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Heteronuclear Eu:Cu trichloroacetate and its polynuclear Eu analogue; their spectroscopy and magnetism

J. Legendziewicz*, M. Borzechowska
Faculty of Chemistry, University of Wrocław, 14 F. Joliot-Curie Str., 50-383 Wrocław, Poland

Abstract

Single crystals of europium trichloroacetates of formulae $Eu(CCl_3COO)_3 \cdot 2H_2O$ (**1**) and $CuEu_2(CCl_3COO)_8 \cdot 6H_2O$ (**2**) were obtained. They are isomorphic with the respective Er and (Nd:Cu) compounds. Absorption, excitation, emission as well as magnetic susceptibility measurements in the 1.7–300 K range were carried out. The spectroscopic and magnetic data were analysed. The absorption spectra of compounds **1** and **2** at room and low temperature were compared and the differences in the splitting of the levels described as a result of the CF effect and the effect of the d-electron ion. The emission of Eu^{3+} was completely quenched in the heteronuclear single crystal (**2**) at 293 and 77 K. The oscillator strengths of the f–f transitions were calculated and the radiative processes analysed. Weak vibronic components recorded in the low-temperature excitation and emission spectra were promoted by localised M–L and internal ligand modes. The number of Stark components of the $L'S'J'$ levels in both systems (**1** and **2**) was analysed and the symmetries of the metal centres determined and compared with the results of X-ray analysis. The value of the splitting of the first excited state, $^7F_1$, was used to explain the LT and HT magnetic properties of the systems under investigation. The role of the heteroatom was considered and related to the data of earlier reported respective systems. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Heteronuclear Eu:Cu trichloroacetate; Europium trichloroacetate; Absorption spectroscopy; Luminescence; Magnetism

1. Introduction

In the past two decades a number of heteropolymetallic compounds have been described with the objective of designing novel molecular materials [1–7]. The presence of lanthanides in these compounds plays an important role in modulating the magnetic and spectroscopic properties.

With the aim of gaining insight into the nature and mechanism of 4f–3d metal ion interactions we have synthesised a series of polynuclear (**1**) and Ln:Cu heteronuclear (**2**) trichloroacetates [6–12]. Spectroscopic [7–12], EPR [9,13–16] and magnetic data for the Pr, Nd and (Pr, Nd:Cu) [7–9] systems were reported recently. We now present the results for their europium analogues. Europium compounds were chosen because the $^7F_0$ ground state multiplet and the $^5D_0$ emitting level are nondegenerate. Thus, this ion is especially useful as an optical probe of the ligand and crystal field perturbation on the 4f-electron energy levels and the radiative transition probabilities. Since for the ground state $J = 0$, at low temperatures it is nonmagnetic. Thus, in a heteronuclear system the long range ion–ion interaction can be additionally investigated.

2. Experimental

Polymeric single crystals of $Eu(CCl_3COO)_3 \cdot 2H_2O$ (**1**) and their heteronuclear analogue $CuEu_2(CCl_3COO)_8 \cdot 6H_2O$ (**2**) were synthesised according to the previously described procedure [6,10]. The samples were checked by X-ray analysis before magnetic and spectroscopic measurements. The polymeric trichloroacetates (**1**) are isomorphic with the erbium complex [17]. The heteronuclear compound (**2**) has a similar structure to that previously reported for the Cu:Nd crystal [6].

The absorption spectra were recorded in the 250–1600 nm region at 293 and 4 K using a Cary–Varian 5 spectrophotometer equipped with a helium (Oxford) cryostat. Intensities of the f–f and d–d transitions were calculated and transformed to the oscillator strength values. Magnetic susceptibility measurements were carried

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*Corresponding author. Tel.: +48-71-320-4300; fax: +48-71-328-2348.
E-mail address: jl@wchuwr.chem.uni.wroc.pl (J. Legendziewicz)

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out with a SQUID magnetometer down to 1.7 K in both the low-field and high-field regime. The data were corrected for diamagnetic contributions using Pascal constants.

3. Discussion

Europium trichloroacetate is isomorphic with erbium trichloroacetate [17] and its structure is composed of centrosymmetric dimeric units of two Eu^{3+} bridged by carboxyl groups. These dimeric units are further linked by carboxyl bridges and water molecules to endless chains so that they can be treated as a polynuclear system. The two different centrosymmetric dimeric subunits exist in the chain with two structurally nonequivalent europium centers. Its heteronuclear analoque also forms endless chains in the structure, but composed of noncentrosymmetric units of two Eu^{3+} bridged by carboxyl groups and further coupled by octahedrally coordinated Cu^{2+}. This latter structure is isomorphic with $CuNd_2(CCl_3COO)_8 \cdot 6H_2O$ [6]. The fitting procedure of the coordination polyhedra of the two metal centers in structure **1** shows distorted SAP polyhedra for Er(1) and Er(2) with a better Δ factor (described by the Drew method [18]) compared with the other polyhedra. However, in structure **2** the two metal ions in the noncentrosymmetric units can be described as CSAP for Nd(1) with C.N. 9 and Dod for Nd(2) with C.N.8. Thus, in the former case the symmetry of Eu^{3+} is close to C_{2v} with a different distortion of the coordination polyhedra for the two metal sites (see Table 1). In the latter compound the symmetry of Eu^{3+} would correspond to C_{2v}, D_2 or to the lower C_2 symmetry. These results will be correlated later with the spectroscopic determination on the basis of group theory.

Absorption spectra of europium trichloroacetate are given in Ref. [19] (**1**) and those of heteronuclear trichloroacetate (**2**) are shown in Figs. 1 and 2. The absorption bands observed in these spectra correspond to transitions from the $^7F_0$ ground state multiplet to the excited ^5D_J, ^5L_J and ^5G_J ^5H_J levels, but also from the first $^7F_1$ and second $^7F_2$ multiplets. For the europium heteronuclear analogue (**2**) the absorption spectrum is dominated by the d–d transitions of Cu^{2+} with high intensities (see Table 2) and in the UV region by the L→M C-T states of both Eu^{3+} and Cu^{2+}. A comparison of the two types of spectra of compounds **1** and **2** points to a lower energy of the C-T state for Cu^{2+}. Both the d–d and C-T transitions can play an important role in quenching the Eu^{3+} inter-ion emission. Let us analyse the energies of the f–f transitions in both of the above spectra at 293 and 4 K. The energy of separated lines is shifted towards the IR region for **2**, which may be caused by stronger bonding in the heteronuclear compound. The splitting of levels, for example between $^7F_0$ and $^7F_1$, also differs in both systems and is 355 and 374 for **1** and **2**, respectively. Moreover, in the near-IR region, two bands were recorded (at 1400 and 1800 nm) for **2**, which correspond to the $^7F_0 \rightarrow {}^7F_6$ (18 006) transition and internal ligand vibrations (overtones) (1400 and 1800 nm). Although low-temperature (4 K) spectra were recorded for compound **2**, the doublet splitting of the bands (given by noncentrosymmetric dimeric units in the structure) is not well manifested because of the low intensities of the f–f transitions of Eu^{3+} (two orders of magnitude). Such splitting was excellently detected in the $^3H_4 \rightarrow {}^3P_0$ transition at 4 K [8] of the praseodymium (**2**) analogue. The components of the $^7F_0 \rightarrow {}^5D_2$ transition (splitting 59.2 cm^{-1}), composed of five components, were relatively well determined. The splitting of that transition in **1** is 56 cm^{-1}. The results of intensity calculations of the f–f and d–d transitions according to the procedure described in Ref. [20] are shown in Table 2 for two temperatures, 293 and 4 K. Note the drastic decrease of the d–d band intensities at 4 K, reflecting its vibronic nature [7,8,21]. Note also the intensity increase of selected f–f bands at 4 K, again demonstrating depopulation of the $^7F_1$ and $^7F_2$ levels at low temperatures resulting in a population increase of the $^7F_0$ level and, consequently, the intensities from the ground state also increase. Table 3 presents the splitting of the d–d bands due to the J–T effect. It is worth noting the decrease of the splitting going from Pr to Gd in the series of heteronuclear trichloroacetates. This means that the distortion of the O_h symmetry becomes lower. The population of the $^7F_1$ levels at 70 K is 0.07 and 0.06% for **1** and **2**, respectively. This has a strong consequence for the magnetic properties of both types of compounds (**1** and **2**). Also, the splitting of the $^7F_1$ multiplet plays an important role in the magnetic properties. Table 4 shows the energies of the $^7F_0$ level of compounds **1** and **2**, as well as the energies of separated Stark components of other ^7F_J levels in emission. Let us correlate the site symmetry determined from the emission spectrum of compound **1** (see Fig. 3) with that described by X-ray analysis and compare it to the respective results for compound **2**, but based on analysis of the absorption spectra (at 293 and 4 K). The emission spectrum of **1** at 77 K shows one broad, three, five, and nine (7+2 weak) components of the $^5D_0 \rightarrow {}^7F_J$ transitions.

Table 1
Results of the fitting procedure of coordination polyhedra determined by the Drew method [18]

Compound	Position	C.N.		Δ
$Nd_2Cu(CCl_3COO)_8 \cdot 6H_2O$	Nd(1)	9	CSAP	0.1155
			TCTP	0.12446
	Nd(2)	8	Dod	0.08299
			SAP	0.31693
$Er(CCl_3COO)_3 \cdot 2H_2O$	Er(1)	8	SAP	0.04274
			Dod	0.12134
	Er(2)	8	SAP	0.20316
			Dod	0.41528

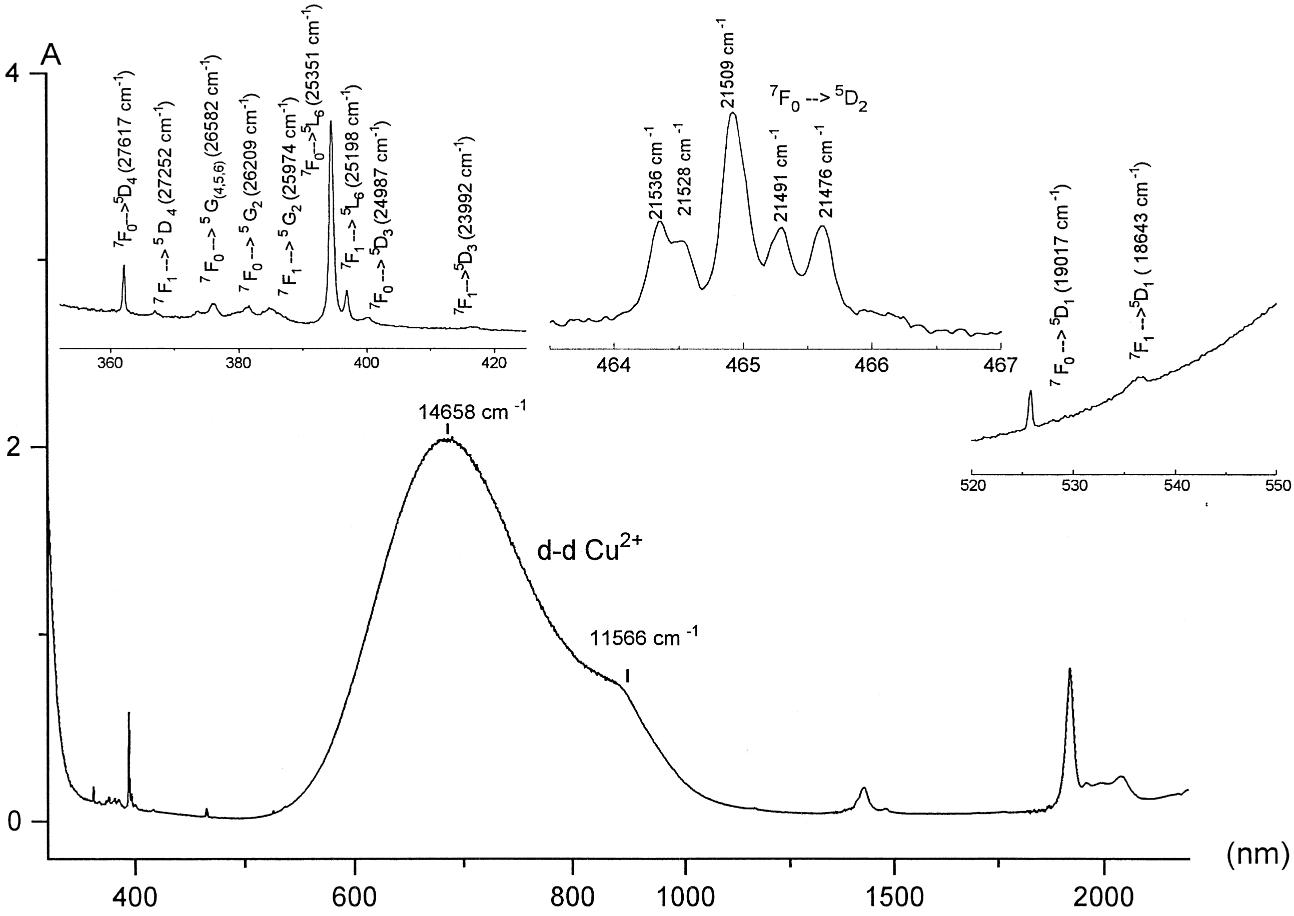

Fig. 1. Absorption spectrum of $CuEu_2(Cl_3CCOO)_8 \cdot 6H_2O$ at 293 K.

Since the 0–0 transition is strongly forbidden in the D_{2d} and D_2 symmetry, the closest point symmetry for the Eu metal site in **1** may be C_{2V}, because the 0–0 transition was detected and is allowed by both magnetic and electric dipole selection rules in this symmetry. Furthermore, the number of remaining components observed in the spectra corresponds to that predicted by group theory.

Much more difficult is the analysis of Stark components in the absorption spectra because of the smaller splitting of the higher excited levels as well as the d–d bands which

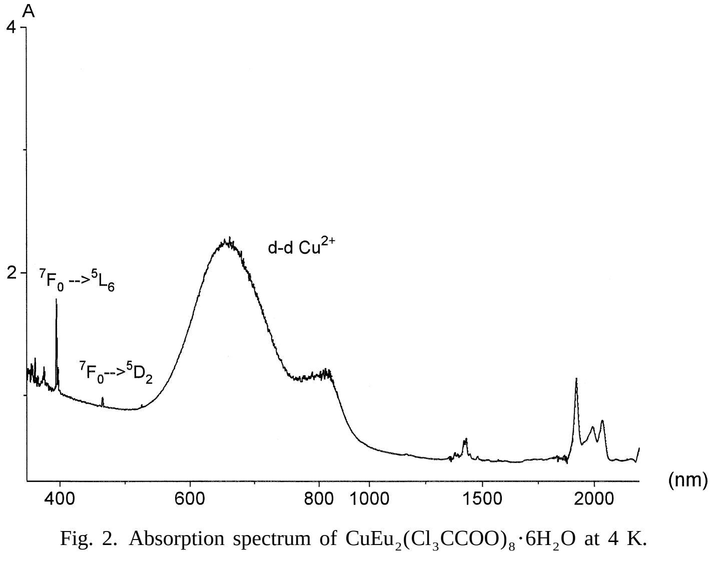

Fig. 2. Absorption spectrum of $CuEu_2(Cl_3CCOO)_8 \cdot 6H_2O$ at 4 K.

Table 2
Oscillator strength values of the f–f ($P \times 10^8$) and d–d ($P \times 10^6$) transitions for Eu and Cu:Eu trichloroacetate crystals at different temperatures

	$Eu(Cl_3CCOO)_3 \cdot 2H_2O$			$CuEu_2(Cl_3CCOO)_8 \cdot 6HO$		
	293 K		4.2 K	293 K		4.2 K
	Energy (cm^{-1})			Energy (cm^{-1})		
$P \times 10^8$						
$^7F_1 \rightarrow {}^5D_0$	16 941	0.75				
$^7F_0 \rightarrow {}^5D_0$			0.11			
$^7F_1 \rightarrow {}^5D_1$	18 656	2.71		18 643	1.43	
$^7F_0 \rightarrow {}^5D_1$	19 012	1.47	1.38	19 017	1.27	
$^7F_0 \rightarrow {}^5D_2$	21 453	7.41	7.30	21 476	8.15	12.33
	21 464			21 491		
	21 485			21 509		
	21 495			21 528		
	21 511			21 536		
$^7F_1 \rightarrow {}^5D_3$	24 033	4.05		23 992	4.41	
$^7F_0 \rightarrow {}^5L_6$	25 358	212.89	165.62	25 351	155.69	225.91
$^7F_1 \rightarrow {}^5G_2$	25 980	47.65		25 974	27.70	
$^7F_0 \rightarrow {}^5G_2$	26 240	46.51		26 209	28.28	
$^7F_0 \rightarrow {}^5G_{(4,5,6)}$	26 613	41.58	41.48	26 582	26.77	
$^7F_1 \rightarrow {}^5D_4$	27 270	5.06		27 252	5.26	
$^7F_0 \rightarrow {}^5D_4$	27 617	22.60	18.51	27 617	20.05	
$P \times 10^6$						
d–d				11 566	498.94	416.14
				14 658		

Table 3
Splitting of d–d bands due to the J–T effect

	Splitting of the d–d band (cm^{-1})
$CuPr_2(Cl_3CCOO)_8 \cdot 6H_2O$	3399
$CuNd_2(Cl_3CCOO)_8 \cdot 6H_2O$	3306
$CuSm_2(Cl_3CCOO)_8 \cdot 6H_2O$	3179
$CuEu_2(Cl_3CCOO)_8 \cdot 6H_2O$	3092
$CuGd_2(Cl_3CCOO)_8 \cdot 6H_2O$	3104

overlap the transition from $^7F_0$ to $^5D_1$ and also from $^7F_1$ and $^7F_2$ to the $^5D_0$ and $^5D_1$ levels. The best line resolution in the spectra of **2** is in the $^7F_0 \rightarrow {}^5D_2$ transition range. This band is split into five relatively broad components confirming two metal centers in the dimer unit. A comparison of the excitation and absorption spectra of compounds **1** and **2** in the $^7F_0 \rightarrow {}^5D_2$ transition region shows differences that correspond with the X-ray data [6,17]. Although the number of components remains the same, the distribution of their intensity is different.

Table 4
Transition energies (cm^{-1}) of the luminescence spectrum of $Eu(Cl_3CCOO)_3 \cdot 2H_2O$ (**1**)

Transition	Energies (cm^{-1})
$^5D_0 \rightarrow {}^7F_0$	17 252
$^5D_0 \rightarrow {}^7F_1$	16 949, 16 886, 16 844
$^5D_0 \rightarrow {}^7F_2$	16 293, 16 233, 16 181, 16 155, 16 077
$^5D_0 \rightarrow {}^7F_3$	15 394, 15 363, 15 340, 15 267
$^5D_0 \rightarrow {}^7F_4$	14 586, 14 482, 14 463, 14 386, 14 370, 14 296, 14 275, 14 261, 14 234

3.1. Magnetic results

For most trivalent rare earth ions only the ground state is thermally populated at room temperature and below, because it is well separated from the first excited state. Thus, in the free-ion approximation the molar magnetic susceptibility for the isolated mononuclear compound can be given by the equation described in Ref. [22]:

$$\chi_J = \frac{N g_J^2 \beta^2 J(J+1)}{3kT} + \frac{2N\beta^2 (g_J - 1)(g_J - 2)}{3\lambda} \tag{1}$$

where T is temperature, $g_J = 3/2 + [S(S+1) - L(L+1)]/2J(J+1)$ and λ is the spin–orbit coupling parameter. The second term in Eq. (1) is the temperature-independent magnetism.

Usually, even for isolated systems, $\chi_M \cdot T$ versus T deviates from this relation as a result of the CF effect, which removes the $2J+1$ degeneracy of the ground state, and the population of excited states at relatively high temperatures (200–300 K). This last case is observed in Eu^{3+}. The ^7F term of Eu^{3+} is split by the spin–orbit coupling into seven S′L′J′ states and their energies are described by $E(J) = \lambda J(J+1)/2$. The λ term is relatively small and the CF components of the first $^7F_1$ and second $^7F_2$ excited states can be thermally populated, as seen in the excitation and absorption spectra of the systems under investigation (see Figs. 1 and 4). According to Kahn et al. [23], $\chi_M \cdot T$ can be described for Eu^{3+} in the HT and LT limits. At the high-temperature limits where $k \cdot T \gg \lambda$, $\chi_M \cdot T$ can be regarded as the sum of the orbital and spin

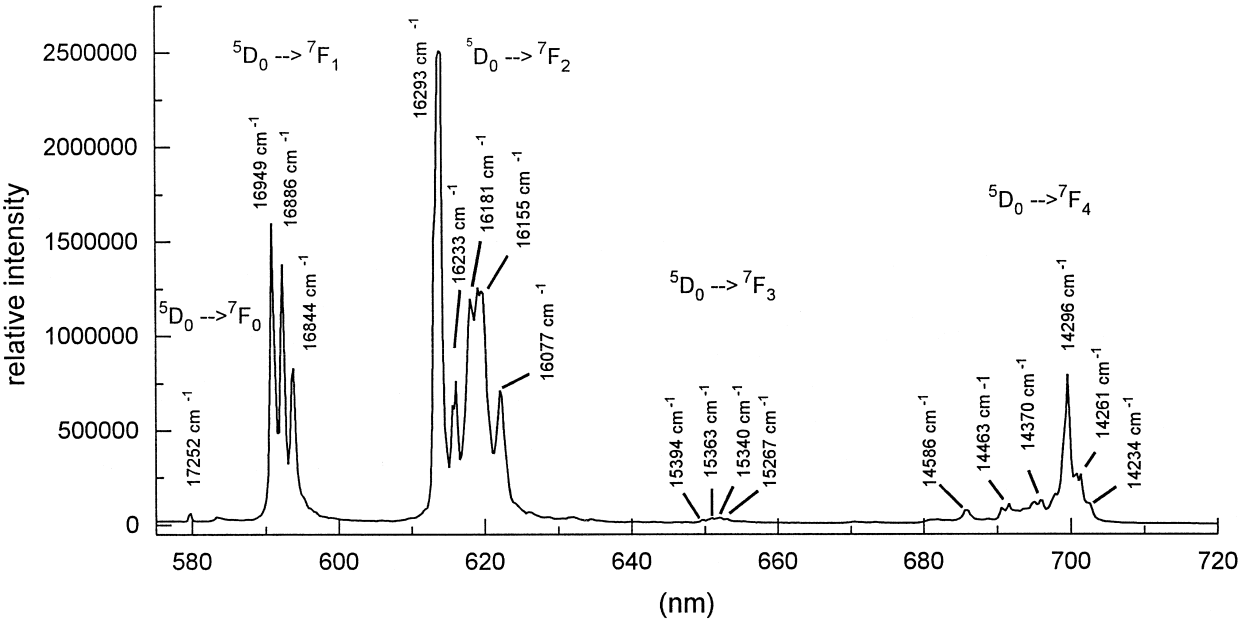

Fig. 3. Luminescence spectrum of $Eu(Cl_3CCOO)_3\cdot 2H_2O$ at 77 K.

contributions and described by Eq. (9) of Ref. [23]. Because of the λ value, only the three lowest states are populated and $\chi_M\cdot T$ does not reach the value of 4.50 cm^3 mol^{-1} K. In our systems, at 293 K, this value was not achieved for **1** nor for **2**. In fact, we obtained values of 1.1185 for **1** and 2.762 for **2** at 300.3 K. These $\chi_M\cdot T$ values are lower in system **1** than that reported by Kahn [22] for the isolated mononuclear europium complex of the $[ML_2(H_2O)_4]$ type. What does this mean? In our case, the splitting between $^7F_0$ and $^7F_2$ is larger and the population of the respective levels is lower. As a result we obtain smaller values of $\chi_M\cdot T$. On the other hand, the two europium ions linked in dimeric units by carboxyl groups interact even at higher temperatures when the excited states are populated, consequently this can lead to a decrease of $\chi_M\cdot T$. In the low-temperature limit, $\chi_M\cdot T$ should be 0 because $^7F_0$ is nonmagnetic. However, at the LT limit, $\chi_M\cdot T$ is nonzero. Coupling between $^7F_0$ and $^7F_1$ states through Zeeman perturbation leads to values arising from the $\chi(0)$ term and finite $\chi_M\cdot T$. In the low-temperature limit, and according to Caro and Porcher [24], $\chi_M\cdot T$ can be related to λ and described as

$$(\chi_M)_{LT} = 8N\beta^2/\lambda = 2.086\times 10^{-3}/(\lambda \text{ in cm}^{-1})$$

Let us now analyse our magnetic data. Figs. 5a,b and 6a,b show plots of χ_M and $\chi_M\cdot T$ versus T for compounds **1** and **2**, respectively. Let us discuss the results for compound **1**.

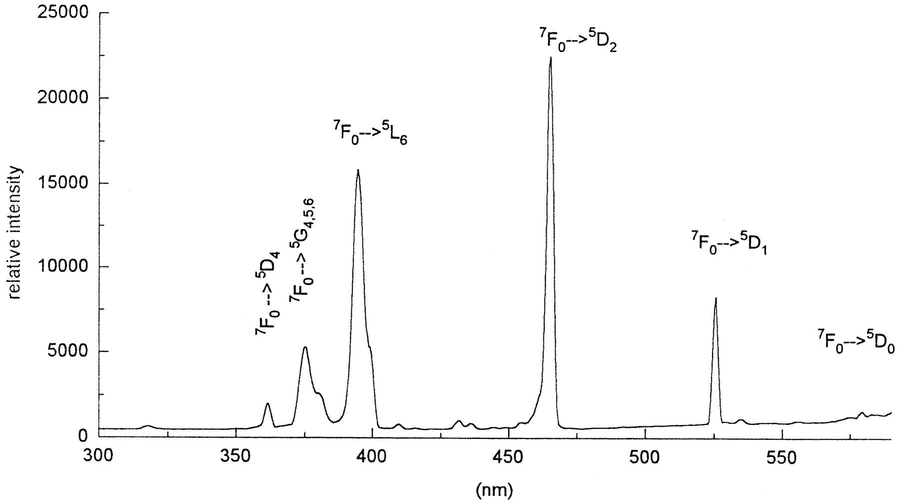

Fig. 4. Excitation spectrum of $Eu(Cl_3CCOO)_3\cdot 2H_2O$ at 77 K.

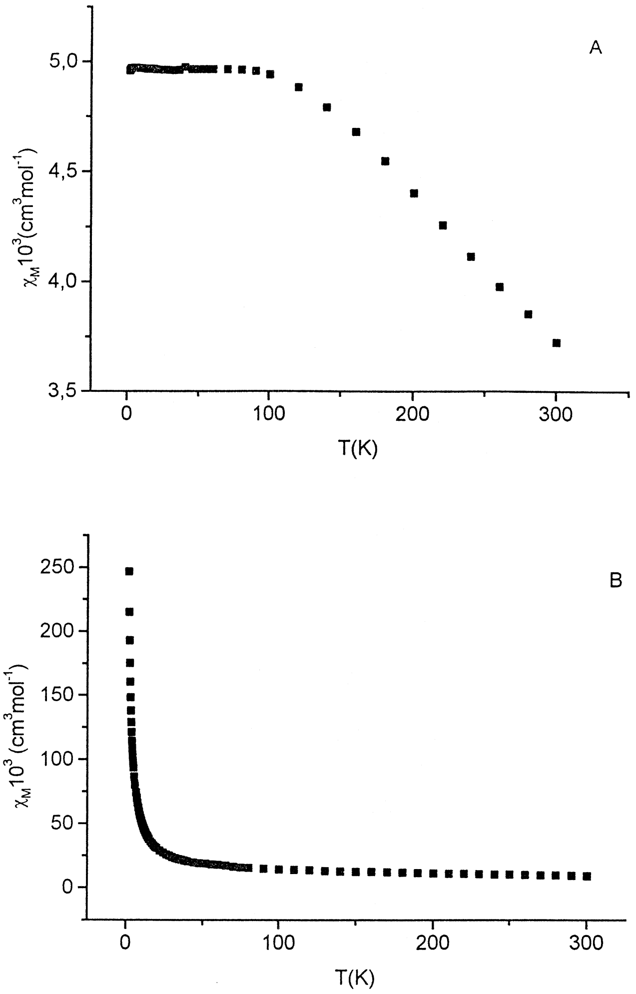

Fig. 5. Experimental magnetic data plotted as χ_M versus T calculated per molecule of complex. (A) $Eu(Cl_3CCOO)_3 \cdot 2H_2O$; (B) $CuEu_2(Cl_3CCOO)_8 \cdot 6H_2O$.

As T decreases, χ_M increases and tends to a plateau at ≈100 K. When the temperature is further reduced to 1.99 K, χ_M remains the same. As mentioned earlier, at 300 and 50 K (plateau), χ_M is equal to 3.73×10^{-3} and 4.97×10^{-3} $cm^3 mol^{-1}$, respectively. Both these values are lower than those reported by Kahn [22] for isolated Eu^{3+} mononuclear complex, although the shape of the relation χ_M versus T is similar. The relation $\chi_M \cdot T$ versus T is also similar to that for the isolated Eu^{3+} complex. However, the values of $(\chi_M \cdot T)_{HT}$ tend to the value 1.1185 $cm^3 mol^{-1}$ K (again smaller than in the isolated complex) and continuously decrease to 0.0085 at 1.7 K

Below 100 K, $\chi_M \cdot T$ versus T is strictly linear with slope $(\chi_M)_{LT} = 5.00 \times 10^{-3}$ $cm^3 mol^{-1}$, lower in comparison with the isolated system [23]. The λ values calculated from Eq. (10) of Ref. [24] lead to 420 cm^{-1} if the mean value of $\chi_M = 4.97 \times 10^{-3}$ is used. The splitting between ${}^7F_0$ and ${}^7F_1$ determined from our emission and absorption spectra at 77 and 300 K is 370 and 355 cm^{-1}, respectively. These values differ from that obtained from magnetic data (417 cm^{-1}). When applying Eq. (11) of Ref. [24] one can evaluate the χ_M values and obtain a value of 5.81×10^3 using our 359 cm^{-1} energy of the ${}^7F_1$ Stark components obtained from emission spectra at 77 K (see Table 4). This value is too high compared with our experimental data. It may again indicate the interaction of two Eu^{3+} in the dimer unit.

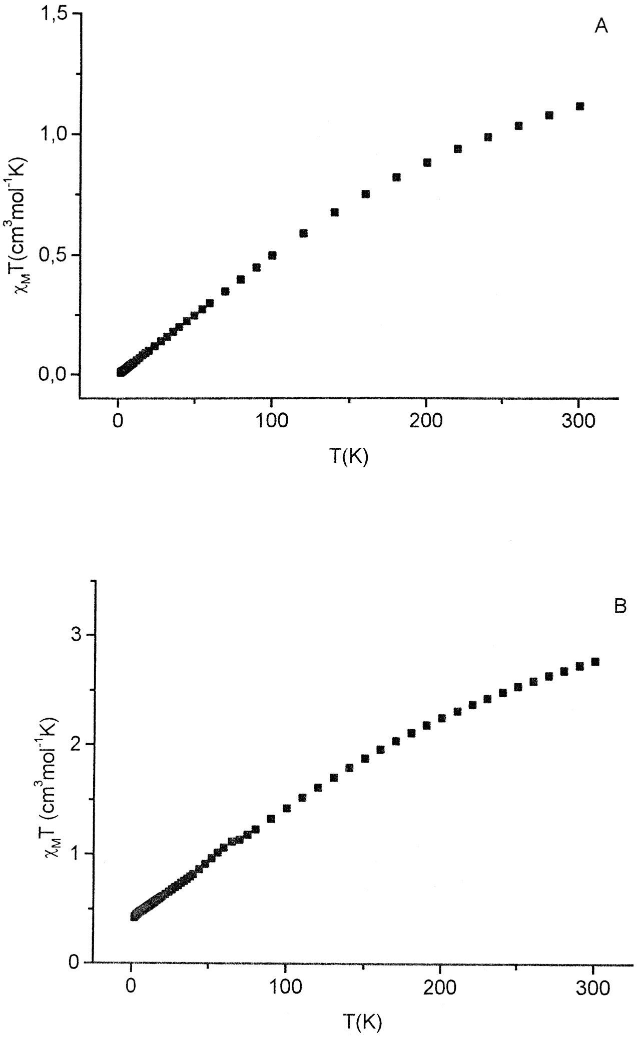

Fig. 6. Experimental magnetic data plotted as $\chi_M \cdot T$ versus T calculated per molecule of complex. (A) $Eu(Cl_3CCOO)_3 \cdot 2H_2O$; (B) $CuEu_2(Cl_3CCOO)_8 \cdot 6H_2O$.

Note now that the plot of χ_M versus T for the heteronuclear trichloroacetate $CuEu_2(CCl_3COO)_8 \cdot 6H_2O$ has a drastically different shape. It looks like our previous relation for $CuNd_2(CCl_3COO)_8 \cdot 6H_2O$ [7]. At 300.3 K, it is equal to 9.1964×10^{-3} $cm^3 mol^{-1}$ and slowly increases to 14.2003×10^{-3} $cm^3 mol^{-1}$ at 100.17 K, then increases strongly to 246.5254×10^{-3} $cm^3 mol^{-1}$ at 1.71 K. However, the plot of $\chi_M \cdot T$ versus T is similar to that for compound **1**, but the value at 300 K (2.76168) does not correspond to the sum of the values (3.1, which could be observed for isolated ions) nor to the 2.63 value obtained from our results for compound **1**. Our experimental value is lower than the values obtained for isolated ions, but higher than that obtained as the sum of $\chi_M \cdot T$ for **1** plus 0.4 for isolated Cu^{2+}. On the other hand, at 1.7 K, it reaches a value of 0.42342 cm^3 mol^{-1} K. If we consider the value of 0.019 for two Eu^{3+} plus 0.4 for isolated Cu^{2+}, the obtained values are close to the measured value of 0.419 (measured value 0.42342 cm^3 mol^{-1} K at 1.7 K). Considering again the splitting between the $^7F_0$, $^7F_1$ level (374 cm^{-1}) in heteronuclear compound **2** and applying Eq. (10) from Ref. [24] we obtain the values $\chi_M = 5.5775 \times 10^{-3}$ and $\chi_M \cdot T = 1.67325 + 0.4 = 2.07325$, i.e. lower values than determined experimentally. In fact, the above magnetic data indicate that both types of compounds ((**1**) and (**2**)) cannot be treated as isolated ions and that the values obtained from approximate calculations are far from the theory applied to isolated systems.

4. Summary

1. Comparative spectroscopic studies of polynuclear $Eu(Cl_3CCOO)_3 \cdot 2H_2O$ and heteronuclear $CuEu_2(Cl_3CCOO)_8 \cdot 6H_2O$ compounds were performed.
2. The splitting of d–d bands given by the Jahn–Teller effect was determined on the basis of the low-temperature spectrum of **2**.
3. Comparison of the respective energy transitions in the polynuclear and heteronuclear trichloroacetates shows shifts of the bands towards lower energies in the latter system.
4. Europium emission is effectively quenched in the spectra of the heteronuclear trichloroacetate.
5. Magnetic data for the two systems under investigation differ significantly; a rather antiferromagnetic ordering was found.

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