

X-ray powder diffractometry and NMR studies of europium-dibenzoylmethane complexes

J. Ts. Zaharieva, M. M. Milanova, N. Vasilev¹, B. Morgenstern², D. S. Todorovsky*

Faculty of Chemistry, University of Sofia, 1, J. Bourchier Blvd., Sofia 1164, Bulgaria

¹*Institute of Organic Chemistry, Bulgarian Academy of Sciences, Acad. G. Bonchev Str., Bl. 9, Sofia 1113, Bulgaria*

²*Chair of Inorganic Chemistry, Saarland University, 66123 Saarbrücken, Germany*

Received November 8, 2010; Accepted January 12, 2011

The X-ray powder diffractogram of the europium complex $\text{Eu}(\text{DBM})_3$ (DBM – dibenzoylmethane) is reported for the first time. It is shown that the mixed-ligand complex $\text{Eu}(\text{DBM})_3\text{dpp}$ (dpp - 1,4-diphenyl-1,10-phenanthroline) is X-ray amorphous. The ^1H and ^{13}C NMR spectra of $\text{Eu}(\text{DBM})_3$, $\text{Eu}(\text{DBM})_3\text{phen}$ (phen – 1,10-phenanthroline) and $\text{Eu}(\text{DBM})_3\text{dpp}$ are interpreted and their applicability as a tool for evaluation of the stoichiometry of the complexes, the content of water and the completeness of the synthetic reaction is shown.

Key words: europium complexes, ^1H , ^{13}C NMR spectroscopy, X-ray diffractometry.

1. INTRODUCTION

Due to their fluorescent properties, the complexes of lanthanides (Ln) with β -diketonates (incl. dibenzoylmethane, HDBM) have a lot of applications [1] as active components of organic LED, laser materials, NMR shift reagents, luminescent labels in biomedical investigations, optical sensors, promising materials for high-density recordable optical materials, etc. Europium β -diketonates are distinguished due to their narrow emission bands resulting from the electron transition between 4f levels. The organic components of the complexes, efficient photon absorbers, play the role of “antenna”, transferring the energy to the $^5\text{D}_0$ long-lived visible light emitted state of the metal ion, thus giving significant advantage of Eu(III) when used as spectroscopic probe [1].

Recently the chemistry and application of the lanthanide diketonates have been object of the reviews [2, 3]. Some peculiarities of the lanthanide dibenzoylmethanates synthesis have been discussed in [4]. The literature data on their crystal structure are limited due to the difficulties to be obtained in crystal state. Some β -diketonates cannot be prepared in such a state even if they are produced by a solid state reaction [5]. Results from X-ray crystal structure determination are published for the mixed-ligand, DBM-containing complex $\text{Eu}(\text{NO}_3)(\text{DBM})_2(\text{TBPO})_2$, where TBPO –

triphenylphosphine oxide [1]. Tetrakis-complexes can be prepared relatively easier in crystal state. The structure of tetrakis (dibenzoylmethanato) europates has been studied in relation to triboluminescence phenomena observed with some of them. Crystals have been prepared by the Hurt's method [6] (for example by the reaction of EuCl_3 and dibenzoylmethane with morphine in absolute ethanol [7]). As a counter ion triethylammonium [7-9], dimethylbenzyl ammonium [10-12], 2-hydroxyethylammonium and pyrrolidinium [12] were used (the structure of the compounds with the two latter ions is not reported). Recently, the structure of tetrabutylammoniumtetrakis(dibenzoylmethanato) europium(III)/dimethyl sulfoxide (1:1) has been reported [13].

However, to our best knowledge, the only published X-ray powder diffraction data (without exact values of interplanar distances and relative intensities) for complexes of the type $\text{Ln}(\text{DBM})_3$ (Ln–lanthanides) are those for La- and Tb-dibenzoylmethanates [5].

The first ^1H and ^{13}C NMR data for anhydrous tris(dibenzoylmethanato)(o-phenanthroline)-europium(III) complexes are reported in [14] in rather general form. No spectra, neither detailed assignment of the shifts is given. Data on $\text{Eu}(\text{DBM})_3$ and DBM-4,7-diphenyl-1,10-phenanthroline are not available.

In the present paper the results from X-ray powder diffractometry and ^1H and ^{13}C NMR spectroscopy observations of $\text{Eu}(\text{DBM})_3$ and of

* To whom all correspondence should be sent:
E-mail: nhdt@wmail.chem.uni-sofia.bg

complexes of the type $\text{Eu}(\text{DBM})_3\text{Q}$ (Q - 1,10-phenanthroline /Phen/ or 4,7-diphenyl-1,10-phenanthroline /dpp/) are reported.

2. EXPERIMENTAL

Materials

HDBM (purum, > 98 %, Fluka), 1,10-phenanthroline (phen, 99 %) and 4,7-diphenyl-1,10-phenanthroline (dpp, >98 %), both from Alfa Aesar and $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ (>99 %, Fluka) as starting materials and ethanol (> 96 %) as a solvent were used for complexes production.

Complexes preparation

$\text{Eu}(\text{DBM})_3$ was prepared by the method proposed in [15]. To 48 cm³ of an ethanol solution containing 6 mmol HDBM, 12 cm³ 0.5 M NaOH and 10 cm³ aqueous solution containing 2 mmol EuCl_3 were added. The solution was boiled at reflux (60 °C) and stirred for 4 h. The formed crystals were filtered and dried at 110 °C for 7 h under vacuum and were stored in a vacuum desiccator. The content of H and C was determined by means of the elemental analyzer Vario EL III V5.018 and for a product stored for 2 months, the following percent content was found: H 4.44, C 65.19; calculated for $\text{Eu}(\text{DBM})_3$: H 4.40, C 65.53.

$\text{Eu}(\text{DBM})_3\text{phen}$ and $\text{Eu}(\text{DBM})_3\text{dpp}$ were synthesized by the method [16]. Saturated ethanol solutions of EuCl_3 and of DBM were mixed and a 0.5 M aqueous solution of NaOH was added adjusting DBM: EuCl_3 mole ratio = 3 and pH = 6. The solution was stirred at ambient conditions for 4 h; the crystals formed were filtered, washed with absolute ethanol and dried at room temperature. Ethanol solution of 1,10-phenanthroline or 4,7-diphenyl-1,10-phenanthroline was added to the crystals, the suspension was stirred for 4 h, filtered, the separated crystals were washed with absolute ethanol, and dried in a desiccator over silica gel at reduced pressure.

X-ray diffractometry

The X-ray powder diffractograms were taken on a powder diffractometer Siemens D500 at CuK_α , 40 kV, 2θ step 0.02°/2s.

NMR spectroscopy

¹H and ¹³C NMR spectra of the complexes were recorded using a Bruker DRX Avance 400 MHz NMR spectrometer (resonance frequencies: 400.13 MHz for ¹H and 100.6 MHz for ¹³C{¹H}). Chemical shifts were given in ppm relative to

tetramethylsilane (dimethylformamid-d₇, DMF) as internal standard ($\delta = 0$ ppm) or on a Bruker Avance DRX250 instrument in CD₃Cl solution. The spectra were referred to the solvent signal. The assignment of the ¹H and ¹³C spectra was accomplished by measurement of DEPT-135 and 2D inverse detected heteronuclear (C-H) correlation (HSQC for DRX250 or HMQC for the DRX400).

$\text{Eu}(\text{DBM})_3$: ¹H NMR (400.13 MHz, DMF-d₇, 21° C): $\delta = 2.35$ (s, 1H, 2-CH), 5.55(d, J=7.2Hz, 4H, o-Ph), 6.65(t, J=7.2Hz, 4H, m-Ph), 6.77(t, J=7.2Hz, 2H, p-Ph). ¹³C NMR (100.6 MHz, DMF-d₇, 21° C): $\delta = 58.7$ (2-CH), 94.1(i-Ph), 124.4(o-Ph), 125.2(m-Ph), 131.3(p-Ph), 165.6(C=O).

$\text{Eu}(\text{DBM})_3\text{phen}$: ¹H NMR (250 MHz, CDCl₃, 25° C): $\delta = 3.22$ (s, 3H, 2-CH), 6.19(bs, 12H, o-Ph), 6.84(bs, 18H, m-Ph and p-Ph), 8.94(d, J=7.5Hz, 2H, 3,8-H), 10.19(bs, 2H, 2,9-H), 10.61(s, 2H, 5,6-H), 10.96(d, J=7.7Hz, 2H, 4,7-H). ¹³C NMR (69 MHz, CDCl₃, 25° C): $\delta = 60.2$ (2-CH), 93.1(i-Ph), 109.6(3,8-C), 116.8(4a,6a-C), 124.6(m-Ph), 124.8(o-Ph), 129.3(5,6-C), 130.8(p-Ph), 150.3(4,7-C), 168.1(10a,10b-C), 173.0(C=O), 180.3(2,9-C).

$\text{Eu}(\text{DBM})_3\text{dpp}$: ¹H NMR (250 MHz, CDCl₃, 25° C): $\delta = 3.26$ (s, 3H, 2-CH), 6.22(bs, 12H, o-Ph), 6.86(bs, 18H, m-Ph and p-Ph), 8.09(bs, 2H, p-Ar), 8.36(bs, 4H, m-Ar), 8.90(bs, 2H, 3,8-H), 9.06(bs, 4H, o-Ar), 10.13(bs, 2H, 5,6-H), 11.34(s, 2H, 2,9-H). ¹³C NMR (69 MHz, CDCl₃, 25° C): $\delta = 60.7$ (2-CH), 93.6(i-Ph), 110.8(3,8-C), 111.5(4a,6a-C), 124.6(m-Ph), 124.8(o-Ph), 126.4(5,6-C), 129.7(m-Ar), 130.0(p-Ar), 130.8(p-Ph), 133.1(o-Ar), 162.4(10a,10b-C), 173.7(C=O), 183.2(2,9-C).

3. RESULTS AND DISCUSSION

X-ray diffractometry

The X-ray diffractogram of the powdered $\text{Eu}(\text{DBM})_3$ is shown on Fig. 1. The interplanar distances (d) and the relative intensities of the

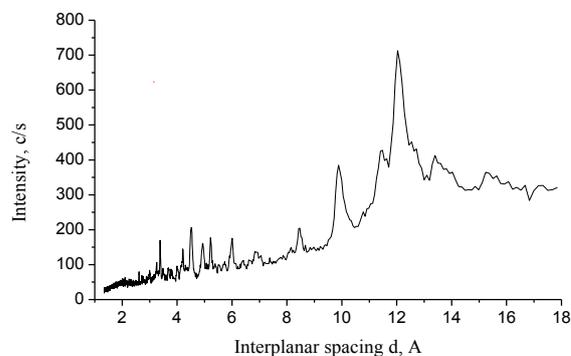


Fig. 1. X-ray diffractogram of $\text{Eu}(\text{DBM})_3$.

peaks are shown in Table 1 compared with the data for HDBM (JCPDS 34-1688), La(DBM)₃ and Tb(DBM)₃ evaluated from the X-ray diffractogram picture reported in [5]. It is seen that the diffractograms of the complexes of the different lanthanides are similar and rather different from that of the pure ligand. The interplanar distances are large as could be expected accounting for the large ligand size. The crystallization is not completed and X-ray amorphous phase exists in the sample studied. Introducing an additional large ligand in

Eu(DBM)₃.dpp inhibits the crystallization and the complex is X-ray amorphous.

NMR spectroscopy

The coordination mode of the lanthanide ion in solution was examined by measuring ¹H, ¹³C, ¹³C DEPT and ¹H,¹³C-HSQC (250 MHz)/HMQC (400 MHz) NMR spectra of the complexes. All NMR spectra confirmed the structure and purity of the target complexes.

Table 1. Interplanar distances (d, Å) and relative intensities (I, %) for dibenzoylmehane (HDBM) and Ln(DBM)₃

| HDBM (JCPDS 32-1641) | | La(DBM) ₃ [5] ¹ | | Tb(DBM) ₃ [5] ¹ | | Eu(DBM) ₃ | |
|----------------------------|-----|---------------------------------------|-----|--|-----|----------------------|-----|
| d | I | d | I | d | I | d | I |
| 5.41 | 90 | 11.00 | 100 | 15.40 | 100 | 15.23 | 51 |
| 5.27 | 30 | 6.62 | 61 | 12.83 | 67 | 13.41 | 57 |
| 5.20 | 100 | 5.50 | 72 | 7.70 | 74 | 12.02 | 100 |
| 4.52 | 40 | 4.81 | 60 | 7.00 | 51 | 11.48 | 19 |
| 4.30 | 18 | 4.28 | 86 | 5.13 | 69 | 9.88 | 68 |
| 4.11 | 40 | 4.05 | 51 | 4.53 | 65 | 8.47 | 22 |
| | | | | | | 6.90 | 15 |
| 3.97 | 25 | 3.67 | 68 | 3.85 | 73 | 6.01 | 26 |
| 3.84 | 10 | 3.50 | 64 | 3.50 | 75 | 5.21 | 30 |
| 3.619 | 65 | 3.35 | 31 | 3.21 | 61 | 4.93 | 23 |
| 3.368 | 14 | 3.21 | 51 | 3.08 | 75 | 4.52 | 42 |
| 3.132 | 25 | 3.08 | 48 | 2.96 | 43 | 4.20 | 18 |
| | | 2.85 | 55 | | | 3.38 | 35 |
| | | | | | | 3.26 | 13 |

¹The data are evaluated from the published diffractogram [5].

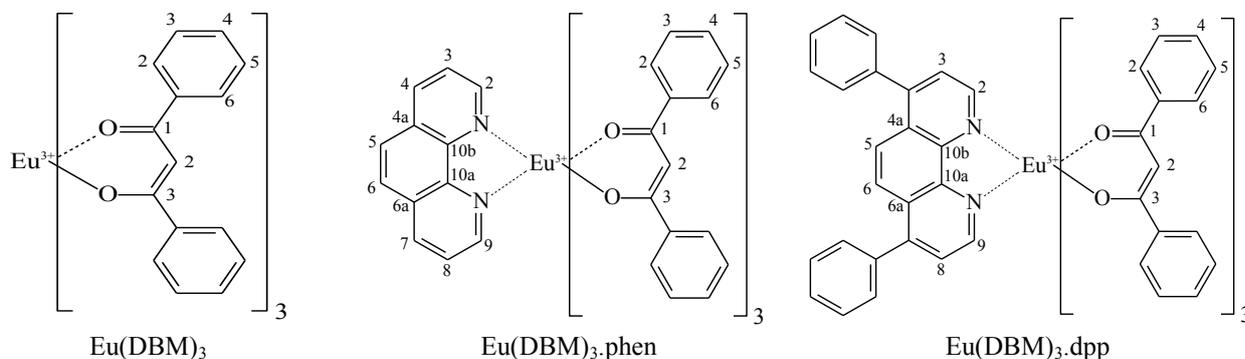


Fig. 2. Structure and numbering of the studied complexes.

The structure and numbering of the studied complexes are shown on Fig. 2. The peaks assignments are presented in the experimental section.

The integral intensity of the peaks in proton spectra is in good agreement with the number of hydrogen atoms in the studied complexes. The signals at 2.30 ppm in Eu(DBM)₃, 3.22 ppm in Eu(DBM)₃.phen and 3.26 ppm in Eu(DBM)₃.dpp were assigned to 2-CH protons in the complexes.

Recently, chemical shifts of β-protons in Eu(III) complexes with β-diketonates were reported in the range of 2.74 to 3.43 ppm [17]. The peaks of aromatic protons for the Eu(III) complexes are shifted to a higher field, compared to the same peaks in the spectra of the starting ligands. That is due to the strong paramagnetic properties of the Eu(III) ions which usually deshield the adjacent nuclei in the second coordination sphere. In the studied complexes the ligands are directly

coordinated to Eu(III) and the Fermi contact term is expected to prevail over the pseudocontact shifts and therefore the resonances are shifted upfield [18]. In fact, such kind of β -diketonate complexes of Eu(III) are lanthanide shift reagents and can be used for transforming second order NMR spectra into first order [18].

The expected ^1H NMR resonances of aromatic protons are significantly broadened upon coordination. There is no change in the symmetry of ligands upon coordination and all resonances are in the same form and position as for free ligands, indicating uniform interaction of all C=O groups with Eu(III) ion within the ^1H NMR time scale.

All ^1H and ^{13}C NMR spectra of $\text{Eu}(\text{DBM})_3$, $\text{Eu}(\text{DBM})_3\cdot\text{phen}$ and $\text{Eu}(\text{DBM})_3\cdot\text{dpp}$ complexes are clean from peaks of free ligands, indicating the completeness of the complexation process.

Determination of the content of water in the complex is possible comparing the signal intensities of the shifts at 2.3 ppm (s, 3H, 2-CH) and at 3.96 ppm in the spectrum taken from solution of the complex in dry DMF. The latter signal belongs to hydrogen which is not correlated with carbon and is ascribed [4] to the hydrogen from water. (The proton from the enolic form of the ligand, the only alternative source of the 3.96 ppm shift, exhibits at 16.89 ppm [14]). It was shown by this way that a complex dried at a pressure of ~ 3 kPa contains ~ 1 mol $\text{H}_2\text{O}/\text{mol}$ complex. The routine synthetic procedure, described in the Experimental part, requires the drying to be performed at 0.7 Pa. If this procedure is followed, the final product is practically anhydrous.

4. CONCLUSIONS

The X-ray powder diffraction pattern of $\text{Eu}(\text{DBM})_3$ is reported for the first time. ^1H , ^{13}C spectra of $\text{Eu}(\text{DBM})_3$, $\text{Eu}(\text{DBM})_3\cdot\text{phen}$ and $\text{Eu}(\text{DBM})_3\cdot\text{dpp}$ are interpreted in details. The capability of the NMR study concerning determination of stoichiometry of the complexes, coordination mode, presence of water and free ligands in the final product is shown.

The measured ^1H and ^{13}C NMR and ^1H , ^{13}C HSQC spectra of $\text{Eu}(\text{DBM})_3$ in DMF- d_7 , $\text{Eu}(\text{DBM})_3\cdot\text{phen}$ in CDCl_3 and of $\text{Eu}(\text{DBM})_3\cdot\text{dpp}$ in CDCl_3 are available as

supporting materials from the authors upon request.

Acknowledgements: The work is performed with the financial support of the Bulgarian Fund for Scientific Investigation (contract VUH 05/2005) and by the contract for bilateral co-operation between the Saarland University and University of Sofia.

REFERENCES

1. J.-C. G. Bünzli, E. Moret, V. Foiret, K. J. Schenk, W. Mingzhao, J. Linpei, *J. Alloys Comp.* **207/208**, 107 (1994).
2. K. Binnemans, in: Handbook on the Physics and Chemistry of Rare Earths, Vol. 35, K.A. Gschneidner, Jr., J.-C.G. Bünzli, V.K. Pecharsky Eds., Chapter 225, p. 111, Elsevier, 2005.
3. K. Binnemans, *Chem. Rev.* **109**, 4283 (2009).
4. J. Zaharieva, M. Milanova, D. Todorovsky, Synthesis Reactivity Inorganic, Metal-Organic, Nano-Metal Chemistry (2010) (in press).
5. Lu Jingci, Y. Kelan, Ch. Junsheng, L. Chongshan, Su Qingde, *J. Shanghai Univ.* **3**, 167 (1999).
6. C. R. Hurt, N. McAvoy, S. Bjorklund, N. Filipescu, *Nature*, **212**, 179 (1966).
7. Xi-R. Zeng, R.-G. Xiong, X.-Z. You, K. K. Cheung, *Inorg. Chem. Commun.* **3**, 341 (2000).
8. L. M. Sweeting, A. L. Rheingold, *J. Am. Chem. Soc.*, **109**, 2562 (1987).
9. F. A. Cotton, L. M. Daniels, P. Huang, *Inorg. Chem. Commun.*, **4**, 319 (2001).
10. L. M. Sweeting, A. L. Rheingold, *J. Phys. Chem.* **92**, 5648 (1988).
11. X.-F. Chen, X.-H. Zhu, R. S. S. Sundara, S. Ozturk, H.-K. Fun, X.-Z. You, *J. Mater. Chem.*, **9**, 2919 (1999).
12. R.-G. Xiong, X.-Z. You, *Inorg. Chem. Commun.*, **5**, 677 (2002).
13. M. Milanova, J. Zaharieva, B. Morgenstern, K. Hegetschweiler, D. Todorovsky, *Z. Kristallogr.*, NCS 225 (2010), 17-22/ DOI 10.1524/ncrs.2010.008.
14. M. O. Ahmed, J.-L. Liao, X. Chen, S.-An Chen, J. H. Kaldis, *Acta Cryst.*, **E59**, m29-m32 (2003).
15. L. R. Melby, N. J. Rose, E. Abramson, J. C. Caris, *J. Am. Chem. Society*, 5117 (1964).
16. Q.G. Meng, L.S. Fu, S.B. Wang, H. J. Zhang, H. R. Li, X. H. Chuai, Y.H. Li, S.Y. Zhang, *Thin Solid Films* **388**, 87 (2001).
17. S. Stanimirov, A. Vasilev, E. Haupt, I. Petkov, T. Deligeorgiev, *J. Fluoresc.*, **19**, 85 (2009).
18. S. P. Babailov, Yu. G. Krieger, *J. Structural Chem.*, **39**, 580 (1998).

РЕНТГЕНО-ДИФРАКТОМЕТРИЧНИ И ЯМР ИЗСЛЕДВАНИЯ НА ЕВРОПИЕВИ ДИБЕНЗОИЛ-
МЕТАНАТИ

Й. Цв. Захариева, М. М. Миланова, Н. Василев¹, Б. Моргенщерна², Д. Ст. Тодоровски*

Химически факултет, Софийски университет, бул. Дж. Баучер 1, София 1164, България

¹ *Институт по органична химия с Център по фитохимия, Българска академия на науките, ул. Г. Бончев, бл. 9,
София 1113, България*

² *Катедра Неорганична химия, Саарландски университет, Саарбрюкен 66123, Германия*

(Резюме)

В работата за пръв път се съобщават праховите рентгенограми на комплекса на европия $\text{Eu}(\text{DBM})_3$ (DBM – дибензоилметан). Показано е, че смесено-лигандният комплекс $\text{Eu}(\text{DBM})_3.\text{dpp}$ (dpp – 1,4-дифенил-1,10-фенантролин) е рентгено-аморфен. ^1H и ^{13}C ЯМР спектрите на $\text{Eu}(\text{DBM})_3$, $\text{Eu}(\text{DBM})_3.\text{phen}$ (phen – 1,10-фенантролин) и $\text{Eu}(\text{DBM})_3.\text{dpp}$ са интерпретирани и е показана тяхната приложимост като средство за оценяване на стехиометрията на комплексите, съдържанието на вода в тях и пълнотата на реакцията на синтез.