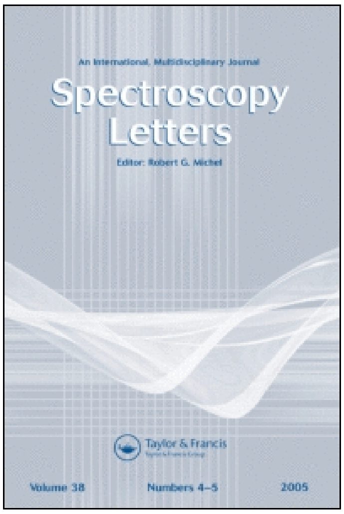


**Spectroscopy Letters**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

# Inductive Effect of Substituents and their Influence on the Rate of Temperature Quenching of $Eu^3$ Luminescence in mixed Ligand Europium β- Diketonates

V. E. Karasyov[a]; A. G. Mirochnick[a]; R. N. Shchelokov[a]
[a] Institute of Chemistry Far East Science Centre, Academy of Sciences of the USSR, Vladivostok- 22, USSR

**To cite this Article** Karasyov, V. E. , Mirochnick, A. G. and Shchelokov, R. N.(1982) 'Inductive Effect of Substituents and their Influence on the Rate of Temperature Quenching of $Eu^3$ Luminescence in mixed Ligand Europium β- Diketonates', Spectroscopy Letters, 15: 12, 931 — 943

**To link to this Article: DOI:** 10.1080/00387018208068028

**URL:** http://dx.doi.org/10.1080/00387018208068028

SPECTROSCOPY LETTERS, 15(12), 931-943 (1982)

# INDUCTIVE EFFECT OF SUBSTITUENTS AND THEIR INFLUENCE ON THE RATE OF TEMPERATURE QUENCHING OF $Eu^{3+}$ LUMINESCENCE IN MIXED LIGAND EUROPIUM $\beta$- DIKETONATES

KEY WORDS: Luminescence Spectra, Europium,
$\beta$- diketones

V.E.Karasyov, A.G.Mirochnick and R.N.Shchelokov

Institute of Chemistry Far East Science Centre,
Academy of Sciences of the USSR. Vladivostok- 22,
690022. USSR.

The mechanism of dissipation of electronic excitation energy of rare earth element( REE) ions into the vibration components of the closer and the farther surroundings is a problem of considerable theoretical and practical interest. Temperature quenching of REI luminescence in chelates was studied in a number of papers/1 - 6/ which revealed the importance of the energy position of the lower triplet levels of the organic ligand and the resonance excited level of the REE ion. As the temperature is raised, the two dominating processes are /7/ temperature quenching and partial redistribution of electrons from the lower Stark's components of the REI excited level to the higher ones. These two factors are , as a rule used to explain the observed temperature dependences of luminescence lines.

The present investigation deals with the effect of donor- acceptor activity of terminal groups of the organic ligand on radiationless dissipation of $Eu^{3+}$ electronic excitation energy to the surrounding ligands.

The following Eu$\beta$ - diketonates with mixed ligands were employed:

1. Tris -$\beta$- diketones Eu $(\beta)_3$Phen, where $\beta$ is DPM (dipivaloylmethane), AA (acetylacetone), BA (benzoylacetone), DBM (dibenzoylmethane), TTA (thenoyltrifluoroacetone), HFAA (hexafluoroacetylacetone), TFAA (trifluoroacetylacetone), and Phen is 1,10 - phenanthroline.

2. Tetrakis - $\beta$ - diketones:

   a) DPhG $[Eu(\beta)_4]$ where $\beta$ is AA,BA,TTA, and DPhG is diphenylguanidine,

   b) $M[Eu(AA)_4]$ , M is Li,Na;

3. Europium ternary complexes with $\beta$ - diketones, a nitrato-group and phosphine oxides:

   a) Eu $(\beta)_2$ $NO_3(TPPO)_2$, where $\beta$ is BA,DBM, TTA, TPPO - triphenylphosphineoxide;

   b) Eu $(\beta)_2$ $NO_3(TBPO)_2$ , where $\beta$ is DBM, TTA , TBPO - tributylphosphine oxide

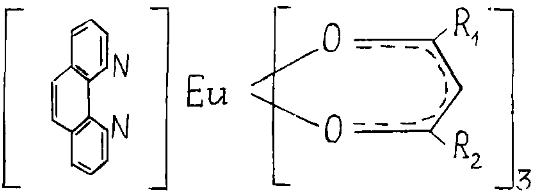
4. Europium carboxylatodibenzoylmethanates:

   $[Eu(DBM)_2(RCOO)]2H_2O$ , R is $CH_3$ , $C_3H_7$ .

The luminescence of polycrystalline $\beta$ - diketonates was excited by the UV light of a DRSh - 250 lamp passed through an UFS- 6 filter and registered by an SDL -1 spectrometer with an automatic recorder.

Investigated was the temperature dependence of line intensities of Stark's components of $^5D_0 - {}^7F_j$ transitions( j = 0,1,2 ) by continuous excitation in the 100 - 300 K temperature range. The temperature was raised by gradual evaporation of nitrogen in a flow-through quarts Dewar flask. The intensity of each line was measured at least at 12 temperatures. Temperature -induced radiationless losses of $Eu^{3+}$ luminescence were measured in terms of the activation energy ($E_a$) inferred from the slope of the ln I = F( 1/ T )curve plotted according to the Arrenius equation /1,2/ (I - relative intensity of the luminescence band, T- temperature).

## 1. Tris -β - diketonates.



Comparative analysis of donor properties of similar ligands with differ ent substituents requires that the complexes under consideration have the same composition, coordination number, dentacity of the ligands and more or less similar geometrical parameters. These requirements are met by compounds of composition Eu $(\beta)_3$Phen , where β are β -diketon es: AA, DPM, BA, DBM, TTA, TFAA, HFAA, and Phen- 1,10-phenanthroline. All these species are mononuclear com plexes in which every $Eu^{3+}$ is surrounded by six oxygens of the three β - diketon es and two nitrogens of the neutral bidentate ligand, i.e. phenanthroline.

Europium $\beta$ - diketonate complexes with aromatic amines posses similar luminescence spectra, which reflects the similarity of their coordination polyhedrons. The structures of $Eu(DPM)_3Phen$ and $Eu(AA)_3Phen$ were reported in /8 / and /9 /, respectively.

Table 1 contains the values of the activation energy for the above series of europium $\beta$ - diketonates. For tris-$\beta$ - diketonates it shows a steady decrease in the following order:

$$DPM > AA > BA > DBM > TFAA \geqslant TTA > HFAA$$

That is, radiationless losses of $Eu^{3+}$ excitation energy consistently decrease when passing from alkyl and aryl substituents to fluorinated ones. The table indicates that $E_a$ does not correlate with the values of energy gaps between the lower triplet levels of the corresponding ligands /2-4/ and the resonance excited level of $Eu^{3+}$. The sequence of $E_a$ values in Table 1 also shows no correlation with the $^5D_0$ - $^5D_1$ gaps, as long as for all the series of europium $\beta$ - diketonates these gaps are approximately the same (~ 1700cm$^{-1}$ Therefore the sequence of activation energies can not be explained by thermal deactivation of the $^5D_0$ exicited resonance level of $Eu^{3+}$ via the ligand triplet levels and higher excited levels of $Eu^{3+}$. It should be also noted that the set of high frequency vibrations of $(CH_3)_3$, $CH_3$ , $C_6H_5$ , $CF_3$ , and C = O groups for the complexes studied is situated in the 600 - 1600 cm$^{-1}$ range ,so that the above - mentioned substantial decrease in $E_a$ when passing from alkyl and aryl substituents to fluorinated ones can be hardly explained in terms of just a decrease in the vibration energy of the ligands.

The spectral luminescent properties of lantanide $\beta$ - diketonates are known to be essentially dependent on thestate of the chemical bond between the REI and the

Table 1. Activation energies and Stark's splitting $\Delta\,{}^7F_1$ of europium chelates.

| Chelate | $E_a$, $cm^{-1}$ | $\Delta\,{}^7F_1$, $cm^{-1}$ |
|---|---|---|
| 1. $Eu(DPM)_3Phen$ | 1300 | 236 |
| $Eu(AA)_3$ Phen | 950 | 243 |
| $Eu(BA)_3$ Phen | 900 | 230 |
| $Eu(DBM)_3PHEN$ | 520 | 220 |
| $Eu(TFAA)_3Phen$ | 350 | 190 |
| $Eu(TTA)_3Phen$ | 350 | 180 |
| $Eu(HFAA)_3Phen$ | 270 | 160 |
| 2. DPhG $[Eu(AA)_4]$ | 770 | 140 |
| DPhG $[Eu(BA)_4]$ | 530 | 130 |
| DPhG $[Eu(TTA)_4]$ | 470 | 100 |
| Li $[Eu(AA)_4]$ | 1110 | 83 |
| Na $[Eu(AA)_4]$ | 1130 | 100 |
| 3. $Eu(BA)_2NO_3(TPPO)_2$ | 1220 | 330 |
| $Eu(DBM)_2NO_3(TPPO)_2$ | 820 | 213 |
| $Eu(TTA)_2NO_3(TPPO)_2$ | 190 | 52 |
| $Eu(DBM)_2NO_3(TBPO)_2$ | 290 | 193 |
| $Eu(TTA)_2NO_3(TBPO)_2$ | 240 | 136 |
| 4. $[Eu(DBM)_2(CH_3Coo)]2H_2O$ | 2990 | 498 |
| $[Eu(DBM)_2(C_3H_7COO)]2H_2O$ | 5050 | 521 |

Errors in $E_a$ 10 - 15 % .

diketone, whereas at the latter point information is very scarce. In mixed ligand complexes special attention should be paid at the competing behavior of ligands with mi xed-type donor atoms. This circumstance is often ignored in studies of REE tris-$\beta$- diketonates.

A bond between a REI and a $\beta$ -diketone is predominantly ionic with a covalent contribution depending on the nature of the ligand. Neutral bidentate ligands such as 1,10- phenanthroline or 2,2'-dipyridyl act as $\sigma$- donors by forming donor-acceptor bonds with the metal. In europium tris-$\beta$- diketonate complexes substitution of water molecules in the first coordination sphere by nitrogen atoms of aromatic amines (1,10 - phenanthroline,2,2' - dipyridyl) leads to a sharp increase in the quantum yield of luminescence. It appears that a stronger $\sigma$ - bond between the metal and the aromatic amine is responsible for a drastic increase in radiationless energy transfer from the ligand to the REI.

A quantitative expression of the inductive effect of the substituents is Taft's constant $\sigma^*$. In the series studied there is a consecutive increase in the negative inductive effect, a decrease in the donation of electronic density to oxygen and, accordingly, the $Eu^{3+}$ - $\beta$ -diketone bond becomes more ionic when passing from alkyl- or aryl- containing $\beta$- diketonates to fluorinated ones. These effects should be accompanied by strenghthening of the REI bond with the neutral molecule of phenanthroline. It seems most likely that the consecutive decrease in radiationless losses in the series of $\beta$-diketonates DPM > AA > BA > > DBM > TFAA $\geqslant$ TTA > HFAA arises from strenghthening and from a more efficient energy transfer from the ligand to the REI. In Fig.1 $E_a$ values are plotted against $\sigma^*$ of the $\beta$ -diketon es. The value of $\sigma^*$ was

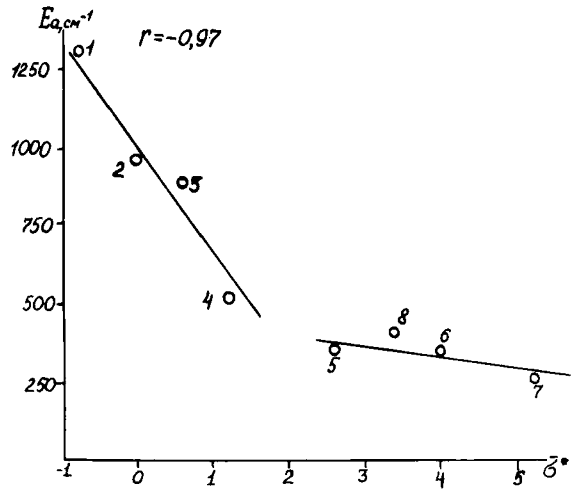


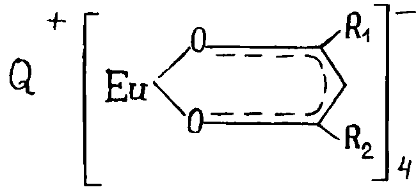
**Fig.1** Correlation between activation energy $E_a$ and total Taft's constant $\sigma^*$ in tris-$\beta$-diketonates $Eu(\beta)_3Phen$:
1 - DPM, 2 - AA, 3 - BA, 4 - DBM, 5 - TFAA
6 - TTA, 7 - HFAA, 8 - BTFA .

r - correlation coefficient

found as a sum of $\sigma^*$ of the $\beta$- diketonate substituents $R_1$ and $R_2$ /10/. Analysis of the results suggests a division of the diketonates in two groups (with fluorinated and non-fluorinated substituents) depending on the donor capacity of the substituents. In either group the dependence in Fig.1 is linear, which favours our assumption that the coordination polyhedrons of the $\beta$ -diketones posses a similar structure. The existence of the two groups is apparently due to the fact that fluorinated $\beta$- diketones have a much higher constant $\sigma^*$. The 1,10 - phenanthroline adducts of

Eu(DPM)$_3$ and Eu(AA)$_3$ have square antiprismatic structures /8,9 /. Sievers et all. /11/ concluded that differences between the later two structures cannot be attributed to the presence of bulky tert-butyl groups Perhaps the greater electron-donating ability of DPM ligand may account for the shortening of the Eu - O bond lengths in the dpm complex. In comparing the structures of REE tetrakis-β- diketones, Poray - Koshitz et all. /12 / arived at the conclusion that for non - fluorinated ligands the tetragonal antiprism is a typical lanthanide coordination polyhedron, and for fluorinated ligands it is the dodecahedron. Poray -Koshitz and collaborators say that this dependency is due to the degree of overlapping of ligand orbitals and REE ion orbitals. Ermolaev et all. /13 / qualitatively evaluated the relative superposition values of Eu$^{3+}$ electron shells with certain ligands and established that fluorinated ligands provide lesser superposition of electron shells than their non-fluorinated analogues.

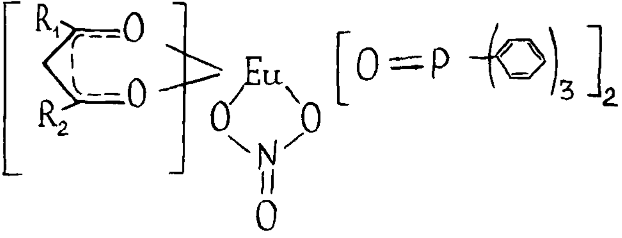
## 2. Tetrakis - β - diketonates.



The structure of tetrakis - β - diketonates of REE was reported in /12 /. In these mononuclear molecules the Eu atom is surrounded by oxygen atoms of four β - diketonate groups forming a dodecahedron. The latter is usually distorted a little ;in Cs[Eu(HFAA)$_4$], for instance, the minimum Eu - O distance is 2.36 A, the maximum one 2.42A /14/.

As is seen from Table 1, tetrakis - β - di - ketonates show asteady decrease in activation energy $E_a$ from 770 $cm^{-1}$ to 470 $cm^{-1}$ in the series AA > BA > TTA. This decrease in radiationless losses is apparently due to the growing inductive effect and the fact that the Eu - O bond becomes more ionic. Thus electron - vibration interactions become weaker and radiationless relaxation of excitation decelerates. It should also be noted that , rather unexpectedly, radiationless losses for DPhG$[Eu(AA)_4]$ proved lower than for M$[Eu (AA)_4]$ ( M= Li, Na) (Table 1), though DPhG does have a large enough set of high frequency vibrations of NH,CN and $C_6H_5$ groups. This suggests a fundamental difference in the bonds between the methyl groups of europium acetylacetonate and the outerspheric cation ($M^+$, DPhG) in these two species. With DPhG$[Eu(AA)_4]$ the DPhG cation accepts electron density from the methyl group ( a hydrogen bond exists), decreases donation of electron density to the chromophore group and, accordingly (see Part1), radiationless losses of electron excitation energy drop. In the case of alkali metal cations ($Li^+$, $Na^+$) there is no direct transfer of electron density from the methyl group and thus the inductive donating effect of the methyl group on the chromophore group changes insignificantly.

### 3. Ternary complexes of europium with β - diketones, nitrato-group and phosphine oxides.



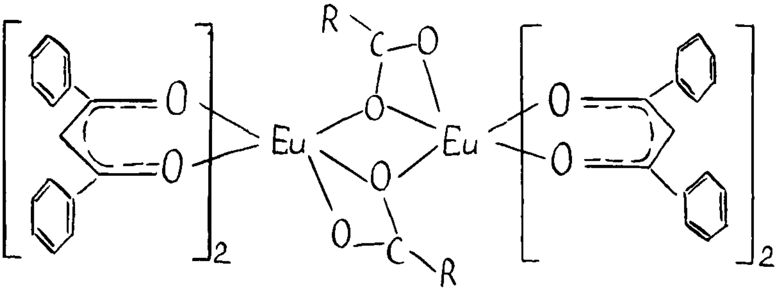
The compounds of composition $Eu(\beta)_2NO_3 2A$ are mononuclear complexes. The europium coordination polyhedron is a dodecahedron whose apexes are occupied by two oxygens of two $\beta$ - diketone groups, two oxygens of the nitrato - group and two oxygens of two phosphine oxide groups. The molecular complexes form a crystal by virtue of Van-der-Vaals bonds.

a) $Eu(\beta)_2 NO_3 (TPPO)_2$. As is seen from Table 1 the activation energy $E_a$ drops drastically (from 1220 $cm^{-1}$ to 190 $cm^{-1}$) in the series BA - DBM - TTA, as it did in the case of compounds considered in Sections 1 and 2. Again, therefore, a direct dependence is observed between radiationless losses of luminescence and the effective electronic charges induced by substituents on the chromophore group atoms. Indeed, when passing from BA and DBM to TTA - containing complexes the negative inductive effect of the substituent increases, while the bond between $Eu^{3+}$ and the $\beta$ - diketone oxygen atom becomes less covalent. At the same time the donor-acceptor bond $Eu^{3+}$ - neutral phosphine oxide should be strengthened and the efficiency of excitation energy transfer from the ligand to the REI should increase.

b) Considering ternary complexes with one and the same $\beta$ - diketone (DBM,TTA) but with different phosphine oxides (TPPO,TBPO), one might expect radiationless losses would be greater for the complexes with TBPO (bearing in mind high frequency vibrations). This, however, disagrees with the experimental values of activation energy: for $Eu(DBM)_2NO_3(TPPO)_2$ $E_a$ (820 $cm^{-1}$) is greater than for $Eu(DBM)_2NO_3(TBPO)_2$ (290$cm^{-1}$

Ternary complexes with TTA display approximately the same low values of $E_a$ ( 190 and 240 $cm^{-1}$ ). Therefore the actual activation energies can not be interpreted if we take into account only the effect of the vibration component of phosphine oxides energy on the efficiency of excitation energy transfer. Comparative analysis of inductive effects of substituents in phosphine oxides shows /10/ that the oxygen atoms of the chromophore group receive more electron density in tributhylphosphine oxide ( $\sigma^* = -0.39$ ) than in TPPO ( $\sigma^* = 1.8$ ). In the latter case, therefore, the donor - acceptor bond between $Eu^{3+}$ and the neutral phosphine oxide molecule is stronger, which promotes excitation energy transfer from the ligand to the REI.

4. Europium carboxylatodibenzoylmethanates.



For europium carboxylatodibenzoulmethanates the values of $E_a$ are as high as 2990cm$^{-1}$ [$Eu(DBM)_2(CH_3COO)$] $2H_2O$ and 5050cm$^{-1}$ [$Eu(DBM)_2(C_3H_7COO)$] $2H_2O$ . Apart from the high value of radiationless losses, it was found in a study of optical properties of Eu carboxylatodibenzoylmethanates that heating of pre-cooled (to - 196° )samples to - 30° stops the Eu ion luminescence, which is not resumed at higher temperatures.

Such a pronounced dissipation of electron energy may be attributed to the special structure of europium carboxylatodibenzoylmethanates. An earlier investigation has shown that these species with mixed ligands are of a dimer or polymer structure /15/, with bridges between the E u ions formed by carboxylato - groups displaying a tridentate bridge - cyclic coordination. This stucture leads to a considerable distortion of the inner coordination sphere of Eu ions and enhances their interaction, thus being responsible for the high value of radiationless dissipation of the electron excitation energy. Note that the radiationless process will be more intense in europium iso butyratodibenzoylmethanate, since the electron donor inductive effect of $C_3H_7$ (i) groups ( $\sigma^* = -0.115$) is stronger than that of $CH_3$ groups ( $\sigma^* = 0$ ).

## 5. Stark's splitting of $^7F_1$ level of $Eu^{3}$.

As the donor ligand bond strength increases and the chelating ligand bond becomes weaker, Stark's splitting of the $^7F_1$ level of the Eu ion decreases ( Table 1 ). Analysis of X - ray diffraction evidence /16/ indicates that this effect (i.e. the increase in the symmetry of $Eu^{3+}$ surroundings) may arise from the levelling of distances from the metal to the coordinated atoms of the chelating and the donor ligand.

Acknowledgment. The authors wish to thank Dr. N.I. Steblevskaya for helpful discussions.

## REFERENCES:

1. Harrigan R.W., Crosby G.A, J.Chem.Phys., 1970, v.52, 9, pp.4912-4914.
2. Kreher K., Butter E. Z.Phys.Chem, 1970, v.243, 3-4, s.152.
3. Kleinerman M., Sang-il Choi. J.Chem.Phys, 1968, v.49, 9, pp.3901-3908.

4. Dawson W.R., Kropp J.L., Windsor M.W. J.Chem.Phys, 1966, v.45, 7, pp.2410-24-18.
5. Haas Y., Stein G. J.Phys.Chem, 1972, v.76, 8, pp.1093-1104.
6. Brown T.D., Shepherd T.M. J.Chem.Soc.Dalt. TRans., 1973, v.3, pp.336-341.
7. Levshin V.L., Maksimova N.D., Astakhov A.V. Optika i Spectroskopiya, 1970, v.28, 6, s.1159-1163.
8. Cunningham J.A., Sievers R.E. Proc. 10th Rare Earth Res. CONf., Carefree, Ariz., 1973.
9. Watson W.H., Williams R.J., Stemple N.S. J.Inorg Nucl.Chem., 1972, v.34, 2, pp.501-508.
10. Zhdanov Y.A., Minkin V.I. Correlation analysis in organic chemistry. Rostov na/ Donu, 1966, s. 307, (in Russian).
11. Sievers R.E. et all. Advances in chemistry series 1976, 150, p.231.
12. M.A.Poray-Koshits et all. Itogi nauki i tekhniki Kristallokhimiya (Crystal Chemistry), v.11, Moscow, 1976 (in Russian).
13. Ermolaev V.L. et all. Optika i spektroscopiya, 22, 854, (1967) (in Russian).
14. Burns J.H., Danford M.D. Inorg.Chem., 8(1969) 1780.
15. Karasyov V.E. et all. Zhurnal neorg. khimii, V27 N. 4 ,900(1982) (in Russian).
16. Karasyova E.T. Thesis, Moskwa, (1980), s.26(in Rus).

Received: September 16, 1982
Accepted: October 8, 1982