

Spectroscopy and magnetism of polymeric $\text{Ln}(\text{CCl}_3\text{COO})_3 \cdot 2 \text{H}_2\text{O}$ and their heteronuclear $\text{Ln}_2\text{Cu}(\text{CCl}_3\text{COO})_8 \cdot 6 \text{H}_2\text{O}$ analogues ($\text{Ln} = \text{Sm}, \text{Gd}$)

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In order to study the exchange interactions between f- and d-electron ions two series of compounds, heteronuclear $\text{Ln}_2\text{Cu}(\text{CCl}_3\text{COO})_8 \cdot 6 \text{H}_2\text{O}$ (**1**, Sm; **2**, Gd) and polymeric $\text{Ln}(\text{CCl}_3\text{COO})_3 \cdot 2 \text{H}_2\text{O}$ (**3**, Sm; **4**, Gd) trichloroacetates, were synthesised. Polymeric trichloroacetates **3** and **4** are isomorphous with erbium chloroacetate, whose structure contains dimeric units linked by carboxyl bridges and water molecules into endless chains. Heteronuclear **1** and **2** are isomorphous with $\text{Nd}_2\text{Cu}(\text{CCl}_3\text{COO})_8 \cdot 6 \text{H}_2\text{O}$ reported by us previously. Absorption spectra of single crystals of **1–4** for two orientations of the crystals down to 4 K were investigated. Magnetic susceptibility measurements in the range 300–1.8 K were carried out. Optical and magnetic properties are related to the X-ray data. Electron transition probabilities were calculated and the effect of coupled ion pairs in the polymeric structure on the optical and magnetic properties was analysed. Changes in magnetic properties in relation to the mononuclear systems are discussed.

In the last few years many studies have been devoted to polynuclear and heteronuclear dimeric and polymeric systems. Binucleating ligands may provide unusual structural features and/or magnetic, optical and catalytic properties and allow the preparation of sophisticated molecular optical and magnetic devices, *etc.*^{1–9} For the same reasons, heteronuclear copper lanthanide compounds have been widely studied and also because of their potential applications in superconducting ceramics. In addition, it is well known that lanthanide(III) ions show peculiar physical and chemical properties that make them essential components in the preparation of many new materials. The main features of these materials can be influenced by structural parameters, the anisotropy of the ground state of 4f ions and by the nature and intensity of the exchange and other interactions involving rare earths and d-electron ions. In these systems two paramagnetic metal centres can interact either ferromagnetically or anti-ferromagnetically through the bridging group.

With the aim of shedding light on this field we synthesised two series of polynuclear (**3,4**) and heteronuclear (**1,2**) trichloroacetates. The correlation of their optical and magnetic properties to the X-ray data is the subject of this report.

Experimental

Polynuclear single crystals of $\text{Ln}(\text{CCl}_3\text{COO})_3 \cdot 2 \text{H}_2\text{O}$ ($\text{Ln} = \text{Sm}$, **3**; Gd , **4**) and their heteronuclear analogues $\text{Ln}_2\text{Cu}(\text{CCl}_3\text{COO})_8 \cdot 6 \text{H}_2\text{O}$ ($\text{Ln} = \text{Sm}$, **1**, Gd , **2**) were synthesised according to the procedure described previously.^{10,11} Samples **1–4** were checked by single crystal X-ray diffraction and the cell constants were determined. Polynuclear trichloroacetates **3** and **4** are isomorphous with the erbium complex.¹² Heteronuclear Cu : Ln **1** and **2** have a similar structure to that previously reported for the Cu : Nd crystal.¹⁰

Absorption spectra between 250 and 1600 nm for two orientations (*a* and *b*) of single crystals of compounds **1–4** were recorded in the 293–4 K temperature range using a Cary–Varian 5 spectrophotometer equipped with a helium

(Oxford) cryostat. Intensities of the f–f and d–d transitions were calculated and converted into oscillator strength values and further applied for calculation of the Judd–Ofelt parameters (τ_λ). Raman spectra reported in ref. 13 were used in the vibronic components analysis. Magnetic susceptibility measurements were carried out with a SQUID magnetometer down to 1.7 K in both the low-field and high-field regimes. The data were corrected for diamagnetic contributions using Pascal's constants.

Results and discussion

X-Ray structure characteristics

As all the effects detected in the spectra (intensity, splitting, broadening) depend strongly on the structure of the system under investigation, essential X-ray structural data are given here. The crystal structure of $\text{Nd}_2\text{Cu}(\text{CCl}_3\text{COO})_8 \cdot 6 \text{H}_2\text{O}$ reported by us earlier¹⁰ (and isomorphous with both crystals **1** and **2** investigated here) consists of heteronuclear chains composed of dimers of $\text{Nd}(1)\text{O}_9$ and $\text{Nd}(2)\text{O}_8$ polyhedra, linked through three bidentate and one chelating bridging (tridentate type) carboxylate groups of the trichloroacetate molecules. Thus, a noncentrosymmetric dimeric unit is formed, further connected by planar CuO_4 squares. Two water molecules (OW1, OW2) add to the strongly distorted octahedron and link together the Cu(II) and Nd(II) ions, as do the carboxylic bridges. In this manner endless chains are formed, as shown in Fig. 1. Intrachain M–M distances are as follows: $\text{Nd1–Nd2} = 4.38 \text{ \AA}$; $\text{Cu1–Nd1} = 4.155 \text{ \AA}$; $\text{Cu1–Nd2} = 4.137 \text{ \AA}$. The interchain separations are 9.472 \AA (Nd2–Nd1) and 8.680 \AA (Cu1A–Cu2B). Magnetic properties are affected by the chain structure and may depend strongly on the dimensionality of polymeric systems.

The structure of $\text{Ln}(\text{CCl}_3\text{COO})_3 \cdot 2 \text{H}_2\text{O}$ is an example of a one-dimensional polymer, composed of two different centrosymmetric dimeric subunits bridged by carboxyl units and water molecules.¹²

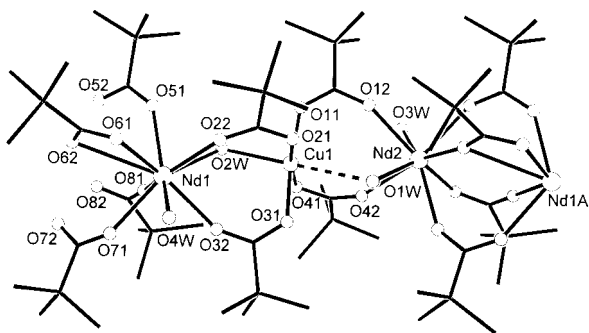


Fig. 1 Part of the one-dimensional $[\text{Nd}_2\text{Cu}(\text{CCl}_3\text{COO})_8(\text{H}_2\text{O})_4]$ chain in the crystal structure of $\text{Nd}_2\text{Cu}(\text{CCl}_3\text{COO})_8 \cdot 6 \text{H}_2\text{O}$.¹⁰

Spectroscopic results

Gd³⁺ and Cu : Gd systems. The Gd³⁺ ion with the 4f⁷ configuration has an $^8S_{7/2}$ ground state and excited state multiplets 6P_J ($J = 7/2, 5/2, 3/2$ in order of increasing energy), 6I_J ($J = 7/2, 17/2, 11/2, 15/2, 13/2$) and 6D_J ($J = 9/2, 1/2, 7/2, 3/2, 5/2$) with increasing energy. These excited states are located in the 32 000–41 000 cm^{-1} range above the ground state.¹⁴

The absorption spectrum of a $\text{Gd}(\text{CCl}_3\text{COO})_3 \cdot 2 \text{H}_2\text{O}$ single crystal in the range 270–314 nm is presented in Fig. 2. Rather broad, unsplit bands were detected and the splitting of these bands does not change with a decrease in temperature to 4 K. Only two transitions from the $^8S_{7/2}$ level to the 6P_J multiplet were detected ($^6P_{7/2}$ and $^6P_{5/2}$, the weakest, $^6P_{3/2}$, was not observed). The $^8S_{7/2} \rightarrow ^6I_J$ transitions at higher energy also do not split cleanly. Such behaviour can indicate disorder in the structure or effects of the ion–ion interaction in the undiluted single crystal, leading to a broadening of the lines. This is so in our case, a fully concentrated single crystal of the gadolinium compound. Although the positions of the f–f absorption lines are weakly dependent on the material type, the absorption lineshape and the Stark splitting differ from material to material. A relatively small splitting is caused by the crystal field (CF) effect. The $^8S_{7/2}$ ground state has a very small Stark splitting¹⁵ (of the order of 0.1 cm^{-1}) so that the absorption spectra reflect directly the splitting of the excited states.^{15–17}

Comparison of the splitting of the 6P multiplets with those in other systems indicates a CF effect for Gd³⁺ in the discussed crystal **4** (7/2, 72 cm^{-1} ; 5/2, 64 cm^{-1}), comparable to those reported for the $\text{GdAl}_3(\text{BO}_3)_4$ single crystal (7/2, 96 cm^{-1} ; 5/2, 62 cm^{-1} ; 3/2, 18 cm^{-1})¹⁸ and larger than in Gd : LaCl_3 (7/2, 50 cm^{-1} ; 5/2, 37 cm^{-1} ; 3/2, 18 cm^{-1}).¹⁹ Intensity analysis of the f–f transitions in the observed spectral

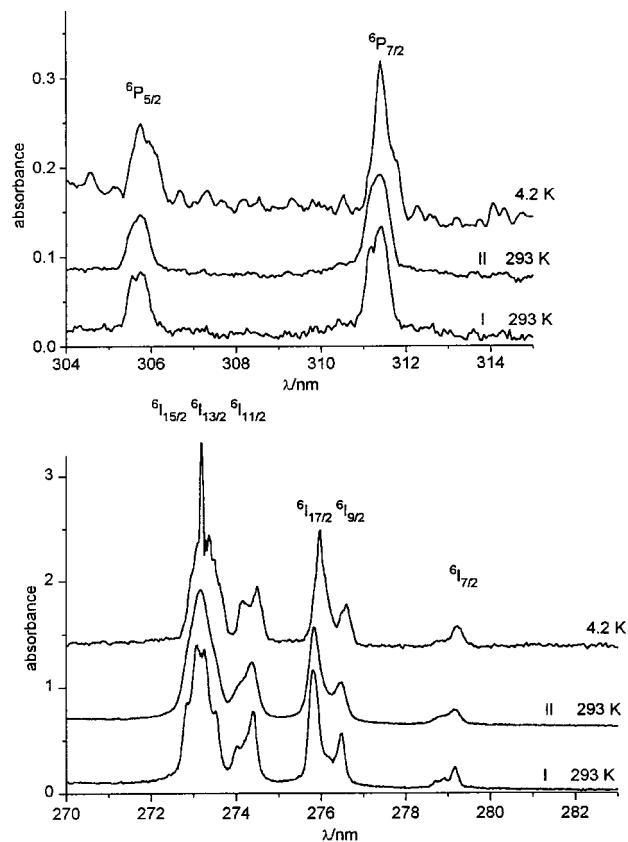


Fig. 2 Absorption spectra of a $\text{Gd}(\text{CCl}_3\text{COO})_3 \cdot 2 \text{H}_2\text{O}$ crystal at 293 K ($d = 0.1355 \text{ cm}$; I: slit = 0.1 nm, II: slit = 0.2 nm) and 4.2 K ($d = 0.117 \text{ cm}$; slit = 0.2 nm).

range is collected in Table 1, for one orientation of both the polynuclear and heteronuclear gadolinium trichloroacetate crystals. In the heteronuclear crystal, oscillator strength values indicate only a small increase in the intensities of the $^8S_{7/2} \rightarrow ^6P_{7/2}$, $^6I_{7/2}$ transitions in comparison to those in crystal **4**. Since the splitting of the $^8S_{7/2}$ level is very small, the decrease in temperature does not reflect the CF effect. Thus, the observed subtle changes in the intensities reflect the vibronic coupling and cooperative effects.

A comparison of the f–f transition intensities in the single crystals under investigation with those reported by Carnall *et al.*¹⁴ in water solution (HClO_4) reveals slightly lower intensities in the single crystal spectra. We have calculated the oscillator strength values for two orientations of the crystals (axes *a* and *b*). It is necessary to calculate the third orientation of the crystal (axis *c*) to obtain the mean values, which can be

Table 1 The oscillator strengths of the f–f ($\times 10^8$) and d–d ($\times 10^6$) transitions calculated from Gd, Cu : Gd and Cu trichloroacetate single crystal spectra at different temperatures

	$\text{Gd}(\text{CCl}_3\text{COO})_3 \cdot 2 \text{ H}_2\text{O}$			$\text{Gd}_2\text{Cu}(\text{CCl}_3\text{COO})_8 \cdot 6 \text{ H}_2\text{O}$		
	λ/nm	293 K	4.2 K	293 K		
$^8S_{7/2} \rightarrow ^6P_{7/2}$	313–309	9.10	9.67	11.99		
$^8S_{7/2} \rightarrow ^6P_{5/2}$	306.5–305	3.67	5.53	7.42		
$^8S_{7/2} \rightarrow ^6I_{7/2}$	280–278	9.79	11.70	13.96		
$^8S_{7/2} \rightarrow ^6I_{9/2}, ^6I_{17/2}$	278–275	69.55	71.31	77.49		
$^8S_{7/2} \rightarrow ^6I_{11/2}, ^6I_{13/2}, ^6I_{15/2}$	275–270	153.72	158.71	162.49		
$^8S_{7/2} \rightarrow ^6D_{9/2}$	253.5–252	13.08				
	$\text{Cu}(\text{CCl}_3\text{COO})_2 \cdot 3 \text{ H}_2\text{O}$			$\text{Gd}_2\text{Cu}(\text{CCl}_3\text{COO})_8 \cdot 6 \text{ H}_2\text{O}$		
	λ/nm	293 K		λ/nm	293 K	4.2 K
	orientation	<i>a</i>	<i>b</i>		<i>a</i>	<i>b</i>
	d–d Cu	500–1400	218.68	269.76	400–1300	407.77
						410.28

compared to those in solution. Since the calculated changes in intensities for two orientations are not high they should not change much, even after correction for the third orientation.

The fitting procedure for the coordination polyhedra of the Ln^{3+} ions in the crystal structures leads to C_{2v} symmetry for the lanthanide centres, both for the polynuclear trichloroacetates and for one Nd ion position in their heteronuclear analogue. Hence, the symmetry of the metal ion in water solutions, C_{3h} ,^{14,20,21} is higher than in the trichloroacetate single crystals.

A comparison of the f-f transition probabilities of crystals **2** and **4** shows a smooth variation of the oscillator strengths. This confirms that the metal centres in both types of crystals have similar environments.

Let us now focus on another aspect of the spectroscopic results, the intensities of the d-d transition in the heteronuclear Gd : Cu system and the monomeric $\text{Cu}(\text{CCl}_3\text{COO})_2 \cdot 3 \text{H}_2\text{O}$ crystal (Fig. 3). Both the intensities and energies of the d-d band are significantly different. Strong distortion of the octahedral symmetry is manifested by an increase of the d-d band intensity in the heteronuclear Gd : Cu crystal. Also, the energy of the split band of **2** at 4 K is shifted to higher values. This effect is accompanied by a shift of the charge transfer (CT) Cu^{2+} band to higher energies ($\approx 280 \text{ nm}$). The energy of this band remains in resonance with the 6I multiplets of the Gd^{3+} ions.

Sm^{3+} and Sm : Cu systems. The absorption spectra of the two samarium compounds, $\text{Sm}_2\text{Cu}(\text{CCl}_3\text{COO})_8 \cdot 6 \text{H}_2\text{O}$ (**1**) and $\text{Sm}(\text{CCl}_3\text{COO})_3 \cdot 2 \text{H}_2\text{O}$ (**3**) are shown in Figs. 4–6. For the Sm^{3+} ion ground state, the $^6H_{5/2}$ multiplet is separated²² from the higher $^6H_{7/2}$ term by $\approx 880 \text{ cm}^{-1}$. In the Sm^{3+} aquaion spectrum this separation was evaluated as 1030 cm^{-1} and seems to be comparable to that in our systems.^{20,21} Such a comparison is possible because of the confrontation of the CF splitting of separated levels for the trichloroacetates and the aquaion spectrum. Experimental and theoretical studies of many of the 206 possible multiplet levels in the $4f^6$ configuration have been made by Magno and Dieke,²³ whose experimental results agree with those obtained by Gobrecht.²⁴ The absorption spectra (1000–2600 nm) have been interpreted as an overlap of the terms of the 6F state with the upper levels of the 6H ground state multiplet. Comparison of our single crystal spectra of the heteronuclear trichloroacetate **1** with data^{20,23–25} at ca. 7000 cm^{-1} reported earlier shows a structure of the lines for the $^6H_{5/2} \rightarrow ^6F_{5/2}$ transition (as assigned in most of the absorption spectra of Sm^{3+} ions) that is too complex if we consider the two non-equivalent sites of the ions in the structure. At 4 K almost all transitions are composed of a sharp doublet structure, indicating two non-equivalent metal centres. However, in the region $7150\text{--}6850 \text{ cm}^{-1}$ very complex bands are observed as mentioned above, in which the number of components corresponds to that expected for the $^6H_{5/2} \rightarrow ^6H_{15/2}$ transition. However, from the low values of the matrix elements of the unit tensor operator $U^{(2)}$ reported by Carnall *et al.* for this transition,²⁰ it is necessary to exclude this assignment. Thus, the complex structure of this band can only be explained by strong vibronic coupling with some vibrations observed in the IR and Raman spectra of lanthanide trichloroacetates, reported by us earlier.¹³ The assignment of vibronic components accompanying the $^6H_{5/2} \rightarrow ^6F_{1/2}$ electronic hypersensitive transition in the high-energy range was made (see Fig. 5, spectrum b). These components are promoted by internal ligand modes and correspond to: (1) $\delta(\text{COO})$ 361 cm^{-1} , (2) $\delta(\text{COO})$ 433 cm^{-1} , (3) $\omega(\text{H}_2\text{O})$ 488 cm^{-1} , (4) $\pi(\text{COO})$ 545 cm^{-1} , (5) $\delta(\text{OCO})$ 620 cm^{-1} , (6) $\tau(\text{OCO})$ 686 cm^{-1} and (7) $\delta(\text{H}_2\text{O})$ 757 cm^{-1} energies calculated from the $E_1 = 6355 \text{ cm}^{-1}$ and $E_2 = 6329 \text{ cm}^{-1}$ zero-phonon lines in the single crystal spectra of

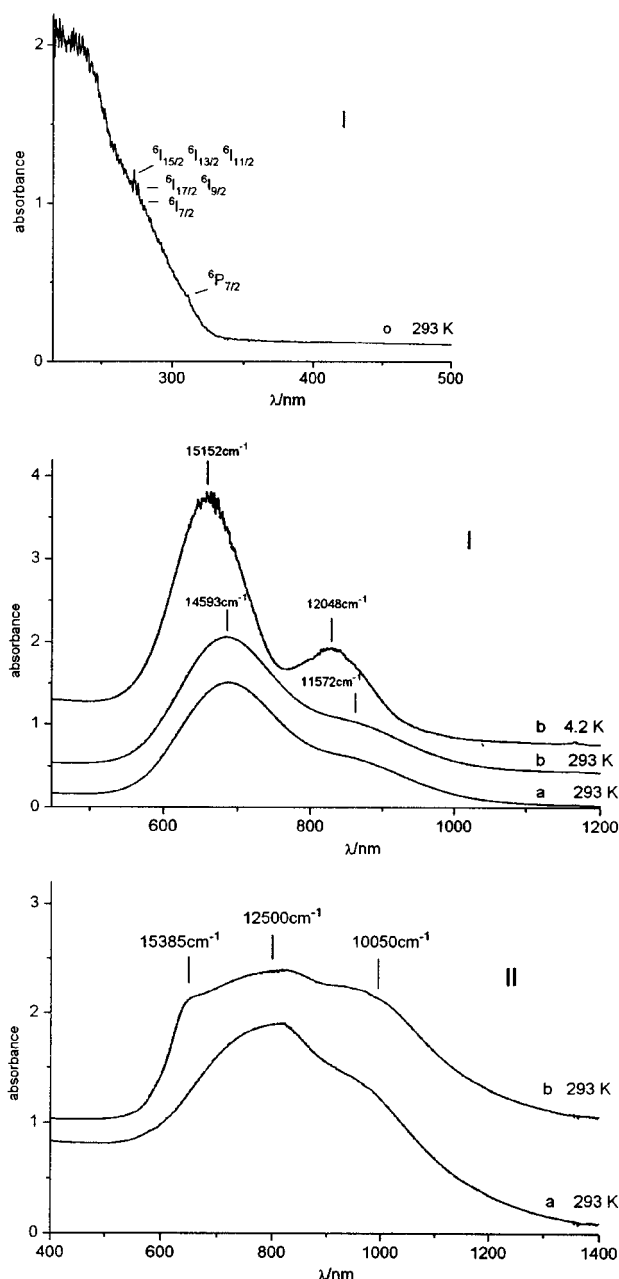


Fig. 3 (I) Absorption spectra of a $\text{Gd}_2\text{Cu}(\text{CCl}_3\text{COO})_8 \cdot 6 \text{H}_2\text{O}$ crystal at 293 K (orientations *a* and *b*; $d = 0.0475 \text{ cm}$; o: in paraffin oil) and at 4.2 K (orientation *b*; $d = 0.067 \text{ cm}$). (II) Absorption spectra of a $\text{Cu}(\text{CCl}_3\text{COO})_2 \cdot 3 \text{H}_2\text{O}$ crystal at 293 K (orientations *a* and *b*; $d = 0.031 \text{ cm}$).

$\text{Sm}_2\text{Cu}(\text{CCl}_3\text{COO})_8 \cdot 6 \text{H}_2\text{O}$ at 4 K. The correct assignment of the levels in this region of the spectra and an explanation of this phenomenon will be made possible by a CF calculation, which will be the subject of future work. If the bands located at 6355 and 6329 cm^{-1} correspond to the two components of the $^6F_{1/2}$ multiplet of the samarium centre (so that the other very weak components observed at 4 K in this region belong to the $^6H_{15/2}$ term) and if the adjacent band at 6620 cm^{-1} corresponds to the $^6F_{3/2}$ transition, the number of components seems to confirm our assignment. The calculated intensities of the f-f and d-d transitions in the Sm : Cu and Sm trichloroacetates at room and helium temperatures along axis *a* are collected in Table 2. The results of the Judd–Ofelt²⁶ parameter calculation are also included. Estimation of the parameters was made with relatively good accuracy and relatively low estimated error. These parameters reproduce quite well the intensities of the Sm^{3+} f-f transitions in compound **1**.

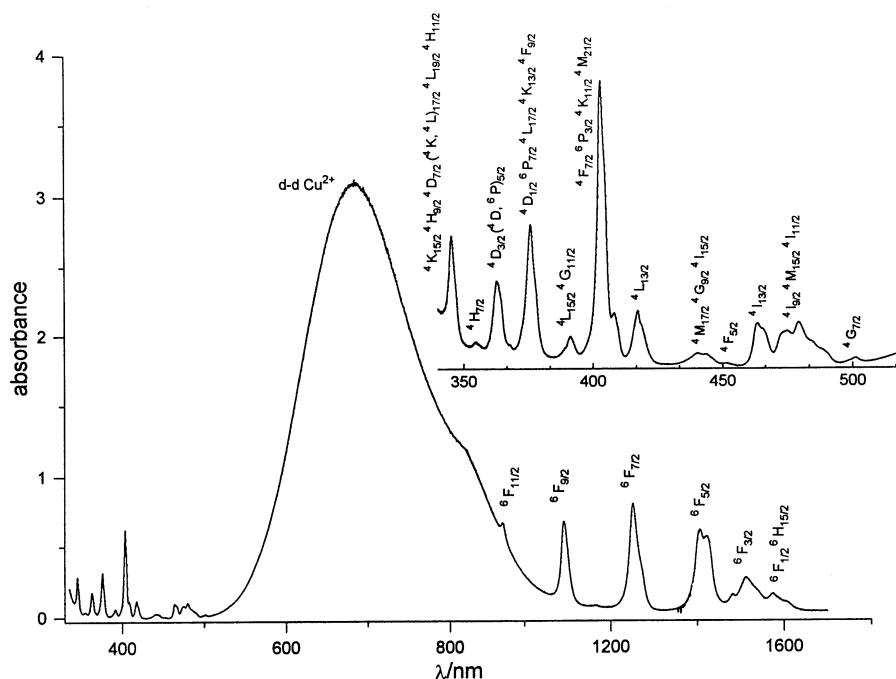


Fig. 4 Absorption spectrum of a $\text{Sm}_2\text{Cu}(\text{CCl}_3\text{COO})_8 \cdot 6 \text{H}_2\text{O}$ crystal at 293 K. The insert shows the expanded spectrum between 320 and 540 nm.

In the 500–1000 nm spectral range the copper d–d band overlaps with the Sm^{3+} transitions. This wide band with no vibronic structure splits into two components at 4 K as a result of the Jahn–Teller (J–T) effect in the deformed octahedron of

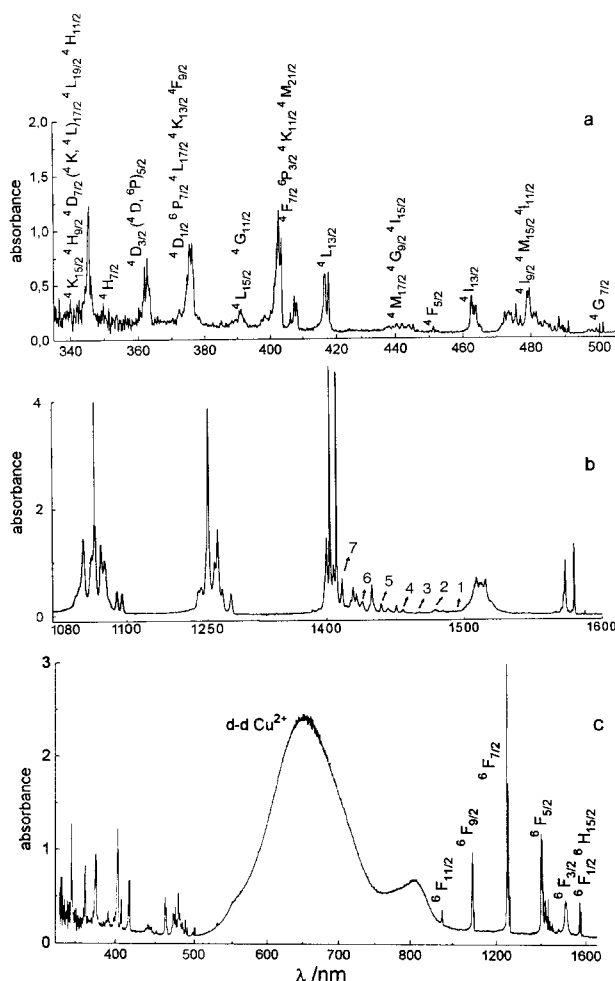


Fig. 5 Absorption spectra of a $\text{Sm}_2\text{Cu}(\text{CCl}_3\text{COO})_8 \cdot 6 \text{H}_2\text{O}$ crystal at 4.2 K. Spectra (a) and (b) show expanded regions of the full spectrum in (c).

the Cu^{2+} environment. Although the energy of the split d–d bands corresponds quite well to that of similar components in the spectra of Nd : Cu and Pr : Cu trichloroacetates reported by us,^{27,28} their intensities vary. They are highest for the samarium spectra ($P_{\text{exp}} = 665.71 \times 10^{-6}$).

Since the first excited state lies at relatively low energy, it can be partially populated at room temperature. We have estimated this population to be 1.3%. Therefore, the population of this term must affect both the spectroscopic and magnetic properties of the systems under investigation. In fact, with a decrease in temperature, the intensities of almost all transitions increase, similarly to the europium single crystal spectra. These results are in contrast to those for the other lanthanide trichloroacetates for which a decrease of intensities is observed at low temperatures.^{11,13}

Magnetic properties

Gd³⁺ and Gd : Cu systems. For most of the trivalent rare earth ions the $2S+1L_J$ free ion ground state is well separated in energy from the first excited state, so that only this ground state is thermally populated at room and low temperatures. For mononuclear systems (in the free ion approximation)

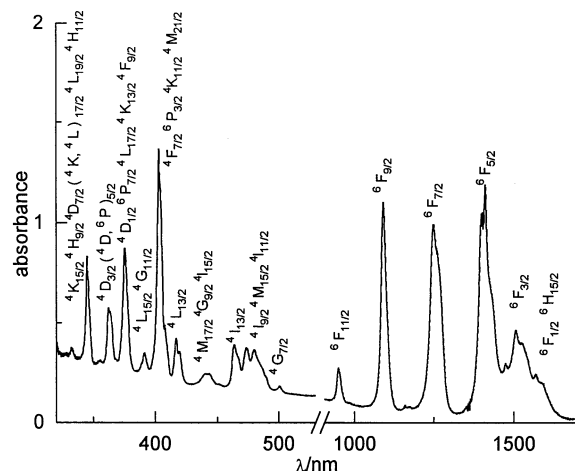


Fig. 6 Absorption spectrum of a $\text{Sm}(\text{CCl}_3\text{COO})_3 \cdot 2 \text{H}_2\text{O}$ crystal at 293 K.

Table 2 The oscillator strengths of the f–f ($\times 10^8$) and d–d ($\times 10^6$) transitions for Sm : Cu and Sm trichloroacetate crystals at different temperatures

	λ/nm	$\text{Sm}_2\text{Cu}(\text{CCl}_3\text{COO})_8 \cdot 6 \text{H}_2\text{O}$		$\text{Sm}(\text{CCl}_3\text{COO})_3 \cdot 2 \text{H}_2\text{O}$	
		293 K	4.2 K	293 K	4.2 K
$^6\text{H}_{5/2} \rightarrow ^6\text{F}_{1/2}, ^6\text{H}_{15/2}$	1786–1538	58.4	58.30	46.55	45.10
$^6\text{H}_{5/2} \rightarrow ^6\text{F}_{3/2}$	1538–1471	161.72	236.42	158.72	21.36
$^6\text{H}_{5/2} \rightarrow ^6\text{F}_{5/2}$	1471–1316	366.69	422.74	344.04	—
$^6\text{H}_{5/2} \rightarrow ^6\text{F}_{7/2}$	1316–1163	383.98	415.46	289.18	—
$^6\text{H}_{5/2} \rightarrow ^6\text{F}_{9/2}$	1136–1020	235.14	352.47	239.58	—
$^6\text{H}_{5/2} \rightarrow ^6\text{F}_{11/2}$	980–909	21.75	42.49	30.56	—
$^6\text{H}_{5/2} \rightarrow ^4\text{G}_{7/2}$	505–493	4.10	14.94	6.84	5.55
$^6\text{H}_{5/2} \rightarrow ^4\text{I}_{9/2}, ^4\text{M}_{15/2}, ^4\text{I}_{11/12}$	493–469	142.95	287.59	162.04	195.10
$^6\text{H}_{5/2} \rightarrow ^4\text{I}_{13/2}$	469–455	71.34	97.10	76.58	62.77
$^6\text{H}_{5/2} \rightarrow ^4\text{F}_{5/2}$	455–450	2.56	5.27	1.58	3.06
$^6\text{H}_{5/2} \rightarrow ^4\text{M}_{17/2}, ^4\text{G}_{9/2}, ^4\text{I}_{15/2}$	450–427	35.2	67.92	35.87	46.65
$^6\text{H}_{5/2} \rightarrow ^4\text{L}_{13/2}$	427–405	80.71	137.26	75.65	91.76
$^6\text{H}_{5/2} \rightarrow ^4\text{F}_{7/2}, ^6\text{P}_{3/2}, ^4\text{K}_{11/2}, ^4\text{M}_{21/2}$	405–392	466.21	382.89	427.04	406.07
$^6\text{H}_{5/2} \rightarrow ^4\text{L}_{15/2}, ^4\text{G}_{11/2}$	392–382	34.76	113.51	36.43	39.58
$^6\text{H}_{5/2} \rightarrow ^4\text{D}_{1/2}, ^6\text{P}_{7/2}, ^4\text{L}_{17/2}, ^4\text{K}_{13/2}, ^4\text{F}_{9/2}$	379–368	237.10	425.53	247.04	240.47
$^6\text{H}_{5/2} \rightarrow ^4\text{D}_{3/2}, (^4\text{D}, ^6\text{P})_{5/2}$	368–356	129.31	283.40	127.84	136.50
$^6\text{H}_{5/2} \rightarrow ^4\text{H}_{7/2}$	356–350	5.90	—	3.57	—
$^6\text{H}_{5/2} \rightarrow ^4\text{K}_{15/2}, ^4\text{H}_{9/2}, ^4\text{D}_{7/2}, (^4\text{K}, ^4\text{L})_{17/2}, ^4\text{L}_{19/2}, ^4\text{H}_{11/2}$	350–336	130.03	346.30	175.14	176.22
d–d Cu	500–1200	665.71	667.28		

^a The $\tau_{\lambda} \cdot 10^9$ parameters: $\tau_2 = 6.80 \pm 3.20$; $\tau_4 = 13.12 \pm 1.02$; $\tau_6 = 8.94 \pm 0.95$, for $\text{Sm}_2\text{Cu}(\text{CCl}_3\text{COO})_8 \cdot 6 \text{H}_2\text{O}$.

magnetic susceptibilities can be described by the relation²⁹

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

with T being the temperature, g the Zeeman factor and λ the spin-orbit coupling parameter. When considering the magnetic properties of lanthanide compounds one must remember the CF effect and the possible thermal population of the higher states for some ions (Sm and Eu).

In the polynuclear and heteronuclear systems ferromagnetic and antiferromagnetic ordering can be expected at low temperature. In fact, for $4f^1$ through $4f^6$ configurations of Ln(III) ions the angular and spin momenta can lead to antiparallel ordering in the $2S+1L_J$ free ion ground state. Parallel alignment of the Ln(III) and Cu(II) spin momenta can lead to an antiparallel alignment of the angular momenta and to an overall antiferromagnetic interaction. On the other hand, for $4f^8$ through $4f^{13}$ configurations angular and spin momenta are parallel in the ground state ($J = L + S$) and a parallel alignment of the Ln(III) and Cu(II) spin momenta may lead to parallel ordering of the magnetic moments, that is to a ferromagnetic interaction. In this case also, the CF effect complicates the situation.

In our earlier reports we have discussed the spectroscopic and magnetic data of two series of Ln and Ln : Cu trichloroacetates (Ln = Nd, Pr). Here we present results for the gadolinium and samarium polynuclear and heteronuclear analogues. In the first system, $\text{Gd}(\text{CCl}_3\text{COO})_3 \cdot 2 \text{H}_2\text{O}$ (**4**), a simple model can be analysed. Since the Gd^{3+} ion has a $^8S_{7/2}$ ground state, which is almost unsplit (0.1 cm^{-1}) and is located $\approx 32000 \text{ cm}^{-1}$ below the first excited state, the magnetic moment is given by the spin momenta only. The second term of eqn. (1) is negligible and the magnetic susceptibility obeys the Curie law: $\chi_M \cdot T = 21N\beta^2/k$. However, our results are not consistent with the free ion approximation nor the reasoning and results reported for dimeric gadolinium systems by Kahn and coworkers.³⁰ This is understandable because, in contrast to the earlier data reported by Kahn and coworkers,^{30,31} for both types of gadolinium chloroacetates, $\text{Gd}_2\text{Cu}(\text{CCl}_3\text{COO})_8 \cdot 6 \text{H}_2\text{O}$ (**2**) and $\text{Gd}(\text{CCl}_3\text{COO})_3 \cdot 2 \text{H}_2\text{O}$ (**4**), polymeric chains are formed with dimeric subunits, which are further linked to each other by the Cu ion, or in **4**, by

carboxyl groups and water molecules. They differ also from other heteronuclear systems investigated by Kahn *et al.*³²

χ_M and $\chi_M \cdot T$ vs. T for the gadolinium systems **2** and **4** are plotted in Fig. 7. For the polynuclear system **4** $\chi_M \cdot T$ exhibits what looks like antiferromagnetic ordering at low temperature. At very low temperatures the dramatic decrease in $\chi_M \cdot T$ could also be a result of a very small splitting of the $^8S_{7/2}$ multiplet at zero field or additional splitting of the ground state multiplet promoted by a Gd(III)–Gd(III) inter-

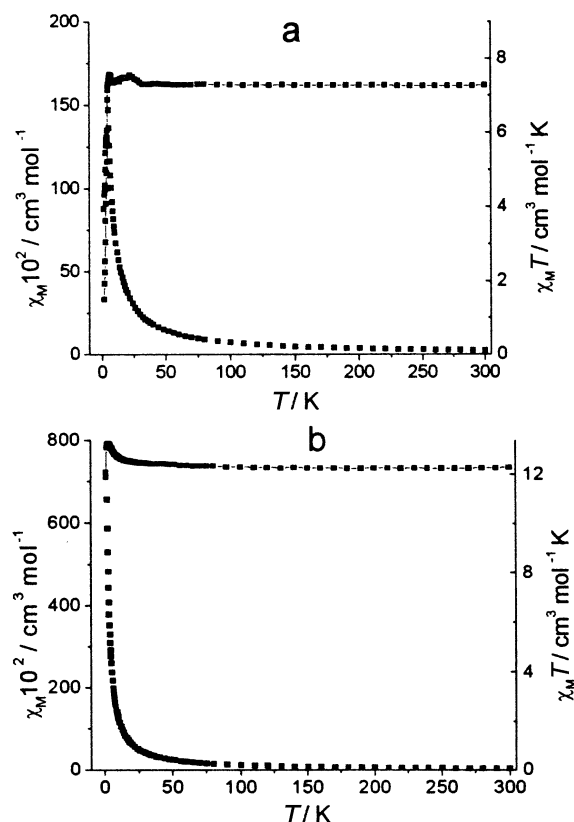


Fig. 7 Experimental (■) magnetic susceptibility χ_M and (—■—) $\chi_M \cdot T$ calculated per molecule in the complex plotted vs. temperature. (a) $\text{Gd}(\text{CCl}_3\text{COO})_3 \cdot 2 \text{H}_2\text{O}$, (b) $\text{Gd}_2\text{Cu}(\text{CCl}_3\text{COO})_8 \cdot 6 \text{H}_2\text{O}$.

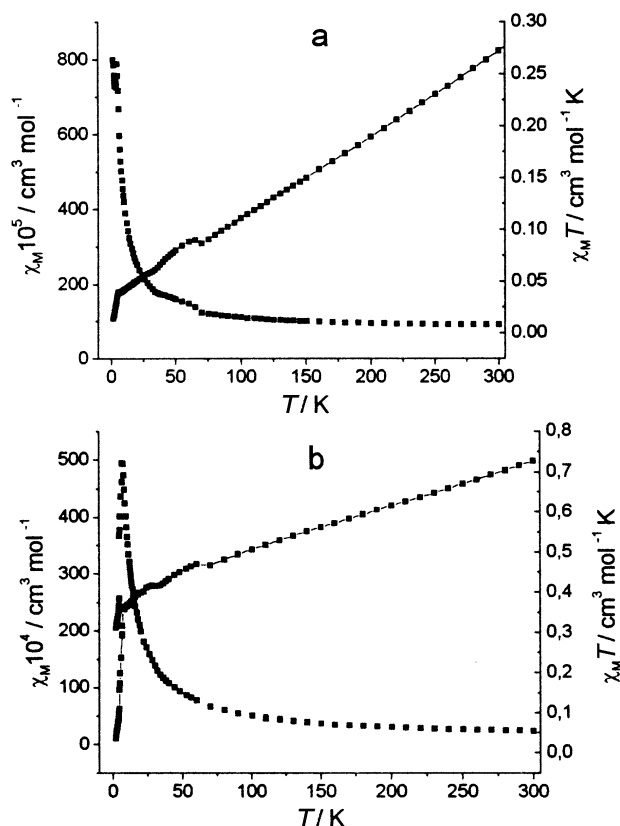


Fig. 8 Experimental (■) magnetic susceptibility χ (—■—) and $\chi \cdot T$ calculated per molecule in the complex plotted *vs.* temperature. (a) $\text{Sm}(\text{CCl}_3\text{COO})_3 \cdot 2 \text{H}_2\text{O}$, (b) $\text{Sm}_2\text{Cu}(\text{CCl}_3\text{COO})_8 \cdot 6 \text{H}_2\text{O}$.

action. On the other hand, for the heteronuclear system $\text{Gd} : \text{Cu}$ ferromagnetic ordering can be considered, but in this case also the relation of $\chi_M \cdot T$ is not comparable to the previously reported results, most probably for the same reason as in the polymeric single crystals of compound **4** since the heteronuclear chain is composed also of $\text{Gd}-\text{Gd}$ dimer units (see Fig. 1). Similar results and relations of $\chi_M \cdot T$ for $\text{Cu} : \text{Gd}$ heteronuclear compounds were reported by Benelli and co-workers.^{33,34} in drastically different heteronuclear chelates.

Sm^{3+} and $\text{Sm} : \text{Cu}$ systems. The Sm^{3+} ion belongs to the first part of the lanthanide series and as we have demonstrated in the spectroscopic section, the 6H ground term is split by spin-orbit coupling into six levels. The first excited $^6H_{7/2}$ term (as was estimated by us) is separated by *ca.* 890–940 cm^{-1} from the $^6H_{5/2}$ ground state and its population is 1.3% at 300 K. Similarly to $\text{Eu}(\text{III})$, $E(J)$ and $\chi(J)T$ decrease with J . There-

Table 3 Magnetic data for $\text{Sm}_2\text{Cu}(\text{CCl}_3\text{COO})_8 \cdot 6 \text{H}_2\text{O}$. $C=0.705$; $\Theta = -20.04$

T/K	$\chi_M \cdot 10^3 / \text{cm}^3 \text{mol}^{-1}$	μ_{eff} / μ_B
1.73	20.61	0.53
2.75	21.57	0.68
3.50	22.85	0.80
4.25	25.66	0.93
5.44	43.60	1.38
6.41	49.44	1.59
7.97	44.89	1.69
9.09	40.20	1.71
10.50	35.22	1.72
20.06	19.90	1.78
52.94	8.68	1.91
100.19	5.05	2.01
160.31	3.58	2.14
220.31	2.89	2.26
300.27	2.42	2.41

fore, for compound **1** $\chi_M T$ decreases as T decreases (the plot is nearly linear for $T = 50$ to 300 K) and leads to a value of 0.36 $\text{cm}^3 \text{mol}^{-1} \text{K}$ as T approaches 6.41 K and drops dramatically with further decrease of temperature to 1.7 K, giving a value of 0.035 $\text{cm}^3 \text{mol}^{-1} \text{K}$ (Fig. 8). The plot of χ_M *vs.* T shows that the magnetic susceptibility slowly increases below 160 K and then dramatically increases below 30 K to reach a value of 49.44×10^{-3} at 6.41 K, then decreases to 20.61×10^{-3} at 1.7 K (see also Table 3). This type of behaviour points to anti-ferromagnetic ordering at low temperatures. Such ordering of spins can be confirmed by the relation of $1/\chi_M$ *vs.* T . In the 300–40 K region it obeys the Curie–Weiss law with a Weiss constant of $\Theta = -20.04$.

Using the free ion approximation, Kahn and colleagues³¹ derived the relation of χ_M for the Sm^{3+} ion in monomeric systems, in which χ_M can be given by the following equation for the six states arising from the 6H ground state multiplet:

$$\chi_M = \frac{\sum_{J=5/2}^{15/2} (2J+1) \chi(J) \exp[-E(J)/kT]}{\sum_{J=5/2}^{15/2} (2J+1) \exp[-E(J)/kT]} \quad (2)$$

where $\chi(J)$ is given by eqn. (1) and $E(J) = \lambda[J(J+1) - 35/4]/2$. Kahn *et al.* obtained excellent theory–experiment agreement. At low temperatures $\chi_M T$ reaches the value of 0.89 $\text{cm}^3 \text{mol}^{-1} \text{K}$ predicted by theory. Our results for the heteronuclear **1** system show completely different behaviour for χ_M and $\chi_M T$ *vs.* temperature (Fig. 8, Table 3) in comparison to the monomeric systems reported by Kahn *et al.*³¹

EPR investigations (300–4 K) of the heteronuclear $\text{Ln} : \text{Cu}$ trichloroacetates show $\text{Ln} : \text{Cu}$ interactions larger than for $\text{Ln} : \text{Ln}$ systems.^{35,36} In addition, in the $\text{Pr} : \text{Cu}$ trichloroacetates $\text{Cu} : \text{Cu}$ interactions appear through the dimeric unit of the lanthanide ions. This was explained by a superexchange interaction involving the s and d orbitals of the Pr^{3+} ion.^{35–37}

Summary

Two types of single crystals, heteronuclear $\text{Sm}_2\text{Cu}(\text{CCl}_3\text{COO})_8 \cdot 6 \text{H}_2\text{O}$ (**1**) and $\text{Gd}_2\text{Cu}(\text{CCl}_3\text{COO})_8 \cdot 6 \text{H}_2\text{O}$ (**2**) and homonuclear $\text{Sm}(\text{CCl}_3\text{COO})_3 \cdot 2 \text{H}_2\text{O}$ (**3**) and $\text{Gd}(\text{CCl}_3\text{COO})_3 \cdot 2 \text{H}_2\text{O}$ (**4**) trichloroacetates were obtained. Their optical and magnetic properties were investigated in the 1.7–293 K range.

Their optical properties indicate marked differences in the structures of these two types of single crystals, with transformation of centro- to noncentrosymmetric lanthanide dimeric subunits.

The f–f transition probabilities were analysed and the Judd–Ofelt parameters calculated with a relatively small error.

Vibronic components were evaluated and assigned on the basis of IR spectra.

The magnetic moments of **1** and **3** decrease with temperature. This can be due to the crystal field effect and anti-ferromagnetic interactions of pairs of ions in compounds **1** and **3**. Magnetic susceptibilities increase with decreasing temperature and ferromagnetic ordering seems to occur in compound **2**.

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