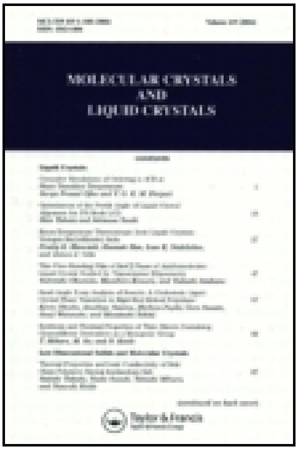

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# Intense Mechanoluminescence from Europium Tris(2-Thenoyltrifluoroacetone) Phenanthroline

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# INTENSE MECHANOLUMINESCENCE FROM EUROPIUM TRIS(2-THENOYLTRIFLUOROACETONE) PHENANTHROLINE

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Abstract Four new kinds of europium complexes were synthesized and their mechanoluminescent properties were investigated. Out of the four, only europium tris(2-thenoyltrifluoroacetone) phenanthroline ( $Eu(TTA)_3(phen)$ ) exhibited intense mechanoluminescence. Its spectra were measured and found to be essentially the same as that of the photoluminescence, indicating an identical emitting species. The excitation mechanisms of mechanoluminescence are also discussed.

## INTRODUCTION

When some solids are subject to stress beyond a certain level, emission of light occurs. This mechanically induced luminescence is known as mechanoluminescence (ML)[1]. A large number of inorganic salts[2] and organic molecular crystals[3] show ML. Many attempts have been made to elucidate the mechanism of excitation bringing about ML, but no general principles have yet to emerge.

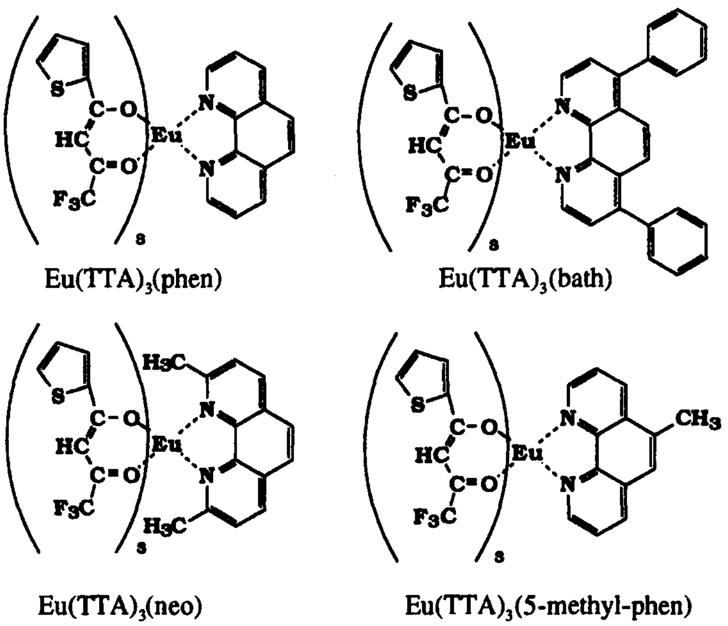
Complexes of rare earth metals are known to exhibit strong luminescence under suitable conditions. This leads to the expectation that they can be used as mechanoluminescent materials. Indeed, it was reported that a dibenzoylmethide complex of europium showed intense ML[4]. However, it was also stated that any other europium complexes tried showed no such activity.

Searching for more efficient mechanoluminescent materials, we have synthesized four kinds of europium complexes whose ML functions have never been investigated before. We did find that one of them demonstrated strong light emission when it underwent mechanical stimuli. In this paper, we describe the experimental details and the complex's mechanoluminescent behavior and discuss possible mechanisms.

## EXPERIMENTAL

The molecular structures and abbreviations of the europium complexes used in this study are shown in Fig.1. These were synthesized by the method of Melby[5] and Bauer[6]. Purification was performed by recrystallization from acetone solutions. For Eu(TTA)$_3$(phen) and Eu(TTA)$_3$(neo), just leaving the solution at room temperature gave crystallites of a few hundred μm, while heating was necessary for Eu(TTA)$_3$(bath) and Eu(TTA)$_3$(5-methyl-phen) to obtain powdery deposit. All complexes were identified by NMR and elemental analysis. The results of elemental analysis and melting point of europium complexes are shown in Table 1.

ML and photoluminescence (PL) spectra were measured with a polychromator-photodiode array multichannel spectrophotometer system (IMUC-7000 : OTSUKA ELECTRONICS ). For ML experiments, the complexes were rubbed with a steel



Eu(TTA)$_3$(phen) Eu(TTA)$_3$(bath)

Eu(TTA)$_3$(neo) Eu(TTA)$_3$(5-methyl-phen)

FIGURE 1 Molecular structures and abbreviations of europium complexes

TABLE 1 Elemental analysis and melting point for europium complexes

| | C (%) | | H(%) | | N(%) | | (℃) |
|---|---|---|---|---|---|---|---|
| Complex | Calcd. | Found. | Calcd. | Found. | Calcd. | Found. | M. P. |
| Eu(TTA)$_3$(phen) | 43.43 | 43.4 | 2.02 | 2.0 | 2.81 | 2.8 | 248~250 |
| Eu(TTA)$_3$(bath) | 50.22 | 50.7 | 2.46 | 2.4 | 2.44 | 2.6 | 118~119 |
| Eu(TTA)$_3$(neo) | 44.58 | 45.3 | 2.36 | 2.3 | 2.74 | 2.8 | 172~175 |
| Eu(TTA)$_3$(5-methyl-phen) | 44.01 | 43.9 | 2.20 | 2.1 | 2.77 | 2.8 | 231~232 |

spatula in a glass vessel put in front of the polychromator slit. For PL experiments, the compounds in the same glass vessel were irradiated by Hg lamp (366nm). Emission spectra obtained were corrected for the instrumental response. All experiments were done at room temperature in air.

## RESULTS AND DISCUSSION

Out of the four complexes in Fig.1, only Eu(TTA)$_3$(phen) was found to show ML, which was strong enough to be visible in daylight, placing the compound among the most intense mechanoluminescent solids. Figure 2 shows the ML spectrum of Eu(TTA)$_3$(phen) together with its PL spectrum. The two spectra are almost identical except for the difference in magnitude around 616nm. PL of europium complexes are known to originate from europium ion$^{7)}$. The similarity between the ML and PL spectrum of Eu(TTA)$_3$(phen) shows that the former is also attributable to the emission from europium ion. The slight difference around 616nm may be explained by an effect of the mechanical stress perturbing the ligand field surrounding europium ion$^{7)}$, changing the relative strength of the emission lines.

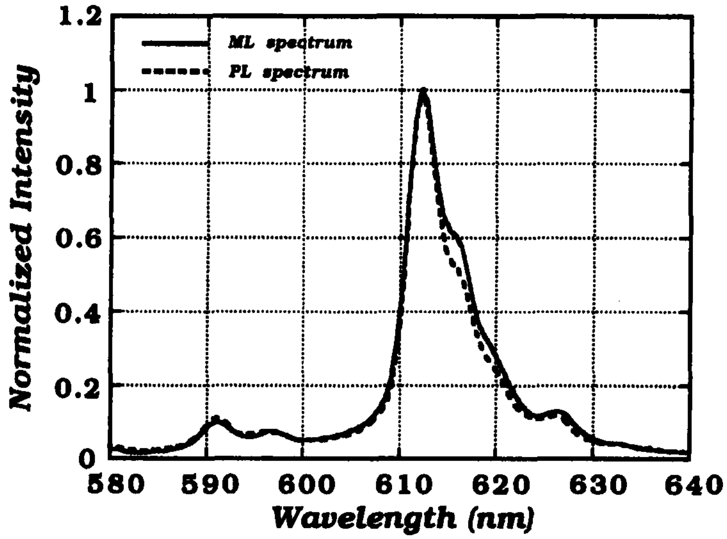


FIGURE 2 ML and PL spectra of Eu(TTA)$_3$(phen)
(slit : 0.1mm)

For ML, three excitation mechanisms have been mainly proposed: frictional electrification$^{8)}$, discharge$^{9)}$ and piezoelectricity$^{10)}$. We discuss these possibilities on the basis of our results. The first one is the excitation caused by frictional electrification between the complexes and grinding rod. We checked this by using four different materials for grinding: steel, glass, plastic and wood, which should give different extent of frictional electrification. No difference was found among the four, however, excluding this possibility. There still remains a possibility that an interaction between the complex and the glass vessel or between crystallites of the complex causes frictional electrification. Also internal electrification caused by cracking in crystal should be considered.

The second possibility is the discharge of atmospheric gas, which was shown to be responsible for the ML of such compounds as sucrose[9]. In the present case, however, the fact that the ML spectrum agreed with that of PL eliminates this possibility.

The third possibility is the deformation of crystal, in other words, piezoluminescence. In crystals of polar space groups, externally applied mechanical energy generates piezoelectric charges on the crystal surface along the direction of polarity, which results in the creation of a high electric field. This high electric field might be large enough to produce electronically excited states by certain mechanisms involving electron impact or generation molecular excitons[11]. In order to elucidate the possibility of piezoluminescence, the analysis of crystal structures and piezoelectric properties should be important. These works are currently under way.

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