Synthesis, optical and magnetic properties of homo- and heteronuclear systems and glasses containing them

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Received (in Montpellier, France) 28th June 1999, Accepted 2nd September 1999

To study the effect of ion pairs (f and d–f) coupled in a polymeric system on their optical and magnetic properties, syntheses of homo- and heteronuclear systems were undertaken. Single crystals of the polynuclear Nd glutarate of formula $[\mathrm{Nd(Glut)(H_2O)_4}]\mathrm{Cl}\cdot 2\mathrm{H_2O}$ (**1**) were obtained. The X-ray diffraction analysis shows the triclinic system and the *P*1 space group. The structure consists of polynuclear two-dimensional chains built of dimeric units with two nonequivalent Nd^{3+} centres. The two Nd^{3+} ions are coordinated by carboxyl groups of the glutarate anion and water molecules. Two different coordination modes of the carboxylate group occur in the structure: simple bridging (bidentate) and chelating bridging (tridentate). There are five oxygen atoms of four carboxylate groups in the direct environment of each Nd ion and four water molecules complete the coordination number at nine. The network of hydrogen bonds stabilises the crystal structure. The above structural characteristics are well manifested in the spectroscopic properties of crystalline **1**. Using the sol–gel technique, neodymium (**2**) and $\mathrm{Nd}^{3+} : \mathrm{Cu}^{2+}$ glutarate (**3**) were incorporated in glass. Glasses of good optical quality were obtained, enabling an analysis of the spectroscopic properties of the investigated systems and consideration of the heteronuclear forms in the glass. The optical and magnetic behaviour of these systems were analysed down to 1.8 K. The effect of the dimensionality of the systems on their optical and magnetic properties is also discussed.

Lanthanides play an important role in modulating the magnetic properties of many materials. Their main features are influenced by the anisotropy of the ground state of 4f ions and by the nature and strength of the exchange interaction between the 4f–4f and/or 4f–3d metals. Recently, polymeric (one- and two-dimensional) and dimeric lanthanide as well as heteronuclear (lanthanide and transition metal) compounds have attracted considerable interest.[1–11] This is motivated by the effect of the dimensionality of the polymeric chains on both the optical and magnetic properties and the applications of such materials.[12] Previously, we reported the X-ray, optical and magnetic properties of a series of polymeric lanthanide trichloroacetates and their heteronuclear ($\mathrm{Cu}^{2+} : \mathrm{Ln}^{3+}$) analogues.[10,13–20] Their EPR and electronic spectra show Ln–Cu and Ln–Ln interactions in the chains.[11,15,17,20] Two other types of glutarates were obtained by us earlier[21,22] and X-ray as well as selected spectral data were analysed. Now we have made an effort to synthesize a new type of polymeric compound also incorporated in silica glass and to analyse its optical and magnetic properties.

Experimental

X-Ray analysis and compound syntheses

A crystal of the title compound was examined on a Kuma KM4CCD diffractometer equipped with a CCD camera. The method used for data collection with KM4CCD, as for other area detectors,[23] was rotational. Precise cell constants were determined by the least-squares method using most of the reflections collected. The data were corrected for Lorentz polarization and absorption effects.[24] The statistics of reflection intensities clearly indicated the *noncentrosymmetric* space group.

The structure was solved by Patterson techniques with the SHELXS86 program.[25] The positions of most non-hydrogen atoms were revealed. The remaining atoms were found by the difference synthesis. The structure was refined by SHELXL93.[26] During the refinement process many constraints and restraints were applied, but most of them were released in the final stages of the refinement. All non-hydrogen atoms were treated anisotropically. The hydrogen atoms of the glutaric fragment were found geometrically. The H atoms in water molecules were not seen clearly on the ΔF maps and were not used in the refinement. The final Flack absolute structure parameter[27] was $-0.02(4)$. The crystal data and refinement details are given in Table 1.

CCDC reference number 440/140. See http://www.rsc.org/suppdata/nj/1999/1097/ for crystallographic files in. cif format.

Single crystals of polynuclear $[\mathrm{Nd(Glut)(H_2O)_4}]\mathrm{Cl}\cdot 2\mathrm{H_2O}$ (**1**) were obtained from a solution of Nd : Glut in a 2 : 3 ratio. Efforts to precipitate the heteronuclear sample in a form appropriate for optical and magnetic studies failed; the substance formed was grease-like. Thus, a heteronuclear system from a mixed solution of Nd : Cu : glutarate (1 : 1 : 3 ratio, where the M : L 2 : 3 ratio was kept) was incorporated in glasses. The polymeric complex **1** was also incorporated in glass for comparison with the heteronuclear system. The sample of **1** was checked by X-ray diffraction techniques before use in the optical and magnetic measurements.

The polynuclear as well as the heteronuclear systems were incorporated in glass according to the method described previously.[28]

Measurement procedures

Absorption spectra were recorded on a Cary-15 spectrophotometer equipped with a helium cryostat at temperatures from

Table 1 Crystal data and structure refinement for $[Nd(C_5H_6O_4)(H_2O)_4]Cl \cdot 2H_2O$ (**1**)

Formula	$C_{10}H_{36}Cl_2Nd_2O_{20}$
M	835.77
Crystal system	Triclinic
Space group	$P1$
a/Å	7.8770(10)
b/Å	8.781(2)
c/Å	10.444(2)
α/deg	110.69(2)
β/deg	95.240(10)
γ/deg	103.48(2)
U/Å^3	645.1(2)
Z	1
μ./mm^{-1}	4.27
T/K	293(2)
No. reflect.	3793
No. indep. reflect.	1894
No. obs. reflect.	1887
R_{int}	0.017
R indices $[I > 2\sigma(I)]$	$R_1 = 0.035$, $wR_2 = 0.098$
R indices (all data)	$R_1 = 0.035$, $wR_2 = 0.098$

293 to 4 K and for the spectral range from 200 to 2500 nm. The f–f and d–d transition probabilities were analysed and the Judd–Ofelt parameters were calculated.[29,30] The calculations were performed according to the procedure already described.[13,21,31] The magnetic susceptibility measurements were carried out with a SQUID magnetometer working down to 1.7 K in both the low- and high-field regions (0–5 T). The data presented in Fig. 7 were obtained at 0.5 T.

Results and discussion

X-Ray data

Coordination around the neodymium ions and the atomic labelling scheme for **1** is presented in Fig. 1. Selected bond lengths and angles concerning the coordination are given in Table 2. Fig. 2 shows the packing in the crystal lattice. The $[Nd_2(Glut)_2(H_2O)_8]^{2+}$ ions form chains along the (1 0 0) direction. In the chain the neodymium ions are bridged into pairs by four carboxylate groups from the glutaric species. Two of the groups are involved in simple bridging bonds and two others in chelating bridging ones (having two contacts to the first metal and one contact to the second metal ion). The Nd–Nd distance is 4.026(1) Å. Additionally, each neodymium ion is coordinated by four water molecules. This leads to a coordination number of nine for both neodymium ions. In the noncentrosymmetric subunits created in the structure the M–O bonds (for the carboxylate groups) vary from 2.444(7) to 2.607(7) Å and the M–O(W) bonds to the water ligands from 2.474(8) to 2.527(8) for one neodymium centre and 2.421(6)–2.622(7) and 2.475(6)–2.551(8) Å for M–O(carboxylate) and M–O(W), respectively, for the second metal centre (Table 2). Finally, this fluctuation in M–L distances for the two Nd^{3+} ions in the dimer unit is not big enough to manifest itself in a doublet splitting of all spectral lines. This type of metal ion inner-sphere coordination of lanthanide glutarate differs from that for the 1 : 1 M : L perchlorate analogue reported by us earlier.[21] It indicates that the size of the anion modifies the form of the inner-sphere carboxylate group coordination and the number of coordinated water molecules. The coordination of the carboxyl group differs from that of the earlier reported 1 : 1 complexes, where only one type of carboxylate group bonding mode was described and a two-dimensional network of chains was formed. In the system presented here two modes of carboxyl group coordination were found, similarly to another type of lanthanide glutarate with a 2 : 3 M : L ratio and having a three-dimensional polymeric structure.[22] In fact, creation of the noncentrosymmetric dimeric units was found

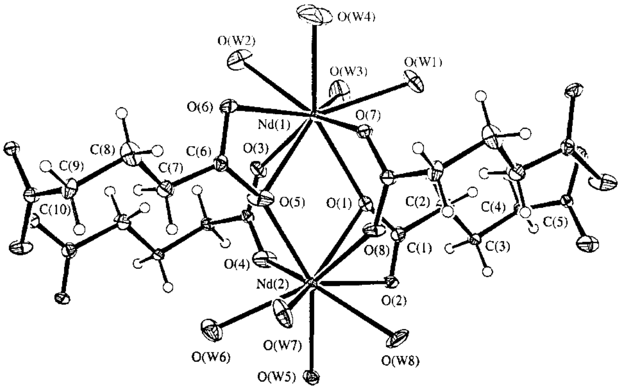

Fig. 1 An ORTEPII view of coordination around the Nd ions in **1**. Displacement ellipsoids are drawn at the 50% probability level: displacement parameters of hydrogen atoms were artificially diminished for clarity. Atomic labels for the asymmetric unit are also presented.

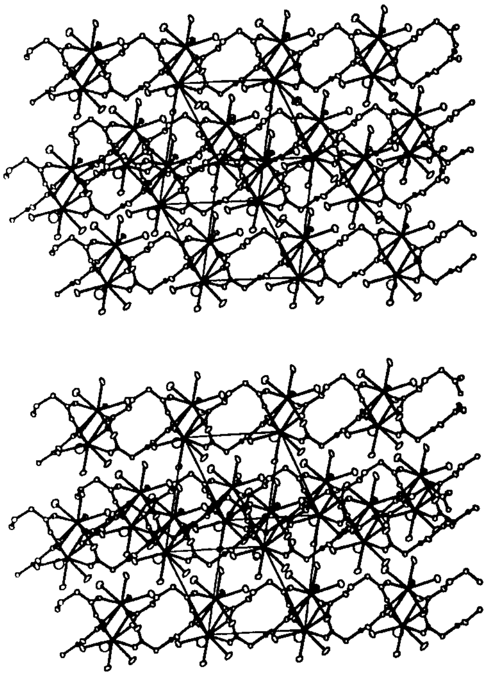

Fig. 2 A stereoscopic packing diagram showing chains formed in the crystal lattice of $[Nd(Glut)(H_2O)_4]Cl \cdot 2H_2O$ (**1**).

Table 2 Selected bond lengths (Å) and angles (deg) for $[Nd(C_5H_6O_4)(H_2O)_4]Cl \cdot 2H_2O$ (**1**)

Nd(1)–O(W1)	2.510(7)	Nd(2)–O(W5)	2.475(6)
Nd(1)–O(W2)	2.474(8)	Nd(2)–O(W6)	2.551(8)
Nd(1)–O(W3)	2.482(9)	Nd(2)–O(W7)	2.518(9)
Nd(1)–O(W4)	2.527(8)	Nd(2)–O(W8)	2.511(8)
Nd(1)–O(1)	2.444(7)	Nd(2)–O(1)	2.519(6)
Nd(1)–O(3)	2.472(7)	Nd(2)–O(2)	2.622(7)
Nd(1)–O(5)	2.607(7)	Nd(2)–O(4)	2.421(8)
Nd(1)–O(6)	2.509(8)	Nd(2)–O(5)	2.361(8)
Nd(1)–O(7)	2.478(7)	Nd(2)–O(8)	2.421(6)
O(1)–Nd(1)–O(3)	75.0(2)	O(1)–Nd(2)–O(2)	49.0(2)
O(1)–Nd(1)–O(5)	70.2(2)	O(1)–Nd(2)–O(4)	73.3(2)
O(1)–Nd(1)–O(6)	121.7(2)	O(1)–Nd(2)–O(5)	73.1(2)
O(1)–Nd(1)–O(7)	75.6(2)	O(1)–Nd(2)–O(8)	65.3(2)
O(3)–Nd(1)–O(5)	70.6(2)	O(2)–Nd(2)–O(4)	75.6(3)
O(3)–Nd(1)–O(6)	91.3(2)	O(2)–Nd(2)–O(5)	120.6(2)
O(3)–Nd(1)–O(7)	137.6(2)	O(2)–Nd(2)–O(8)	91.2(2)
O(5)–Nd(1)–O(6)	52.0(2)	O(4)–Nd(2)–O(5)	76.4(2)
O(5)–Nd(1)–O(7)	71.0(2)	O(4)–Nd(2)–O(8)	133.9(2)
O(6)–Nd(1)–O(7)	79.0(2)	O(5)–Nd(2)–O(8)	73.1(3)

in structures of other types of lanthanide carboxylates, such as amino acid complexes with lanthanides.[10,16,17,31]

Optical data

Fig. 3 and 4 present absorption spectra of the neodymium glutarate single crystal (**1**) in the temperature range 4–293 K. The absorption spectra were recorded in the UV, Vis and IR regions. Calculations of the d–d and f–f electron transition probabilities were performed and the results are collected in Tables 3 and 4. The evaluated values of the oscillator strengths were further used in calculations of the Judd–Ofelt parameters, given at the bottom of Table 3. Calculated intensities of electronic transitions in the single crystal spectra of $[Nd(glut)(H_2O)_4]Cl \cdot 2H_2O$ (**1**) at 4 K are also collected in Table 3. The electron transition probabilities calculated for the systems incorporated in glass and in aqueous solution are also reported.

Both the intensities of the f–f transition and the Judd–Ofelt parameters show a rather high symmetry for the metal centre in the crystal of **1** with an oscillator strength value of 971.18×10^{-8} for a hypersensitive transition. This value is comparable with that observed in the neodymium aquo ion spectra of relatively high symmetry (C_{3h}).[32] The symmetry of the Nd^{3+} ion in compound **1** possibly does not belong to a point group fulfilling the conditions of hypersensivity in the Judd–Ofelt theory, where both intensities and the τ_2 parameter are dramatically higher.[33,34]

Fig. 5 presents a band corresponding to the $^4I_{9/2} \rightarrow {}^2P_{1/2}$ transition of **1** at room temperature. The splitting of the ground state multiplet determined from that transition is equal to 377 cm^{-1}. It was also found from the temperature dependence of the $^4I_{9/2} \rightarrow {}^2P_{1/2}$ and $^4G_{5/2}$, $^2G_{7/2}$ transitions. The splitting of the ground state multiplet is a little smaller than in the single crystal spectra of the 1 : 1 neodymium glutarate of formula $[Nd(Glut)(H_2O)_3]ClO_4$ reported by us earlier.[21]

In system **1** presented here the splitting of the $^4I_{9/2} \rightarrow {}^4F_{3/2}$ band also shows a lower value (38 cm^{-1}). The calculated population of the separated Stark components of the ground state multiplet from 4 to 300 K can help explain the magnetic data at low temperature. The second component of the

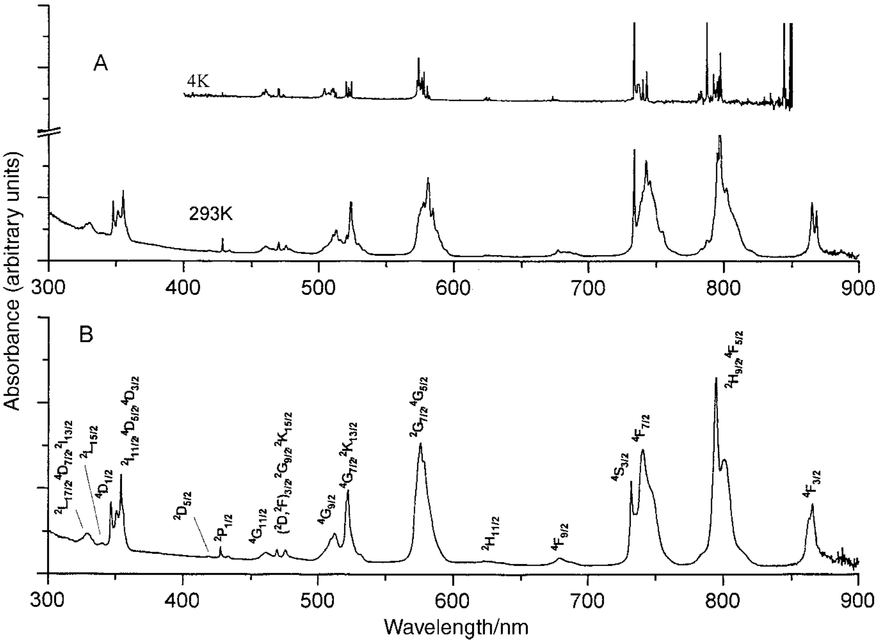

Fig. 3 Absorption spectra of (*A*) the $[Nd(Glut)(H_2O)_4]Cl \cdot 2H_2O$ (**1**) crystal and (*B*) the gel incorporating the 2 : 3 neodymium glutarate complex **2** at 293 K.

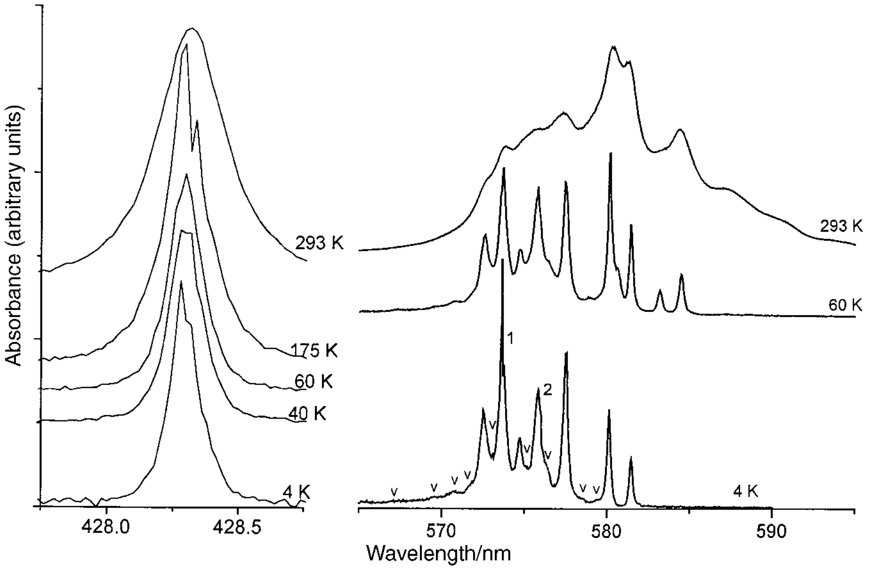

Fig. 4 The temperature dependence of the f–f transitions of the $[Nd(Glut)(H_2O)_4]Cl \cdot 2H_2O$ (**7**) crystal.

Table 3 The oscillator strengths P of f–f transitions and Judd–Ofelt τ^{λ} parameters for various Nd : Glut systems

		Oscillator strength ($P \times 10^8$)			
		$[Nd(Glut)(H_2O)_4]Cl \cdot 2H_2O$ (**1**)		Nd : Glut (2 : 3) (**2**)	
f–f Nd^{3+}	λ/nm	293 K	4 K	2% gel	0.04 M soln
$^4F_{3/2}$	920–840	237.26	95.73	247.89	241.65
$^4F_{5/2}$, $^2H_{9/2}$	835–772	869.21	281.27	896.20	890.22
$^4F_{7/2}$, $^4S_{3/2}$	772–715	926.21	253.94	887.40	885.13
$^4F_{9/2}$	700–659	68.77	25.47	56.34	58.08
$^4G_{5/2}$, $^2G_{7/2}$	610–555	971.18	376.31	1134.37 1301.87(12 K)	1012.18
$^2K_{13/2}$, $^4G_{7/2}$, $^4G_{9/2}$	546–494	721.94	356.07	691.26	681.42
$^2K_{15/2}$, $^2G_{9/2}$, $(^2D,^2F)_{3/2}$, $^4G_{11/2}$	494–443	215.68	224.31	184.65	184.78
$^2P_{1/2}$	473–425	30.05	9.44	34.28	34.11
$^2D_{5/2}$	425–415	6.05		5.28	5.02
$^4D_{3/2}$, $^4D_{5/2}$, $^2I_{11/2}$, $^4D_{1/2}$, $^2L_{15/2}$	365–335	835.88		970.84	968.30
$\tau_{\lambda} \times 10^9$		$\tau_2 = 2.42 \pm 0.34$		$\tau_2 = 2.85 \pm 0.40$	$\tau_2 = 2.13 \pm 0.38$
		$\tau_4 = 4.32 \pm 0.31$		$\tau_4 = 5.18 \pm 0.36$	$\tau_4 = 5.19 \pm 0.35$
		$\tau_6 = 10.53 \pm 0.44$		$\tau_6 = 10.16 \pm 0.53$	$\tau_6 = 10.12 \pm 0.50$

ground state multiplet $^4I_{9/2}$ located at 91 cm^{-1} is populated to the extent of 5.4% at 45 K.

The dramatic decrease of intensities with temperature indicates the strong electron–phonon coupling as well as the crystal field (CF) effect as also observed in ref. 13, 18 and 19. At low temperature, the anti-Stokes components must disappear and the intensities of bands in which the vibronic components are involved must decrease. The electron–phonon coupling is manifested best in the electronic transition $^4I_{9/2} \rightarrow {}^4G_{5/2}$, which obeys the selection rule $\Delta J = 2$ according to the theory of vibronic transition probabilities.[35] Vibronic components associated with this transition are assigned in Fig. 4. They can be promoted by both M–O and the internal ligand modes.

The splitting of the $^4I_{9/2} \rightarrow {}^2P_{1/2}$ Kramers doublet at 4 K points to the existence of two different metal centres with relatively small differences in M–O bond lengths and a symmetry distortion of the separated metal centres in the dimeric unit. In another f–f transition ($^4I_{9/2} \rightarrow {}^4G_{5/2}$, $^2G_{7/2}$), subtle splitting of the Stark component with a doublet structure is not well observed except for some lines (1, 2 in Fig. 4). Changes in the band shape of the $^4I_{9/2} \rightarrow {}^2P_{1/2}$ transition with temperature point to some subtle transformation of the structure in the region of 60–175 K. Instead of simple band broadening with increasing temperature, additional sharp lines appear at 175 K.

In further experiments we used the analysis of the f–f transition intensities in the region of the hypersensitive band of the Nd^{3+} ion and also the splitting of the levels at 4 K as a test in investigations of the heteronuclear $Nd^{3+} : Cu^{2+}$ system formation in glass. The intensity analysis of the d–d bands and the energies of charge transfer (CT) transitions can also provide useful information, especially since we were not able to precipitate the heteronuclear compounds.

In the spectra of **3** the intensities of the $^4I_{9/2} \rightarrow {}^4G_{5/2}$, $^2G_{7/2}$ and $^4F_{5/2}$, $^2H_{9/2}$ bands show formation of the heteronuclear system in glass rather than that of polynuclear chains with one kind of metal centre (see Tables 3, 4). The intensities of both transitions differ from those in the single crystal spectra and of the homonuclear system in solution (Table 3). Most probably they can "borrow" intensity from the d–d bands or create Nd^{3+} centres in the heteronuclear system with different symmetries. The colour (green) of $Nd^{3+} : Cu^{2+}$: Glut (**3**) incorporated in a gel is the same as that of the grease-like sample. The room temperature spectra of the single crystal of **1** and $Nd^{3+} : Cu^{2+}$: Glut (**3**) in gel in the region of the hypersensitive $^4I_{9/2} \rightarrow {}^4G_{5/2}$, $^2G_{7/2}$ transition also indicate formation of different environments for the Nd ion centre in the heteronuclear system.

In addition, an unexpected effect was observed in the spectra of the glutarate complex **2** incorporated in gel. The splitting of the $^4I_{9/2} \rightarrow {}^4G_{5/2}$, $^2G_{7/2}$ transitions at low temperature shows transformation of the lanthanide centre in the structure of the gel in relation to the single crystal [compare Fig. 4 and 6(*C*)]. Moreover, with decreasing temperature an inverse relation of the intensity changes was detected in these systems. The temperature decrease leads to a decrease of the f–f transition intensities in the crystal spectra, whereas an increase of intensity was found in the gel. This effect is most probably due to the rigidity of the gel systems and band broadening in glass as a result of disorder.

A comparison of two spectra at low temperature, for Nd : Glut (**2**) and Nd : Cu : Glut (**3**) incorporated in gel, shows subtle differences in the splitting of the neodymium hypersen-

Table 4 The oscillator strengths P of f–f transitions for $Nd^{3+} : Cu^{2+}$: Glut (**3**) systems

		Oscillator strength ($P \times 10^8$) Nd : Cu : Glut (2 : 3) (**3**)	
f–f Nd^{3+}	λ/nm	2% gel	0.04 M soln
$^4F_{3/2}$	920–840	483.23	340.21
$^4F_{5/2}$, $^2H_{9/2}$	835–772	1386.78	1062.64
$^4F_{7/2}$, $^4S_{3/2}$	772–715	801.30	966.92
$^4F_{9/2}$			
$^4G_{5/2}$, $^2G_{7/2}$	610–555	957.84 1344.70 (4 K)	935.00
$^2K_{13/2}$, $^4G_{7/2}$, $^4G_{9/2}$	546–494	678.14	667.95
$^2K_{15/2}$, $^2G_{9/2}$, $(^2D,^2F)_{3/2}$, $^4G_{11/2}$	494–443		180.11
$^2P_{1/2}$	473–425		34.89
d–d Cu^{2+}	1350–600	112700	22960

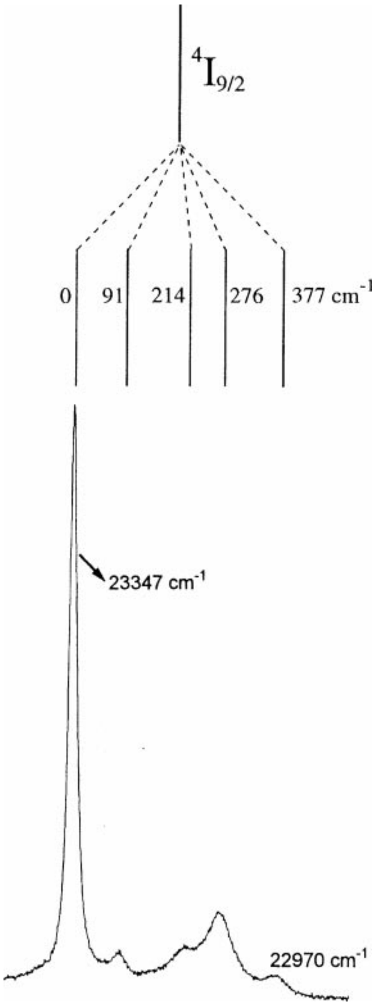

Fig. 5 The $^4I_{9/2} \rightarrow {}^2P_{1/2}$ transition for the single crystal of **1**.

sitive transition as well as its intensity variations in both systems. This could confirm some differences in the direct environment of the Nd^{3+} ions in both **2** and **3**. Moreover, in these cases the decrease in temperature is accompanied by an increase in intensities. One can find in the intensities of the d–d transition an additional argument that seems to confirm the formation of the heteronuclear system in the gel. The oscillator strength values of the d–d band calculated for two different systems of **3**, in solution and gel (see Table 4), confirm creation of the heteronuclear system in gel, a little different than in the Nd : Cu : Glut solution. These spectra also differ from the simple Cu : Glut spectrum.

UV spectra of the two systems, Nd : Cu : Glut **3** incorporated in gel and in a water solution, show dramatic shifts of the Cu^{2+} ion CT band. Formation of the heteronuclear polymeric forms is also manifested in a shift in the energy of the d–d transition [see Fig. 6(*A*) and (*B*)].

Magnetic data

The magnetic data for **1** are plotted as $\chi_M \cdot T$ and $1/\chi_M$ *vs.* temperature (Fig. 7). The magnetic susceptibilities vary with temperature (45–300 K) according to the Curie–Weiss law with $\Theta = -47.35$ (while that evaluated from the whole temperature range is equal to -19.4) showing a degree of antiferromagnetic ordering in solid **1** (Fig. 7). The decrease in the magnetic moment could be due to the crystal field effect (depopulation of the separated Stark components at low temperature) and weak antiferromagnetic ordering of the ion pair coupled in the dimer unit of the polymer structure. Thus at 300 K $\mu_{eff} = 3.09$ μ_B and at 1.8 K we have a magnetic moment equal to 1.69 μ_B, lower than that observed in isolated neodymium systems.[36] Also $\chi_M \cdot T$ is lower when compared to that in the isolated Nd(III) system at room and low temperature.[31] If only the CF effect operates $\chi_M \cdot T$ is expected to reach a plateau at low temperature where only the lowest Kramers doublet is thermally populated. The continuous decrease of $\chi_M \cdot T$ as T approaches 1.7 K indicates that the two local Kramers doublets interact and $\chi_M \cdot T$ reaches a value of 0.38 cm^3 mol^{-1} K^{-1}. Similar results were reported by us for another neodymium polymeric system, the polynuclear and heteronuclear Nd and Nd : Cu trichloroacetates.[10,13,18,19] EPR investigation of the Nd : Cu heteronuclear systems points to stronger Cu–Ln than Ln–Ln ion interaction, too.[20,37,38]

Careful analysis of χ_M *vs.* T shows a maximum at 1.80 K (T_N) that could confirm an antiferromagnetic ordering. The above needs confirmation by measurements of magnetic susceptibilities at different crystal orientations. However, the sizes

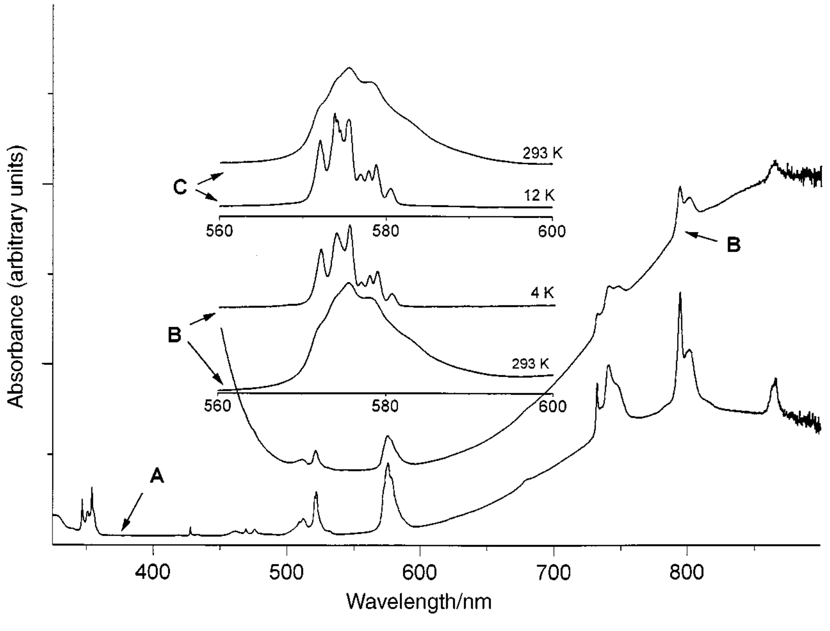

Fig. 6 Absorption spectra of (*A*) Nd,Cu glutarate (**3**) aqueous solution, (*B*) gel incorporating the Nd,Cu glutarate system (**3**) and (*C*) gel incorporating the 2 : 3 neodymium glutarate complex **2**.

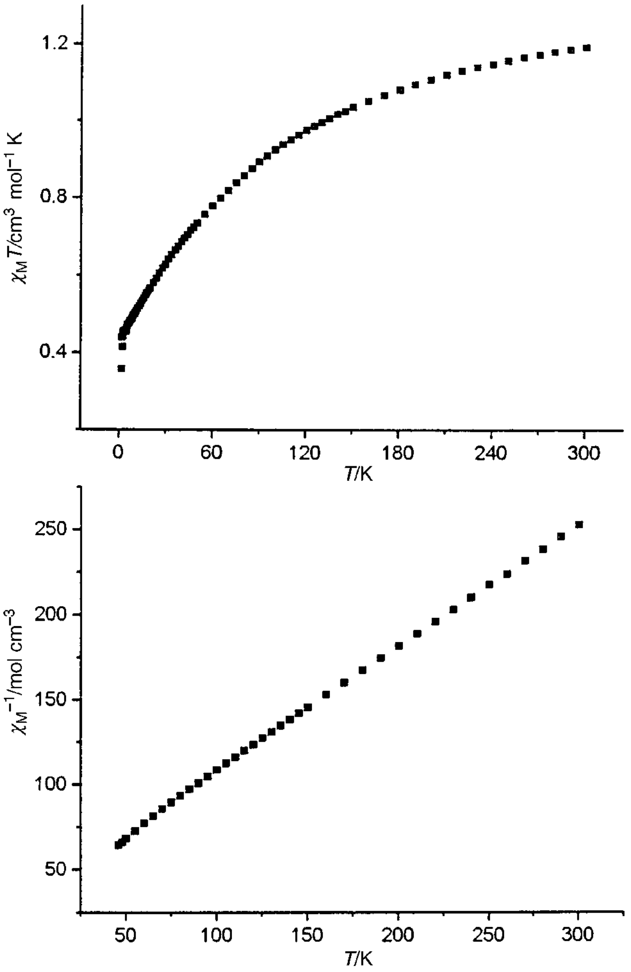

Fig. 7 Experimental magnetic data plotted as $\chi_M \cdot T$ and $1/\chi_M$ calculated per molecule of the $[Nd(Glut)(H_2O)_4]Cl \cdot 2H_2O$ complex (**1**) *vs.* temperature.

of the single crystals obtained made it impossible to perform such experiments.

Applying the splitting of the ground state multiplet determined from the spectral data (Fig. 5), magnetic susceptibilities in the range of 2–300 K were calculated according to the relation

$$\chi = \frac{8N\mu_B^2}{kT} \cdot \left[\frac{81 + 49\exp\left(\frac{-\Delta_1}{kT}\right) + 25\exp\left(\frac{-\Delta_2}{kT}\right) + 9\exp\left(\frac{-\Delta_3}{kT}\right) + \exp\left(\frac{-\Delta_4}{kT}\right)}{1 + \exp\left(\frac{-\Delta_1}{kT}\right) + \exp\left(\frac{-\Delta_2}{kT}\right) + \exp\left(\frac{-\Delta_3}{kT}\right) + \exp\left(\frac{-\Delta_4}{kT}\right)} \right] + \mathrm{TIP} \qquad (1)$$

where Δ_n is the energy gap between Kramers levels of the ground state multiplet with respective m_j quantum numbers and TIP is the temperature independent paramagnetism. The calculated values are in good agreement with experimental data.

The exchange integral J_0 equal to -0.005 cm^{-1} was calculated using

$$\chi_M = \frac{2N\mu_B^2 g^2}{kT\left[3 + \exp\left(\frac{-J_0}{kT}\right)\right]} + \mathrm{TIP} \qquad (2)$$

This equation can be applied to the interpretation of magnetic properties of lanthanide ions with odd values of J at very low temperatures[39]. The value of the effective quantum number in the Heisenberg Hamiltonian was assumed to be $S' = 1/2$. Very good agreement of the calculated values with the experimental ones was obtained in the range of 1.7–15 K.

Conclusion

1. Among others, three different systems were investigated: polymeric $[Nd(Glut)(H_2O)_4]Cl \cdot 2H_2O$ single crystal, neodymium glutarate (2 : 3) incorporated in gel and Nd : Cu glutarate incorporated in gel. Their optical and magnetic properties were investigated in the 1.7–293 K temperature range.

2. The structure of **1** consists of polynuclear two-dimensional chains built of dimers with two nonequivalent Nd^{3+} centres (Fig. 1). The two Nd^{3+} ions are coordinated by the carboxyl groups of the glutarate anion and water molecules. Two different coordination modes of the carboxylate group occur in the structure: simple bridging (bidentate) and chelating bridging (tridentate).

3. Low temperature spectra of **1** show two symmetry centres for the metal ion, determined on the basis of the ${}^4I_{9/2} \rightarrow {}^2P_{1/2}$ transition. The intensity of the ${}^4I_{9/2} \rightarrow {}^2G_{7/2}$, ${}^4G_{5/2}$ hypersensitive transition shows a rather high symmetry for the metal centre with an oscillator strength value $\cong 971.18 \times 10^{-8}$ for one orientation of the crystal and is lower than in the neodymium complexes reported earlier.[21] Vibronic components are associated with electronic transitions, satisfying the selection rule $\Delta J = 2$. The dramatic decrease in intensities with decreasing temperature is a result of depopulation of the ${}^4I_{9/2}$ ground state multiplet of Nd^{3+} and vibronic coupling.

4. Subtle differences in the spectral properties of two other systems (**2** and **3**) indicate some rearrangement of the direct environment of the neodymium ion in gel. A comparison of the spectral properties of two systems incorporated in gel, Nd and Nd : Cu glutarate, points to the same small differences in the structure of the Nd centre in both these systems. The spectra at 4 and 12 K show a split of levels caused by a relatively small disorder of the metal centres in gel. Dramatic differences of the d–d transition intensities and their energies in comparison with those of the simple Cu glutarate system allow us to conclude that a mixed Nd : Cu compound is formed in gel.

5. The magnetic moment and magnetic susceptibilities of $[Nd(Glut)(H_2O)_4]Cl \cdot 2H_2O$ decrease with temperature, which might be caused by the crystal field effect and antiferromagnetic ordering at low temperature for pairs of ions coupled in the dimer unit.

Acknowledgements

This work was supported by the Polish Committee for Scientific Research (grant 3T09A 086 10). The authors are grateful to Małgorzata Borzechowska, M.Sc., for her help in preparing the magnetic data for publication.

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Paper 9/05284D