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Comparative spectroscopic and magnetic studies of two types of Ln and Ln:Cu trichloroacetates

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Abstract

Heteronuclear copper–lanthanide complexes have attracted much attention as models for the theoretical investigation of magnetic exchange involving d and f electrons and because of their potential application in superconducting ceramics. Synthesis, structural, spectroscopic and magnetic characterization of one-dimensional polymeric $Ln(Cl_3CCOO)_3 \cdot 2H_2O$ (Ln=Nd, Eu, Dy) (**I**) and heteronuclear $CuNd_2(Cl_3CCOO)_8 \cdot 6H_2O$ (**II**) single crystals was undertaken. The structure of (**II**) is constructed from dimers of two crystallographically independent types of $NdO_{8(9)}$ polyhedra linked by carboxyl bridges. These dimers are separated by square planar coordinated copper ions which are bridged to the lanthanide by four carboxyl groups and two water molecules. The chains are further connected via a hydrogen bonding system to layers. The optical and magnetic properties were investigated in the 4.2–293 K temperature range and are discussed on the basis of X-ray data. Electronic spectra reveal marked differences in the structures of these two types of compounds. The spectra allow the determination of the splitting pattern of the ground state multiplet of the Nd^{3+} ion. Vibronic components were detected in the europium excitation spectra and their assignments were made on the basis of Raman data. The temperature dependence of χ_M and μ_{eff} shows a decrease of the magnetic moment with temperature and the reverse relation for magnetic susceptibility in mixed Nd:Cu crystals. The cooperative interaction of ion-pairs coupled in polymeric chains could be considered based both on spectroscopic and magnetic investigations. © 1998 Elsevier Science S.A.

Keywords: Copper; Lanthanides; Magnetic properties; Spectroscopy; Trichloroacetates

1. Introduction

In recent years many studies have been devoted to the synthesis of polynuclear compounds because of their unusual structural features and/or magnetic, optical and catalytic properties [1–17]. Several studies also concerned the modeling of some metalloenzymes containing different metal ions and applying lanthanide ions as spectroscopic probes. It is well known that lanthanide(III) ions show peculiar physical and chemical properties which make them essential components in the preparation of new materials. The presence of lanthanides also plays an important role in modulating the bulk magnetic properties of many materials. The main features of these materials are essentially influenced by the anisotropy of the ground state of the 4f metal ion and/or by the nature and intensity of the exchange interaction involving rare earth ions. In the literature there are only a few reports of studies on the actual nature of the exchange mechanism in 4f–4f and 4f–3d pairs [1–9,15–17]. To improve the properties of the rare earth-containing materials, more information is needed on the nature of the exchange interaction and the dependence of the magnetic anisotropy on structural parameters, as well as the effects of 4f–3d pairs on the spectroscopic properties. With the aim of shedding light on this field, we started investigations on the synthesis, structure, spectroscopy and magnetic characterisation of simple molecular systems, where rare earth ions are in close contact with paramagnetic centers. A series of polynuclear (Ln:Cu, Ln:Ln) trichloroacetates $CuLn_2(Cl_3CCOO)_8 \cdot 6H_2O$ and $[\{Ln(Cl_3CCOO)_2(H_2O)\}_2(Cl_3CCOO)_2(H_2O)]_n \cdot nH_2O$ were obtained. Their structure and optical and magnetic properties are the subject of this report.

2. Experimental

Single crystals of polynuclear $Ln(Cl_3CCOO)_3 \cdot 2H_2O$ (Ln=Nd, Eu, Dy) and heteronuclear $CuNd_2(Cl_3CCOO)_8 \cdot 6H_2O$ were obtained according to the procedure described in Refs. [1,10–13]. Samples were checked by the X-ray

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method. Neodymium, dysprosium and europium trichloroacetates are isomorphic with $Er(Cl_3CCOO)_3 \cdot 2H_2O$ [14]. A single crystal with the structure as reported previously for $CuNd_2(Cl_3CCOO)_8 \cdot 6H_2O$ was investigated [1].

Absorption spectra were recorded at 293 and 4.2 K on a Cary-Varian 5 spectrophotometer equipped with a helium flow cryostat in the region 190–950 nm. The intensities of the optical lines were calculated using the program TAUS, transformed to the oscillator strength values and applied to the τ_λ parameter calculation.

Excitation spectra were recorded using an Aminco SPF-500 spectrofluorometer at 77 K ($\lambda_{em}=624.5$ nm).

Raman spectra reported in Ref. [13] were used for the analysis of vibronic components.

The magnetic susceptibility measurements were carried out with two apparatus: (i) a Faraday-type magnetometer working down to 4.2 K and (ii) with a SQUID magnetometer working down to 1.7 K in both the low-field and high-field regions. The data were corrected for diamagnetic contributions using Pascal's constants.

3. Results and discussion

Absorption and excitation spectra of (Nd, Eu)$(Cl_3CCOO)_3 \cdot 2H_2O$ in the UV and visible region are dominated by the f–f transitions, and for europium spectra in the high energy region (>300 nm) also by the charge transfer (CT) band. In contrast to the above, for heteronuclear $CuNd_2(Cl_3CCOO)_8 \cdot 6H_2O$ single crystals (further denoted as Nd:Cu) the strongest broad bands belong to Cu^{2+} (the CT at $\approx$265 nm and the d–d band with a maximum located at 683 nm at room temperature) which are overlapped by neodymium f–f transitions. Since all the effects detected in the spectra (intensity, splitting, broadening) depend strongly on the structure of the system, essential X-ray structural data are as follows.

The crystal structure of $CuNd_2(Cl_3CCOO)_8 \cdot 6H_2O$ [1] consists of heteronuclear chains constructed from dimers of two types of $Nd(1)O_9$ and $Nd(2)O_8$ polyhedra, linked through three bidentate trichloroacetate ligands and one chelating bridging (tridentate type). Thus a noncentrosymmetric dimer unit is formed, connected by CuO_4 planar squares. Two water molecules (OW1, OW2) add to a strongly distorted octahedron. Intrachain metal–metal distances are as follows: Nd(1)–Nd(2), 4.38 Å; Cu(1)–Nd(1), 4.155 Å; Cu(1)–Nd(2), 4.137 Å. The interchain separation is equal to 9.472 Å (Nd(2)–Nd(1)) and 8.680 Å (Cu(1)A–Cu(2)B). The angle Nd(1)–Cu(1)–Nd(2) is close to 168°, while OW1–Cu(1)–OW2 is 167.7°.

The structure of $Ln(Cl_3CCOO)_3 \cdot 2H_2O$ is an example of a one-dimensional polymeric system, composed of two different centrosymmetric dimeric subunits [11,14].

Absorption spectra of the heteronuclear Cu:Nd for two orientations of the crystal at room temperature and 4.2 K are presented in Fig. 1. The broad absorption band at 293 K (683.3 nm = 14 635 cm^{-1}) for the Cu^{2+} ion splits into two broad components (15 306 cm^{-1}, 12 000 cm^{-1}) upon decreasing the temperature to 4.2 K, whereas the fine complex structure of the Stark components of two inequivalent Nd^{3+} ions in the crystal at 4.2 K are recorded. Besides, anisotropy of intensities is well manifested in the spectra depending on the crystal orientation. Results of the oscillator strength calculations for both f–f and d–d transitions are collected in Table 1. Note that the strongest differences in intensities are those of the hypersensitive transition of the Nd^{3+} ions. Note also the remarkable changes in the intensities of the Cu^{2+} bands. This is reasonable since the coordination polyhedron of a copper ion can be described as a distorted octahedron and the Jahn–Teller effect should be considered.

The low temperature electronic spectrum of the single crystals revealed no vibrational fine structure. A structure of this kind is usually observed in the spin-allowed d–d spectra of centrosymmetric metal complexes and several *ungerade* vibrational modes are generally responsible for inducing intensity, and the resulting peaks overlap to produce a smooth featureless band envelope [18].

The broad band splits at low temperatures into two components, with the same spread as at room temperature,

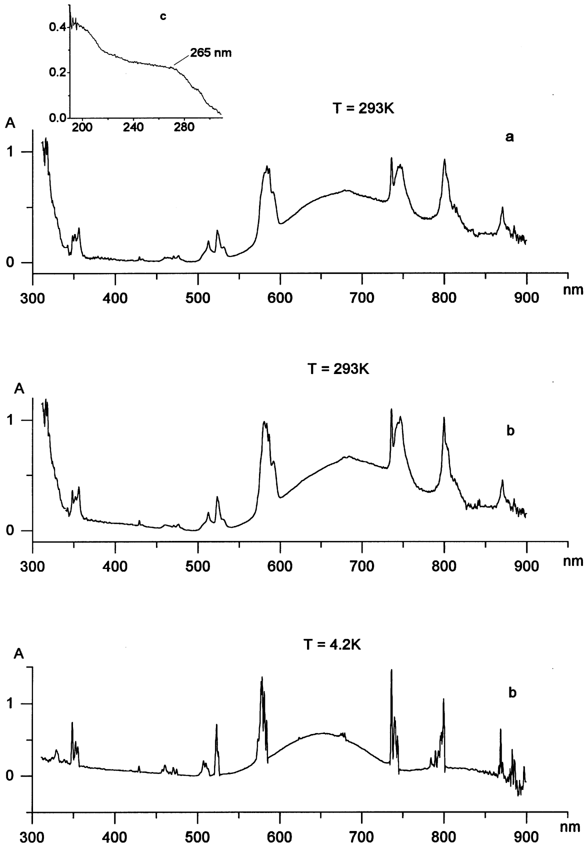

Fig. 1. Absorption spectra of a $CuNd_2(Cl_3CCOO)_8 \cdot 6H_2O$ crystal at different orientations (a,b) and different temperatures ($T=293$ and 4.2 K); (c) CT transition for crystal powder in a thin layer of paraffin oil.

Table 1
The oscillator strength values of f–f transitions $P\times10^8$ and d–d transitions $P\times10^6$ for a $CuNd_2(Cl_3CCOO)_8\cdot6H_2O$ crystal at different orientations and temperatures ($C_{Nd}=2.575$ M)

		$CuNd_2(Cl_3CCOO)_8\cdot6H_2O$				$Nd(Cl_3CCOO)_3\cdot2H_2O$	
		a		b		[11]	
	(nm)	293 K	4.2 K	293 K	4.2 K	293 K	4.2 K
${}^4F_{3/2}$	900–850	188.29	183.09	186.27	142.21	148.46	146.54
${}^4F_{5/2}$ ${}^2H_{9/2}$	830–775	880.51	436.84	832.43	429.53	677.98	407.25
${}^4F_{7/2}$ ${}^4S_{3/2}$	775–725	1013.93	479.84	1054.99	524.99	906.09	420.88
${}^4F_{9/2}$	700–670	58.90	61.87	76.46	52.27	58.78	34.95
${}^4G_{5/4}$ ${}^2G_{7/2}$	600–540	2254.74	1152.69	2925.39	1318.07	1345.50	706.77
${}^2K_{13/2}$ ${}^4G_{7/2}$ ${}^4G_{9/2}$	540–490	614.30	639.86	713.98	645.44	694.77	512.80
${}^2K_{15/2}$ ${}^2G_{9/2}$ $({}^2D,{}^2F)_{3/2}$ ${}^4G_{11/2}$	490–450	215.67	235.09	218.20	207.44	207.37	250.17
${}^2P_{1/2}$	450–425	41.34	32.36	41.63	36.42	40.04	27.44
${}^2D_{5/2}$	425–410	34.60	12.64	30.33	12.87		
${}^4D_{3/2}$ ${}^4D_{5/2}$ ${}^2I_{11/2}$ ${}^4D_{1/2}$ ${}^2L_{15/2}$	370–345	955.96		988.40	956.678	858.95	
$P\times10^6$							
d–d Cu^{2+}	900–500	193.45	181.53	294.56	181.44		

also confirming noticeable interaction of copper with lanthanide ions, additionally observed in the EPR spectra [2]. Proof of the above is afforded in the analysis of diluted $La_{1-x}Nd_x$:Cu single crystal spectra. Results of intensity calculations performed on the absorption spectra in polarized light confirm again the phenomenon detected above. The absorption spectra of a crystal cut perpendicular to the chain axis (010) in π and σ polarized light are shown in Fig. 2. Values of the intensities of both f–f and d–d transitions, as well as of the CT bands, are compiled in Table 2. Their mean values from σ and π polarization of f–f bands were used to calculate the τ_λ parameters from the Judd–Ofelt relation [19,20], which are included in Table 2. The highest oscillator strength values were obtained for ${}^4I_{9/2}\rightarrow{}^4G_{5/2}$, ${}^2G_{7/2}$ and ${}^4I_{9/2}\rightarrow{}^4F_{5/2}$, ${}^2H_{9/2}$; ${}^4F_{7/2}$, ${}^4S_{3/2}$ transitions. These intensities are significantly higher compared with those of pure neodymium trichloroacetates, with polymeric chains composed of dimeric subunits, and also with other polymeric lanthanide acetates, for which P_{exp} for the hypersensitive transition did not exceed a value of $\approx2000\times10^{-8}$ [11,21].

The detected increase of intensities could be caused by interaction with paramagnetic Cu^{2+} ions in the chain, but this also needs additional investigation on other systems. Similarly, the mechanism of this phenomenon needs further consideration. An unexpectedly good estimation of τ_λ parameters was obtained from a limited set of transitions. Decreasing the temperature to 4.2 K was accompanied by a decrease of the oscillator strength values of both f–f and d–d transitions. As before, this effect is more pronounced in this system than in other neodymium single crystal spectra. A simple vibronic theory suggests that for a

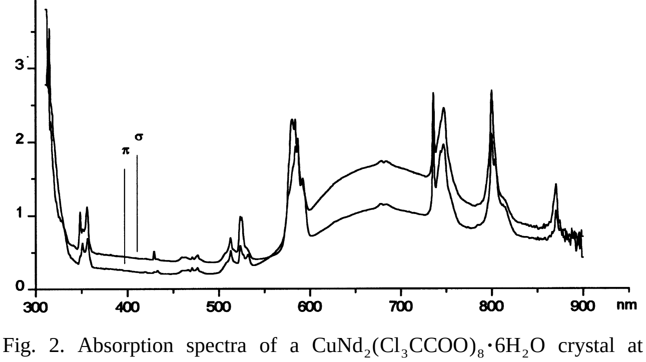

Fig. 2. Absorption spectra of a $CuNd_2(Cl_3CCOO)_8\cdot6H_2O$ crystal at 293 K in polarized light (σ,π).

Table 2
The oscillator strength values of f–f transitions $P\times10^8$ and d–d transitions $P\times10^6$ in polarized light, the $\tau_\lambda\times10^9$ parameter values (calculated from $P_{mean}\times10^8$) and the oscillator strength value of the charge transfer transition (CT) for a $CuNd_2(Cl_3CCOO)_8\cdot6H_2O$ crystal at 293 K; the population of separated Stark components of the ground state vs. temperature is also shown

	σ	π
${}^4F_{3/2}$	173.67	222.97
${}^4F_{5/2}$ ${}^2H_{9/2}$	841.61	804.26
${}^4F_{7/2}$ ${}^4S_{3/2}$	1065.31	1012.07
${}^4F_{9/2}$	71.86	82.05
${}^4G_{5/2}$ ${}^2G_{7/2}$	2989.48	2956.80
${}^2K_{13/2}$ ${}^4G_{7/2}$ ${}^4G_{9/2}$	833.68	703.49
${}^2K_{15/2}$ ${}^2G_{9/2}$ $({}^2D,{}^2F)_{3/2}$ ${}^4G_{11/2}$	194.49	183.98
${}^2P_{1/2}$	42.43	36.82
${}^2D_{5/2}$	17.37	14.25
${}^4D_{3/2}$ ${}^4D_{5/2}$ ${}^2I_{11/2}$ ${}^4D_{1/2}$ ${}^2L_{15/2}$	1088.75	791.79
$\tau_2\times10^9$	13.88 ± 0.36	
$\tau_4\times10^9$	5.29 ± 0.34	
$\tau_6\times10^9$	11.07 ± 0.47	
	$P\times10^6$	
d–d Cu^{2+}	181.22	319.34
CT	2.31×10^{-2}	
Stark components of ${}^4I_{9/2}$	50 K	80 K
0		
21 cm^{-1}	54.62%	68.53%
90 cm^{-1}	7.49%	19.79%
200 cm^{-1}	0.32%	2.73%
325 cm^{-1}		0.125% (70 K)

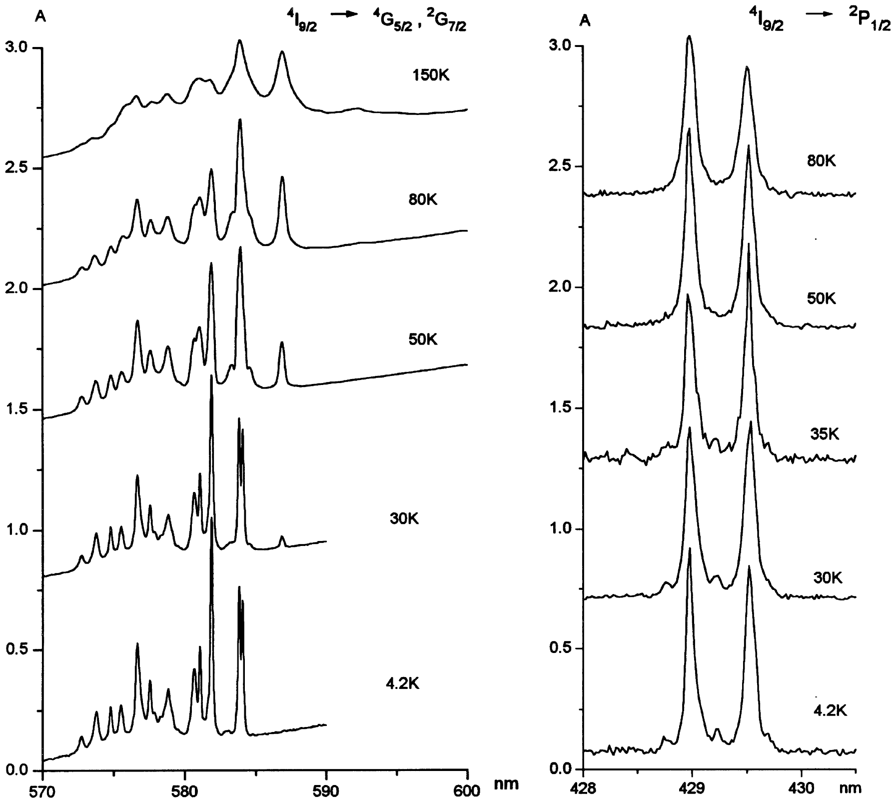

Fig. 3. The temperature dependence of the $^4I_{9/2}\rightarrow{}^2P_{1/2}$ and $^4I_{9/2}\rightarrow{}^4G_{5/2}$, $^2G_{7/2}$ transitions of a $CuNd_2(Cl_3CCOO)_8 \cdot 6H_2O$ crystal.

centrosymmetric complex the intensity P of a d–d electronic transition is related to the temperature T by the expression $\coth^{-1}(P/P_0) = h\nu/2kT$ [18] where P_0 is the intensity at 0 K, k is the Boltzmann constant, and ν is the frequency of the u-perturbing mode.

A meaningful decrease of f–f transitions was detected in the ≈30–50 K temperature range. Between 0 and 40 K the exchange Nd–Cu interaction exceeds the Nd–Nd one, as shown from the EPR spectra, and is dominated by Nd–Cu–Nd fragments [2]. The decrease of intensities of the f–f bands with decreasing temperature could be caused by changes of the population of Stark components of the ground state multiplet, vibronic coupling and other effects.

It is also worth noting the very complex structure of the Nd^{3+} bands at 4.2 K. The number of Stark components exceeds that expected for two nonequivalent structural sites of Nd^{3+} ions. Probably, additional components could be given by a cooperative effect of interacting paramagnetic ions (Fig. 3). The values of the interaction of copper with two structurally inequivalent neodymium ions are different, as found from an EPR investigation [2]. Additional components in the bands corresponding to $^4I_{9/2}\rightarrow{}^2P_{1/2}$ and $^4G_{5/2}$, $^2G_{7/2}$ transitions are shown in Fig. 3. However, the nature of this phenomenon needs further investigation.

Analysis of the temperature dependence of the splitting

Table 3
The electronic and vibronic components in the excitation spectra of a $Eu(Cl_3CCOO)_3 \cdot 2H_2O$ crystal at 77 K

	Energy (cm^{-1})	ΔEnergy (from 0 to the phonon line) (cm^{-1})	
$^7F_0\rightarrow{}^5D_0$	17226		
$^7F_0\rightarrow{}^5D_1$	18993		
$^7F_0\rightarrow{}^5D_2$	21471		
	21575	104	δ(Eu–O)
	21680	209	ν(Eu–O)
	21704	233	ν(Eu–O)
	21834	363	ρ(C=O)
	21954	483	$\bar{\omega}$(H_2O)
	22185	714	δ(OCO)
	22431	960	ν(C–C)
	22857	1386	ν(C–O)
	23095	1624	δ(H_2O)

of $^4I_{9/2} \rightarrow {}^2P_{1/2}$; $^4F_{3/2}$ and $^4G_{5/2}$, $^2G_{7/2}$ transitions made it possible to construct the energy level diagram of the ground state multiplet; their energies are collected at the bottom of Table 2. Splitting of the $^4I_{9/2}$ term is close to 325 cm^{-1} and the components of the two Nd sites are shifted at the $^2P_{1/2}$ level by $\approx$30 cm^{-1}. The population of separated Stark components of the ground state versus temperature is also given at the bottom of Table 2.

Judging from the excitation spectra of the pure europium trichloroacetate vibronic components are clearly shown. Analysis of the vibronic sideband was performed on the basis of the Raman data [13]; the results are collected in Table 3. Vibronic components observed in excitation spectra of electronic transition with $\Delta J = 2$ are stronger than those in emission spectra. Note that the strongest components correspond to the internal ligand vibration of the groups engaged in coordination of metal ion and are consistent with the theory of vibronic transition probabilities.

3.1. Magnetic properties

Experimental magnetic data plotted as magnetic susceptibility χ_M and magnetic moment μ_{eff}, calculated per molecule of complex for pure neodymium and dysprosium trichloroacetate, versus temperature are presented in Fig. 4a,b. In the same figure (Fig. 4c) a similar relation is given for the heteronuclear Nd:Cu trichloroacetate. A slight decrease of the magnetic moment for the neodymium containing crystal when the temperature is decreased might be due to both crystal-field effects around the rare earth metal ion and weak antiferromagnetic interactions. Almost no change of the magnetic moments was seen for dysprosium trichloroacetate in the range 300–80 K other than the increase of the maximum at 2.25 K. This is unexpected compared to the results obtained for the neodymium system. The X-ray crystal tests indicate that the Nd and Dy trichloroacetates are isostructural.

A more pronounced cooperative effect is seen in both magnetic susceptibility and magnetic moment vs. temperature in the heteronuclear Nd:Cu system. The magnetic moment decreases from 4.78 at 300.2 K to 2.89 at 4.2 K (Table 4). This decrease could again be caused by crystal-field effects as well as a cooperative antiferromagnetic interaction of Cu^{2+}:Nd^{3+} and Nd^{3+}:Nd^{3+} ions. The EPR investigations which were followed independently [2] showed that the Cu^{2+}–Nd^{3+} interaction exceeds the Nd^{3+}–Nd^{3+} one. The exchange interactions detected in the 30–4 K region could be described by the Nd(1)–Cu–Nd(2) intrachain fragment. The interactions of Cu^{2+} ions with two nonequivalent neodymium centres are different. Additional components (which could not be caused by the population of the higher Stark components) in the electronic spectrum in the 4.2–30 K temperature range seem to confirm this phenomenon. The explanation of how the Nd^{3+}–Nd^{3+} interaction could be affected by the magnetic properties of heteronuclear systems requires further investigation of heteronuclear systems with diamagnetic La^{3+} ions. Thus far, we have not been able to synthesize that type of single crystal. The magnetic susceptibility data change with temperature according to the Curie–Weiss law with $\Theta = -54.1$ and -50.1 K for Nd^{3+}–Cu^{2+} and Nd trichloroacetates (Table 4), which could also confirm the weak antiferromagnetic exchange coupling between the

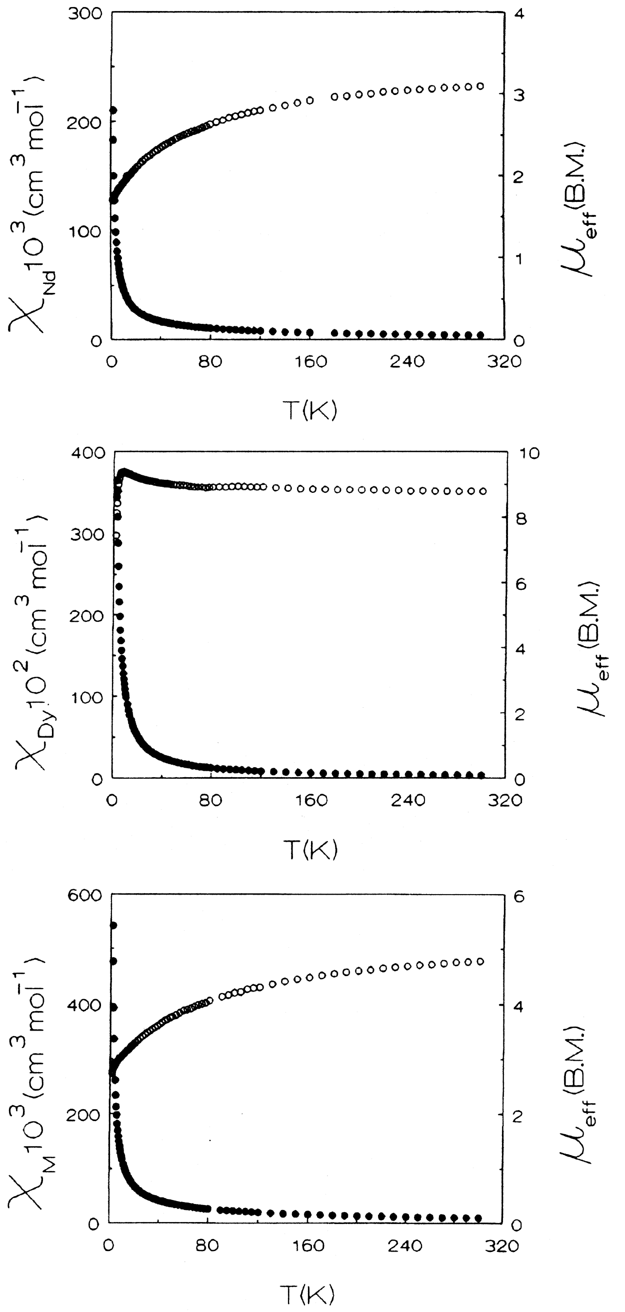

Fig. 4. Experimental magnetic data plotted as magnetic susceptibility χ (●) and magnetic moment μ_{eff} (○), calculated per molecule of complex, vs. temperature: (a) $Nd(Cl_3CCOO)_3 \cdot 2H_2O$, (b) $Dy(Cl_3CCOO)_3 \cdot 2H_2O$, (c) $CuNd_2(Cl_3CCOO)_8 \cdot 6H_2O$.

Table 4
The magnetic data of $CuNd_2(Cl_3CCOO)_8 \cdot 6H_2O$

Temperature (K)	$\chi_M \times 10^6$ ($cm^3\ mol^{-1}$)	μ_{eff} (B.M.)	C	Θ
1.72	0.542	2.73	3.36	−54.1
4.0	0.261	2.89	For neodymium and	
19.0	0.0702	3.27	dysprosium trichloroacetate	
30.0	0.0503	3.48	1.39	−50.1
50.0	0.0354	3.77	9.46	+5.4
100.2	0.0220	4.20		
150.3	0.0164	4.45		
220.3	0.0122	4.65		
300.2	0.00951	4.78		

metal ions. For the dysprosium system the Weiss constant is equal to +5.4 K. The mechanism of the f–d system interaction is the subject of further studies. At the moment we are not able to explain the magnetic properties of Dy^{3+} polynuclear one-dimensional polymeric systems.

4. Summary

(1) Two types of single crystals, i.e. simple $(Nd,Eu,Dy)(Cl_3CCOO)_3 \cdot 2H_2O$ and mixed $CuNd_2(Cl_3CCOO)_8 \cdot 6H_2O$ trichloroacetates, were obtained. Their optical and magnetic properties were investigated in the 4.2–293 K range.

(2) The centrosymmetric dimers in structure (**I**) become noncentrosymmetric lanthanide dimers in structure (**II**), reflecting the influence of Cu^{2+} ion on the chain composition and M–M interaction.

(3) The effect of the polymeric structure is manifested both in the intensities and splitting patterns of spectral lines.

(4) Vibronic coupling detected in excitation spectra of europium trichloroacetates is stronger than that in emission spectra. Assignments of the vibronic components were made on the basis of Raman data.

(5) Cooperative interactions of ion-pairs coupled in the polymeric chain quenches the magnetic moment when the temperature is decreased to 4 K, both in simple and mixed single crystals. This effect is confirmed by EPR data.

(6) The results obtained, as well as our earlier spectroscopic investigation, allow us to assume a superexchange interaction in the systems tested, most probably mediated by phonons [15–17]. Attempts to specify the detailed nature of this interaction will be the subject of future studies.

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