus ΔE for the electric dipole allowed $^5D_0 \rightarrow ^7F_2$ transitions. The equations representing the lines in the graphs and also the linear regression coefficients were calculated using the LOTUS 123 program (Lotus Development Corporation, © 1985).

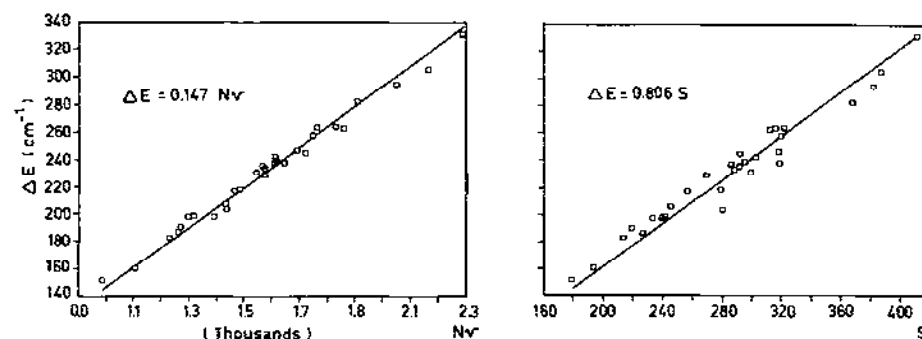


Fig. 10. Maximum Stark splitting of 7F_2 (Eu³⁺) versus N_v and S in C_{3v} symmetry.

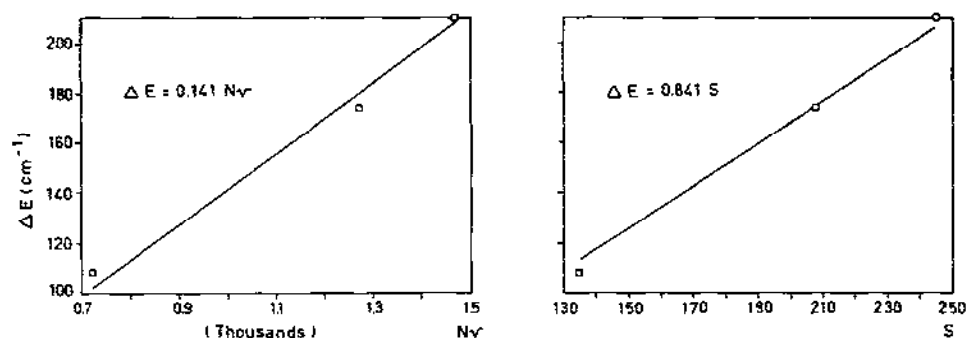


Fig. 11. Maximum Stark splitting of 7F_2 (Eu^{3+}) versus N_v and S in D_3 symmetry.

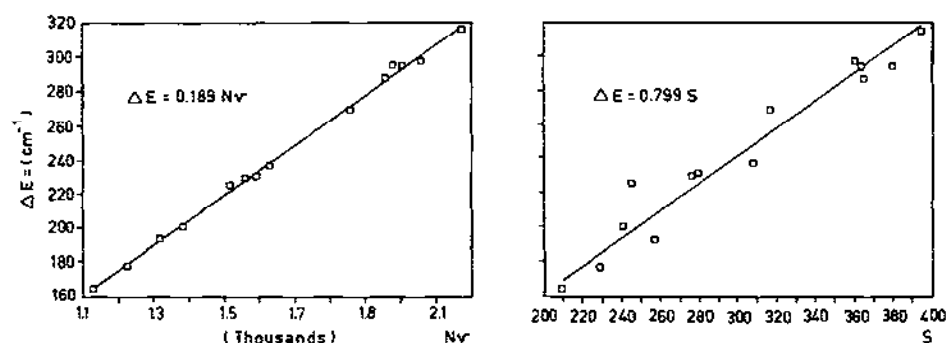


Fig. 12. Maximum Stark splitting of 7F_2 (Eu^{3+}) versus N_v and S in D_{3d} symmetry.

F. FINAL REMARKS

When we analyse these data, we can see that the values of N_v for the 7F_1 manifold are equal in modulus to $Y_2^0 \langle r^2 \rangle$ for all three symmetries.

Comparing the N_v and S values of the 7F_2 manifold in an attempt to establish a spectrochemical series of the ligands based on the crystal-field splitting, it was observed that

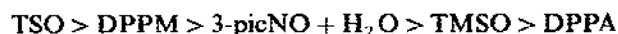
(a) taking the N_v and ΔE values for all compounds containing NCS^- as counter-ion, with C_{3v} symmetry, the splitting of the levels follows the order:

TMU > 2-picNO (CN = 7) > DDPA > 2-picNO (CN = 6)
> DMA > 4-picNO > TSO > pyzNO > 3-picNO > TMSO

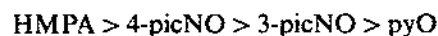
(b) using S and ΔE for the same compounds, a different order, with some inversion, was obtained:

TMU > DDPA > DMA > 2-picNO (CN = 7) > 4-picNO > 2-picNO (CN = 6)
= TSO > 3-picNO > pyzNO > TMSO

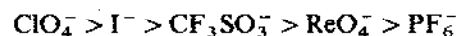
(c) using compounds containing Cl^- as counter-ion, the order is the same for N_v and S :



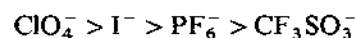
(d) using $\text{H}_3\text{C-SO}_3^-$ as counter-ion, the order for both parameters is:



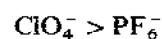
(e) in the case of compounds with D_{3d} symmetry with TMSO as ligand and the same apparent coordination number and using N_v and S parameters, the anions, despite the fact that they are not directly coordinated to the central ion due to their basicity, influence the splitting as:



(f) with TSO as ligand, an inversion in order is observed:



(g) with pyzNO as ligand



(h) in general, the following order is observed when the same counter-ion, the same symmetry (D_{3d}) and the same coordination number is used



The scalar parameters S were plotted in relation to N_v for the three symmetries under consideration. A reasonable correlation was obtained in all cases, indicating that these parameters are both consistent and reflect the same trends.

To correlate the splittings with chemical properties of the different ligands is not an easy task since we may have different coordination numbers, the structures are not known, and the ligands have different basicities, geometries and bulkiness. Nevertheless, the bonding is essentially electrostatic and it is possible to conclude that basicity is the predominant factor.

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