Synthesis, Luminescence, Energy Transfer of Binary and Ternary Rare-Earth Complexes with 5-Sulfosalicylic Acid and 1,10-Phenanthroline

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A series of binary and ternary complexes of rare earth (Gd, Eu, Tb) with 5-sulfosalicylic acid and 1,10-phenanthroline were synthesized. The low-temperature phosphorescence spectra and lifetimes of these complexes were measured. The triplet level energies of ligands were determined and the energy match between the triplet state energies of ligands and the resonance emitting energies of Ln^{3+} was discussed. The intramolecular energy migration in the complexes was studied in detail. The luminescence intensities and luminescence lifetimes were also obtained and in good agreement with the theoretical prediction of luminescence properties.

There has been a growing interest in the luminescence properties of lanthanide complexes (Eu^{3+} and Tb^{3+}) with organic ligands because of their potential application as luminescent material and as a label and probe for a variety of chemical and biological studies [1—3]. In the past thirty years or so, systematic studies [4, 5] were reported on the energy coupling between the triplet state energy of β-diketone ligands and the emitting energy level of Ln^{3+}, the relationship between the energy match and luminescence properties, and intramolecular energy transfer in rare-earth complexes systems. Relatively little attention has been paid to the studies of rare-earth complexes with aromatic carboxylic acids. As shown in Ref. [6], the rare-earth β-diketonates are very liable and instable towards moisture, while rare-earth complexes with aromatic carboxylic acids can overcome these drawbacks due to their polymeric network and chain structure. So in the present work, 5-sulfosalicylic acid was selected as ligand of Gd^{3+}, Eu^{3+}, Tb^{3+}, and the binary and ternary (1,10-phenanthroline is the second ligand) complexes were prepared. The triplet state energies of organic ligands were measured and the energy coupling between them and the emitting energy level was studied.

RESULTS AND DISCUSSION

The compositions of the prepared complexes were confirmed by elemental analysis and are shown in Table 1, where HSSAL = 5-sulfosalicylic acid and phen = 1,10-phenanthroline.

The TG—DTA curves of $REH(SSAL)_2 \cdot 6H_2O$, $RE(phen)_2Cl_3 \cdot 4H_2O$, and $REH(SSAL)_2 \cdot 5H_2O$ (RE = Gd, Eu, Tb) in air atmosphere indicate that the thermal decomposition processes of these rare-earth complexes show different ways. The binary complexes of rare earth with 5-sulfosalicylic acid show three steps, they lose five water molecules and transform to the complexes with one water molecule, then lose the one water molecule, which is accompanied by the endothermic effect, and at last, the anhydrous complexes decompose to the rare-earth oxides (Eu_2O_3, Gd_2O_3, Tb_4O_7) with the accomplishment of a strong exothermic effect. On the other hand, the TG—DTA curves of binary rare-earth complexes with 1,10-phenanthroline show two steps: the first is to lose two water molecules and yield the anhydrous salts being accompanied by an endothermic effect; the second is that the anhydrous complexes then decompose to the corresponding oxides, which is accompanied by a strong exothermic effect. TG—DTA curves of the ternary complexes with 5-sulfosalicylic acid and 1,10-phenanthroline show three steps, the first is dehydration, the second is to lose one heterocyclic ligand, and the last is the decomposition of the carboxylic acid ligand. The processes of dehydration are accompanied by endothermic effects and the processes of decomposition are accompanied by strong exothermic effects. The final products of decomposition of the complexes of rare earth are mixtures of oxides and carbon. Table 2 gives the data of TG—DTA result of $EuH(SSAL)_2 \cdot 6H_2O$, $Eu(phen)_2Cl_3 \cdot 2H_2O$, and $EuH(SSAL)_2 \cdot 5H_2O$ which are stable in the temperature range 1163—1273

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Table 1. The Compositions of Rare-Earth Complexes by Elemental Analysis

Complex	w_i(found)/%				w_i(calc.)/%			
	C	H	N	RE	C	H	N	RE
$GdH(SSAL)_2 \cdot 6H_2O$	23.99	2.78		22.74	24.05	3.01		22.51
$EuH(SSAL)_2 \cdot 6H_2O$	24.05	2.77		22.34	24.23	3.03		21.91
$TbH(SSAL)_2 \cdot 6H_2O$	24.32	2.69		23.00	23.99	3.00		22.69
$Gd(phen)_2Cl_3 \cdot 2H_2O$	43.30	2.94	8.20	23.97	43.65	3.03	8.49	23.84
$Eu(phen)_2Cl_3 \cdot 2H_2O$	43.76	2.92	8.23	23.65	44.01	3.06	8.56	23.22
$Tb(phen)_2Cl_3 \cdot 2H_2O$	43.80	2.89	8.19	24.31	43.54	3.02	8.47	24.03
$GdH(SSAL)_2 \cdot phen \cdot 5H_2O$	36.00	3.01	3.01	18.53	36.25	3.14	3.25	18.27
$EuH(SSAL)_2 \cdot phen \cdot 5H_2O$	36.17	2.98	3.01	18.00	36.47	3.16	3.27	17.76
$TbH(SSAL)_2 \cdot phen \cdot 5H_2O$	36.02	2.96	3.03	18.22	36.18	3.13	3.25	18.43

Table 2. Temperature Range of Dehydration and Decomposition of Binary and Ternary Europium Complexes with 5-Sulfosalicylic Acid and 1,10-Phenanthroline and their Products in Air Atmosphere

Complex	Product		Product		Product	
	Temp. range		Temp. range		Temp. range	
	w_i(found)/%	w_i(calc.)/%	w_i(found)/%	w_i(calc.)/%	w_i(found)/%	w_i(calc.)/%
$EuH(SSAL)_2 \cdot 6H_2O$	$EuH(SSAL)_2 \cdot 5H_2O$		$EuH(SSAL)_2$		Eu_2O_3	
	418—505		520—580		780—1180	
	2.7	2.6	13.7	13.0	73.1	74.7
$Eu(phen)_2Cl_3 \cdot 2H_2O$	$Eu(phen)_2Cl_3$				Eu_2O_3	
	375—416				433—520	
	5.2	5.5			26.0	26.9
$EuH(SSAL)_2 \cdot phen \cdot 5H_2O$	$EuH(SSAL)_2 \cdot phen$		$EuH(SSAL)_2$		Eu_2O_3	
	428—538		474—520		780—1190	
	10.1	10.5	20.1	21.0	21.2	20.5

Table 3. The Lowest Triplet State Energies of Binary Gd^{3+} Complexes with HSSAL and Phen and the Energy Differences between them and the Resonant Energy Level of Eu^{3+} and Tb^{3+}

Complex	$\tilde{\nu}$(Triplet state energies)/cm^{-1}	$\tilde{\nu}(\Delta E(T_r - {}^5D_0))$/cm^{-1}	$\tilde{\nu}(\Delta E(T_r - {}^5D_4))$/cm^{-1}
$GdH(SSAL)_2 \cdot 6H_2O$	24316	7052	3816
$Gd(phen)_2Cl_3 \cdot 2H_2O$	22075	4811	1575

K. These results of TG—DTA were in a good agreement with those of elemental analysis.

Low-temperature phosphorescence spectra of Gd^{3+} binary complexes with sulfosalicylic acid and phen were measured. The shortest wavelength of emission bands was assumed to be 0—0 transition, so the lowest triplet state energies of ligands were determined and the energy differences between them and the resonance energy level of central Eu^{3+} and Tb^{3+} ions ($\Delta E(T_r - {}^5D_j)$, $j = 0$ or 4) was calculated. The result is shown in Table 3.

Intramolecular energy transfer efficiency depends chiefly on two energy transfer processes [7]: one is from the lowest triplet level of ligand to the resonance level of RE^{3+} by resonant exchange interaction [8], and the other is just an inverse energy transfer by thermal deactivation mechanism [9]. Both energy transfer rate constants depend on the energy difference ($\Delta E(T_r - {}^5D_j)$) between the triplet state energy of the ligands and the emitting energy of Eu^{3+} and Tb^{3+} The detailed discussion was shown as follows:

For the resonant exchange interaction

$$k_{ET} = Pda \quad (-2Rda/L) \tag{1}$$

$$Pda = (2\pi Z^2/R) \int Fd(E)\, E_a(E) d(E) \tag{2}$$

For the thermal deactivation mechanism

$$k(T) = A \exp(-E_a/RT) \tag{3}$$

where k_{ET} and $k(T)$ are the rate constants of resonant exchange interaction and thermal de-excitation, respectively, Pda is the transition probability from en-

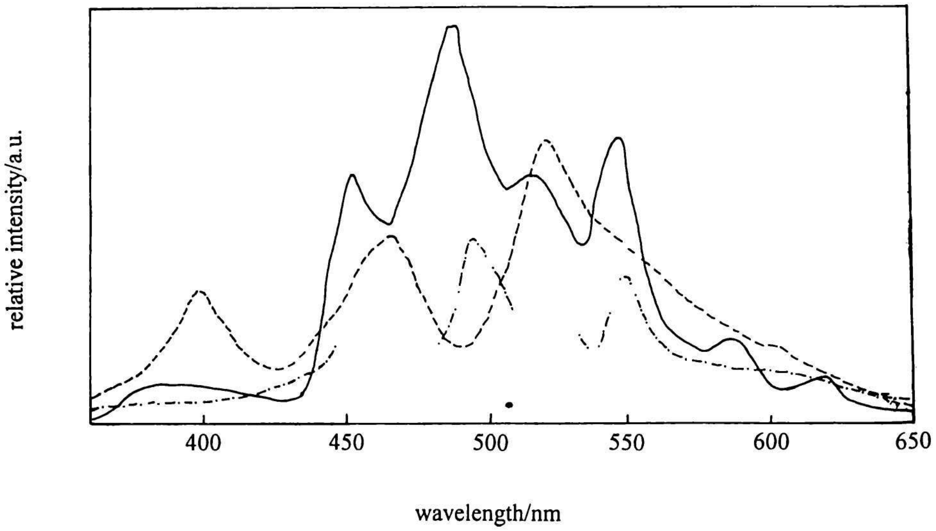

Fig. 1. The low-temperature phosphorescence spectra of Gd(phen)$_2$Cl$_3$ 2H$_2$O (——) ($\lambda_{\text{ex}} = 302.0$ nm), GdH(SSAL)$_2$ 6H$_2$O (- - -) ($\lambda_{\text{ex}} = 345.6$ nm), and GdH(SSAL)$_2$ · phen · 5H$_2$O (– – –) ($\lambda_{\text{ex}} = 322.0$ nm) (5×10^{-4} mol dm^{-3} ethanol and DMF mixed solution) (77 K).

Table 4. The Phosphorescence Lifetimes of Gd^{3+} Complexes and the Energy Transfer Efficiencies from HSSAL to Phen

Complex	Phosphorescence lifetimes τ/s	Energy transfer efficiencies/%
GdH(SSAL)$_2$ · 6H$_2$O	2.74	
GdH(SSAL)$_2$ · phen · 5H$_2$O	0.67	74.82

ergy donor (carboxylic acid ligand) to energy acceptor (RE^{3+}), Rda is the intermolecular distance between donor and acceptor, and L is van der Waals radius, which is considered to be equal to the constant for intramolecular energy migration process, $F\text{d}(E)$ and $E_{\text{a}}(E)$ are the experimental luminescence spectrum of energy donor (sensitizer) and the experimental absorption spectrum of energy acceptor (activator), respectively. The term of $2\pi Z^2/R$ is a constant relating to the mutual orbital distance. E_{a} in eqn (*2*) is the activation energy of the inverse energy transfer and may be equal to $\Delta E(T_{\text{r}} - {}^5D_j)$. From eqn (*1*), it can be seen that the overlap between the luminescence spectrum of ligands and the absorption spectrum of central RE^{3+} increased with the decreasing of $\Delta E(T_{\text{r}} - {}^5D_j)$, namely k_{ET} increased with the decreasing of the energy difference. On the other hand, from eqn (*3*) conclusion can be drawn that $k(T)$ also shows the same change tendency as k_{ET} with the decreasing of $\Delta E(T_{\text{r}} - {}^5D_j)$. So it can be deduced that $\Delta E(T)$ should be neither too large nor too small, there would be an optimal value. On the basis of the discussion, three carboxylic acids will sensitize Tb^{3+} more efficiently than Eu^{3+} due to the suitable energy difference between them and Tb^{3+}, while the energy match between phen and Eu^{3+} is better, so when phen is the predominant energy donor, it will sensitize Eu^{3+} more effectively.

Fig. 1 shows the phosphorescence spectra of GdH(SSAL)$_2$ · 6H$_2$O, Gd(phen)$_2$Cl$_3$ · 2H$_2$O, and GdH(SSAL)$_2$ · phen · 5H$_2$O. It can be obviously seen that the phosphorescence spectrum of GdH(SSAL)$_2$ · phen · 5H$_2$O was similar to that of Gd(phen)$_2$ · Cl$_3$ 2H$_2$O. The result suggests that phen is the main luminescence sensitizer in the ternary rare-earth complexes and it is convenient for energy migration between carboxylic acid and phen. In order to further interpret the opinion, low-temperature phosphorescence lifetimes of Gd^{3+} complexes were determined (Table 4). From the data it is obvious that the phosphorescence lifetimes of the ternary complexes were all abated compared with the corresponding binary complexes with carboxylic acids. Therefore, it can be deduced that the energy transfer between aromatic carboxylic acids and phen takes place definitely. The intramolecular energy transfer process occurring here is shown in Fig. 2 [10]. The energy transfer rate and energy efficiency can be expressed as below

$$k^*_{\text{ET}} = \tau_1^{-1} - \tau_0^{-1} \qquad (4)$$

$$\eta_{\text{ET}} = k^*_{\text{ET}}(k^*_{\text{ET}} + k_1)^{-1} \qquad (5)$$

where k^*_{ET} and η_{ET} are the energy transfer rate constant and efficiency from carboxylic acids to phen, respectively, τ_1 and τ_0 are the phosphorescence lifetimes

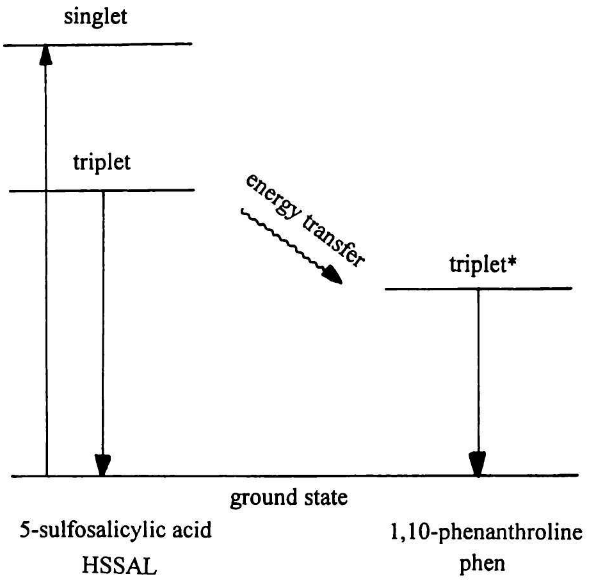

Fig. 2. The intramolecular energy transfer process from 5-sulfosalicylic acid to 1,10-phenanthroline.

of Gd^{3+} ternary complexes and correspondingly binary carboxylic acid complexes, respectively, and k_1 is phosphorescence rate constant. The data are shown in Table 3. According to the value of η_{ET}, the energy transfer between carboxylic acid and phen is very large even in ternary systems, the second ligand, phen being the major energy donor.

So as to demonstrate the above prediction, the fluorescence spectra of Eu^{3+} and Tb^{3+} were measured. Figs. 3 and 4 show the fluorescence spectra of $EuH(SSAL)_2 \cdot 6H_2O$, $EuH(SSAL)_2 \cdot phen \cdot 5H_2O$ and $TbH(SSAL)_2 \cdot 6H_2O$, $TbH(SSAL)_2 \cdot phen \cdot 5H_2O$, respectively. The emission of $EuH(SSAL)_2 \cdot 6H_2O$ at 578.5 nm, 592 nm (596 nm), 612 nm (616 nm), 650 nm, and 698 nm; $EuH(SSAL)_2 \cdot phen \cdot 5H_2O$ at 579 nm, 590 nm (595 nm), 612 nm (618.5 nm), 652 nm, and 697 nm (702 nm) originated from the $^5D_0 \rightarrow ^7F_0$, $^5D_0 \rightarrow ^7F_1$, $^5D_0 \rightarrow ^7F_2$, $^5D_0 \rightarrow ^7F_3$, and $^5D_0 \rightarrow ^7F_4$ transitions and the emission of $TbH(SSAL)_2 \cdot 6H_2O$ at 490 nm (495.5 nm), 543.5 nm (548 nm), 585 nm (590 nm), and 620 nm; $TbH(SSAL)_2 \cdot phen \cdot 5H_2O$ at 489 nm (495.5 nm), 543 nm (548 nm), 585 nm (589.5 nm), and 620 nm originated from the $^5D_4 \rightarrow ^7F_6$, $^5D_4 \rightarrow ^7F_5$, $^5D_4 \rightarrow ^7F_4$, and $^5D_4 \rightarrow ^7F_3$ transitions separately. Among these transitions, the $^5D_0 \rightarrow ^7F_2$ transition of $EuH(SSAL)_2 \cdot 6H_2O$, $EuH(SSAL)_2 \cdot phen \cdot 5H_2O$ and $^5D_4 \rightarrow ^7F_5$ transition of $TbH(SSAL)_2 \cdot 6H_2O$, $TbH(SSAL)_2 \cdot phen \cdot 5H_2O$ show the strongest emission. Table 4 gives the relative luminescence intensities of Eu^{3+} and Tb^{3+} complexes at the strongest emission. The reported luminescence intensity values were obtained by integration of each luminescence spectrum for the entire peak (here for Eu^{3+} complexes $^5D_0 \rightarrow ^7F_2$ and for Tb^{3+} complexes $^5D_4 \rightarrow ^7F_5$). From the result it can be seen that the luminescence intensities of the binary Tb^{3+} complexes are stronger than those of the binary Eu^{3+} ones, which are in good agreement with what predicted from the energy match between the triplet state position and the emission energy level of rare-earth ions. The fluorescence intensities of Eu^{3+} ternary complexes are larger than those of the binary complexes, while it is in contrast for Tb^{3+} complexes, this can be well explained by the difference in energy mismatch between the lowest triplet of phen and first excited rare-earth states because there takes place energy transfer from carboxylic acid to phen in ternary complexes [10]. In order to further illustrate the result, the luminescence

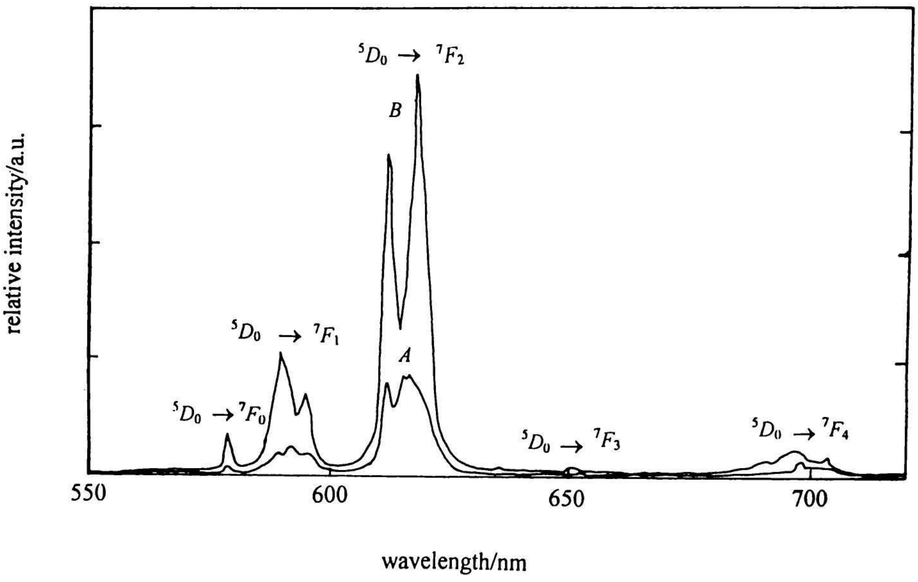

Fig. 3. The luminescence spectra of $EuH(SSAL)_2 \cdot 6H_2O$ (*A*) and $EuH(SSAL)_3 \cdot phen \cdot 5H_2O$ (*B*) (solid sample).

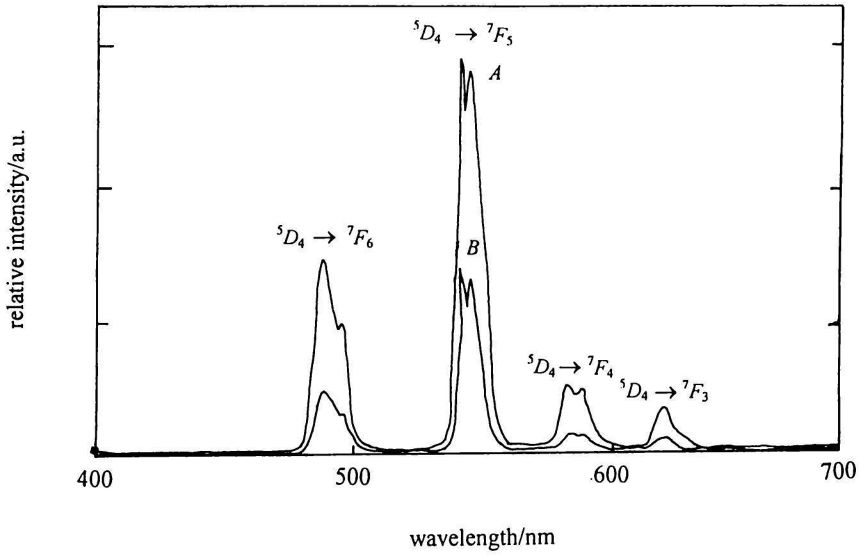

Fig. 4. The luminescence spectra of $TbH(SSAL)_2 \cdot 6H_2O$ (*A*) and $TbH(SSAL)_2$ phen $\cdot 5H_2O$ (*B*) (solid sample).

Table 5. Luminescence Properties of Eu^{3+} and Tb^{3+} Complexes

Complex	λ_{ex}/nm	λ_{em}/nm	Relative intensities/a.u.	Lifetimes/μs
$EuH(SSAL)_2 \cdot 6H_2O$	308.8	610, 618.5	0.093	576
$EuH(SSAL)_2 \cdot phen \cdot 5H_2O$	307.2	612, 616.5	0.28	782
$Eu(phen)_2Cl_3 \cdot 2H_2O$	308.8	614, 620	47.85	838
$TbH(SSAL)_2 \cdot 6H_2O$	275.6	543.5, 548	156.32	1672
$TbH(SSAL)_2 \cdot phen \cdot 5H_2O$	273.6	542, 547	62.59	1147
$Tb(phen)_2Cl_3 \cdot 2H_2O$	274.4	546	19.63	1374

lifetimes were obtained (Table 5). Also draw the same conclusion that the luminescence lifetime of the binary Eu^{3+} complex is much smaller than that of Tb^{3+} complex, and the binary Eu^{3+} complex shows a shorter lifetime (576 μs) than that of ternary one (782 μs). For the Tb^{3+} complexes, however, the binary complex indicated a longer lifetime (1672 μs) than that of ternary one (1147 μs), which is in a good agreement with the results discussed above.

EXPERIMENTAL

The binary rare-earth complexes with 5-sulfosalicylic acid were prepared according to the report in Ref. [11]. The binary complexes of rare earths with 1,10-phenanthroline were prepared by the same method [12]. The ternary rare-earth complexes were synthesized as follows:

An ethanol solution of rare-earth chloride was added to an ethanol solution of 5-sulfosalicylic acid and pH value of the mixture was adjusted to 6—7 by adding aqueous sodium hydroxide (NaOH) with stirring. The mole ratio of the acid to RE^{3+} was 3 1. Then the 1,10-phenanthroline in ethanol solution was added to the reaction mixture in the mole ratio of it to RE^{3+} ion 1 1. The precipitate was filtered off, washed with water and ethanol, and dried first at room temperature, then it was stored over a silica-gel drier.

The compositions of these complexes were determined using an Erba 1106 elemental analyzer. The TG and DTA curves were recorded on a Thermoflex DTA derivatograph at heating rate of 10 K min^{-1} and the samples were heated in air. The luminescence spectra were measured on a SPEX FL-2T2 spectrofluorometer with excitation and emission slit of 0.5 mm. The fluorescence lifetimes were taken on SPEX 1934D spetrophotometer using a 450 W xenon lamp as excitation source. The low-temperature phosphorescence spectra and lifetimes measurements were carried out at 77 K on the same instrument as above.

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