Chromium(III)-trisoxalate, a versatile building block for luminescent materials

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Chromium(III)-trisoxalate, [Cr(ox)3]3− (ox−=C2O42−), incorporated into polymeric networks of composition [NaCr(ox)3][MII(bpy)3] and [NaCr(ox)3][MIII(bpy)3]ClO4 (ox−=C2O42−, bpy−=2,2′-bipyridine, MII=Zn, Fe, Ru; MIII=Rh, Cr), results in interesting features ranging from phonon-assisted and resonant energy migration within the R, line the 2E state to persistent spectral side-hole burning via the latter, and manifestations of specific nearest-neighbour π–π interactions between bipyridine and oxalate.

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1. Introduction

Chromium(III)-trisoxalate, [Cr(ox)3]3− (ox−=C2O42−), constitutes a molecular equivalent of the much studied chromophore provided by Cr3+ doped sapphire known as ruby [1], Al2O3:Cr3+. That is, its pseudo-octahedral coordination sphere is made up by six oxygen ligands in trigonally distorted symmetry. First spectroscopic investigations of this complex, notably diluted in NaMgAl(ox)3·9H2O, in which the Na+ and the Al3+ ions are alternatingly bridged by oxalate in 2D honeycomb layers held together by Mg2+ in the form of its hexaquo complex, indeed showed the ligand-field strength for Cr3+ to be only slightly smaller than for ruby, that is 18250 cm−1 [2] instead of 18520 cm−1 [3] at low temperature as derived from the maximum of the spin-allowed A2→T2 ligand-field transition in the corresponding absorption spectra. As for ruby, the lowest energy spin-forbidden A2→2E transition, at exactly the same energy of 14400 cm−1, was found to consist of the typical doublet of the two R lines with a zero-field splitting (ZFS) of the 2E state of 16 cm−1 [2], the corresponding zero-field splitting of the ground state being 1.3 cm−1 [4]. The former is smaller than the 29 cm−1 found in ruby, the latter is considerably larger than the corresponding 0.39 cm−1 [5]. The quite substantial variation of the the ZFSs in different host lattices is due to a tetragonal component to the ligand field resulting from non-coordinated H2O molecules hydrogen bonded to the oxalate ligands [4,6].

In the above mentioned lightly doped 2D network, Riesen used fluorescence line narrowing (FLN) and transient spectral hole burning (SHB) spectroscopy to determine ground and excited state ZFSs and g-values of [Cr(ox)3]3− to high precision, and to identify the dominating relaxation processes responsible for the temperature dependence of the homogeneous line width as a combination of a direct process and a Raman process [7]. He furthermore established a novel and very efficient mechanism for persistent SHB upon partial deuteration of the water molecules [8], which he attributed to flipping of the hydrogen bonded HOD molecules in the excited state.

In highly doped systems site-selective techniques are very often not successful because the homogeneous line widths are much larger even at low temperatures due to spin-spin and cross relaxation [7,9], and efficient phonon-assisted energy migration as a result of which the energy is transferred non-selectively to shallow traps at the low-energy tail of the inhomogeneous distribution [10] or is scavenged by impurity chromophores or exchange coupled pairs as in highly doped ruby [11]. Nevertheless, neat compounds incorporating [Cr(ox)3]3− as chromophore in stoichiometric ratios show a variety of interesting optical, magnetic and magneto-optical properties. For instance, the 2D analogue of the above-mentioned lattice in which Na+ in the honeycomb structure is replaced by Mn2+ and consequently the [Mg(H2O)6]2+ complex sitting in between the layers by a large monovalent cation, shows interesting magnetic properties in the form of ferrimagnetic order below 6.5 K [12,13]. The helical [Cr(ox)3]3− complex is inherently chiral, but if the cation is chosen to be achiral, as for instance [PPh4]+, the honeycomb layers with alternating Mn2+ and Cr3+ linked by oxalate as bridging ligand, crystallise in such a way that in one layer the [Cr(ox)3]3− complexes all have a configuration and in the next layer they all have another configuration resulting in an overall racemic mixture and an achiral space group [12]. If on the other hand, the enantiopure form of a chiral cation is used, the compound crystallises in a chiral space group with all [Cr(ox)3]3− complexes having one configuration and all Mn2+ centres the other one. This results in spectacular magneto-chiral effects below the ordering temperature [13].
A chiral space group, namely P2₁3, also results upon crystallisation with chiral cations in the form of helical \([\text{M(bpy)}_3]^{2⁺}\) complexes (bpy=2,2’-bipyridine, M=Zn\(^{2+}\), Ru\(^{2+}\), ..., M=Rh\(^{3+}\), Cr\(^{3+}\), ...). In this case, spontaneous resolution of the enantiomers by crystallisation from solution occurs even from racemic mixtures of the complex cation, the templating effect of the first complex incorporated into the lattice determining the chirality of the whole crystallite [14]. In the resulting 3D network structures of general composition \([\text{NaCr(ox)}_3]\)[M(bpy)_3] and \([\text{NaCr(ox)}_3]\)[M’(bpy)_3]ClO_4, respectively, the oxalate ligands alternatingly bridge Na\(^+\) and Cr\(^{3+}\) such that both metal ions have the same chirality, thus forming chiral cavities for a perfect fit of the \([\text{M(bpy)}_3]^{2⁺}\) complexes, the site symmetry of all metal centres being C_3. In contrast to doped oxides and other ionic lattices, the molecular architecture of the above structures separates the \([\text{Cr(ox)}_3]^{3⁻}\) chromophores sufficiently from each other to preclude superexchange between them even at high concentrations. As a result, efficient energy migration within the \(^2\text{E}\) state of Cr\(^{3+}\) is observed with a clear differentiation between resonant and phonon-assisted processes dominating at 1.5 K and above 4.2 K, respectively [15,16]. In particular the former is unique to these molecular compounds. In the 2D network NaMgAl(ox)_3·9H_2O, partially deuterated and heavily doped with Cr, the resonant process creates a series of persistent spectral side-holes [17] based on the mechanism proposed by Riesen [8]. In the 3D mixed crystal series \([\text{NaCr(ox)}_3][\text{Zn}_1\text{Ru}_{1-x}\text{Rh}_x\text{ bpy)}_3]\), specific nearest-neighbour π–π interactions between the oxalate ligand on Cr\(^{3+}\) and bpy ligand on M\(^{2⁺}\) result in the creation of well defined optical sites [18], and external pressure modulates the energy transfer efficiency between \([\text{Cr(ox)}_3]^{2⁻}\) and \([\text{Cr(bpy)}_3]^{2⁺}\) as active chromophores in the co-doped inert host lattice \([\text{NaAl}_1-x\text{Cr}_x(\text{ox})_3][\text{Rh}_1-x\text{Cr}_x\text{ bpy)}_3]\text{ClO}_4[19]\. These four aspects of \([\text{Cr(ox)}_3]^{3⁻}\)-containing systems are briefly reviewed in this paper.

2. Experimental procedures

Pure compounds as well as mixed crystals of the 3D systems were synthesised in the form of polycrystalline powders or small single crystals as described in Refs [12,14]. The mixed crystals of the 2D system were grown from aqueous solution according to Ref. [2]. Single crystal absorption spectra were recorded either on a double beam spectrometer (Cary 5000, spectral resolution 4 cm\(^{-1}\)) or a Fourier transform spectrometer (Bruker IFS 66, spectral resolution 0.25 cm\(^{-1}\)). FLN and low-resolution SHB spectra were recorded on a home-built setup consisting of a 0.85 m double monochromator (SPEX 1404) equipped with a CCD camera (Roper Instruments with 13 μm pixels giving a spectral resolution of 0.25 cm\(^{-1}\)). Non-selective excitation of the Cr\(^{3+}\) luminescence was performed at 532 nm from an intracavity frequency doubled Nd:YAG laser (ILEE VA-I-N-532). For selective excitation at around 14400 cm\(^{-1}\) from FLN and SHB experiments, a single frequency Ti:Sapphire laser (Coherent 699) was used. Temperatures down to 1.4 K were achieved in a helium bath cryostat (Cryo Industries). Further experimental details may be found in Refs [14–21].

3. Results and discussion

3.1. Energy migration within the \(^2\text{E}\) state of Cr\(^{3+}\)

As schematically shown in Fig. 1, in the 3D network \([\text{NaCr(ox)}_3][\text{Rh(bpy)}_3]\text{ClO}_4\), in which Na and Rh are photophysically inert, three different mechanisms for energy migration within the R\(_1\) line of the \(^2\text{E}\) state of Cr\(^{3+}\) can be identified using fluorescence line narrowing techniques [15,16,20]. At and above 3.2 K, the standard phonon-assisted process, also omnipresent in doped ionic lattices [11,21], dominates as can be inferred from the non-selective growing in of the inhomogeneous background in a time-resolved FLN spectrum (Fig. 2a). Below that temperature, an energy-selective and thus resonant process between different components of the ground state of the donor and the acceptor results in a pattern of seven sharp lines within the inhomogeneously broadened R\(_1\) line (Fig. 2b), rather than the customary 3-line spectrum for Cr\(^{3+}\) in dilute systems. The time-resolved FLN spectra clearly demonstrate the sequential nature of the process down the energy-selective ladder of subsets of chromophores spaced by the ZFS of the ground state of 1.3 cm\(^{-1}\). With an inhomogeneous line width of \(\Gamma_{\text{inh}}\) of \(\sim\)4 cm\(^{-1}\) up to 6 steps can be observed. Likewise, a quasi-resonant process between the same ground state components results in a broadening spectra clearly demonstrate the sequential nature of the process down the energy-selective ladder of subsets of chromophores spaced by the ZFS of the ground state of 1.3 cm\(^{-1}\). With an inhomogeneous line width of \(\Gamma_{\text{inh}}\) of \(\sim\)4 cm\(^{-1}\) up to 6 steps can be observed. Likewise, a quasi-resonant process between the same ground state components results in a broadening or spectral diffusion of the individual lines of the multi-line pattern as function of the delay time between the excitation pulse and recording the spectrum. With an upper limit of the homogeneous line width \(\Gamma_{\text{hom}}\) of 600 MHz (0.02 cm\(^{-1}\)) [16] probably due to efficient spin-spin relaxation in the concentrated compound, as compared to the 20 MHz for a dilute system [6], and the above value for the inhomogeneous line width, the concentration of resonant species at the centre of the inhomogeneous distribution is approximately \(10^{10}\) cm\(^{-3}\), estimated from the ratio of the homogeneous to the inhomogeneous line widths. From the homogenous line width of 600 MHz, a value for the critical radius \(R_c\) for dipole-dipole interaction of 34 Å according to Förster theory [22] can be estimated [16]. The corresponding critical concentration of \(6 \times 10^{19}\) cm\(^{-3}\) is indeed smaller than the effective concentration.

In the related system, \([\text{NaCr(ox)}_3][\text{Ru(bpy)}_3]\), the inhomogeneous line width is only \(\sim\)1 cm\(^{-1}\). As a consequence, fewer steps across the inhomogeneously broadened line are possible. However, assuming that the homogeneous width is the same, the concentration of resonant species is increased four-fold, and thus the resonant process is expected to be more efficient. This manifests itself in a considerably faster spectral diffusion of the individual sharp line in the time-resolved FLN spectra (Fig. 2c).
distinctly different from the spectral evolution for the phonon-assisted process [20]. Surprisingly, for \([\text{NaCr(ox)}_3][\text{Zn(bpy)}_3]\) the spectral diffusion is even faster despite an intermediate inhomogeneous line width (Fig. 2d), approaching the limit given by the homogeneous line width within 200 \(\mu\)s as opposed to the 2000 \(\mu\)s for the Ru based compound (Fig. 3). The reason for this is not clear as yet, we may however conclude that the homogeneous line width for this system is larger than for the other two. This could
be a result of an enhancement of the spin-spin relaxation mediated by the \( \pi-\pi \) interaction between bipyridine and oxalate ligands in Zn based compound. Indeed, in Section 3.4 we demonstrate that for \( [Zn(bpy)_3]^{2+} \) this interaction is larger than for \( [Ru(bpy)_3]^{2+} \) [18].

3.2. Persistent spectral side-hole burning via resonant energy transfer

In the related 2D network \( NaMgAl(ox)_3 \cdot 9H_2O \) partially deuterated and weakly doped with \( Cr^{3+} \), Riesen et al. demonstrated extremely efficient persistent spectral hole burning in the \( R_1 \) line based on mechanism that involves the flipping of HOD molecules upon selective excitation [9]. In highly doped mixed crystals \( NaMgAl_{1-x}Cr_x(ox)_3 \cdot 9(H_2O/D_2O) \), for instance with \( x=0.2 \), resonant energy migration in the shape of a multi-line pattern can also be observed at 1.4 K (Fig. 4a). At the same time, the selective excitation does not only burn a central hole at the excitation wavelength but also side-holes at the energies of the subsets excited by the resonant energy migration. This becomes apparent in the dips in the non-selectively excited luminescence spectrum following prior selective excitation within the \( R_1 \) line for a few minutes. It can also be viewed in the comparison of the single crystal absorption spectra recorded before and after selective excitation (Fig. 4b). The corresponding difference spectra (Fig. 4c) reveal that the hole burning is photophysical in nature in so far as the absorption in between the holes significantly increases as a result of the slight shift in energy of the state of a given ion upon the flip of HOD molecules. Furthermore, there is a bias towards lower energies in the background of the difference absorption spectrum due to a contribution of non-resonant energy transfer processes. At this stage, the hole width in the spectra of Fig. 4c is limited by the resolution of the double monochromator. Determining the effective homogeneous line width as function of chromium concentration in this system using SHB spectroscopy will yield better values for this important parameter with regard to resonant energy migration.

3.3. Tuning resonant energy transfer by external pressure

In the co-doped system \( [NaAl_{1-x}Cr_x(ox)_3][Rh_{1-y}Cr_y(bpy)_3]ClO_4 \) energy transfer occurs from the \( 4E \) state of the initially excited \( [Cr(ox)_3]^{3+} \) as donor to \( [Cr(bpy)_3]^{3+} \) as acceptor via a resonant process due to the spectral overlap of the sharp \( 4A_2 \rightarrow 4E \) emission of the donor and the \( 2A_2 \rightarrow 2T_1 \) spin-flip transitions of the acceptor (Fig. 5). The latter is resonant with the former because of the enhanced nephelauxetic effect of bipyridine as compared to oxalate.

A detailed analysis of the concentration dependence of the acceptor at low donor concentrations revealed two types of energy transfer processes: (a) For those donors which statistically happen to have an acceptor in their nearest neighbour shell, the energy transfer occurs within less than 1 ms, that is, with a quantum efficiency of unity by comparison with the intrinsic lifetime of the excited donor of 1.3 ms in the absence of acceptors. It has been attributed to weak superexchange interaction mediated via the overlap between the oxalate and the bipyridine \( \pi \) orbitals. (b) For those donors that have no acceptors in their nearest neighbour shell, energy transfer is much less efficient, occurring on the time scale of the intrinsic lifetime of the donor via dipole-dipole interaction with a critical radius \( R_c \) of 10.5 Å. At low acceptor levels, the energy transfer efficiency increases linearly with concentration, reaching 25% at \( y=0.05\) of which around \( 1/3 \) is due to the dipole-dipole process [21]. The rate constant for both processes depends upon the spectral overlap integral between the emission of the donor and the absorption of the acceptor [22] indicated in the corresponding spectra depicted in Fig. 5. As the shift of the spin-flip transitions as a function pressure for the two chromophores in the network is not the same (Fig. 6a), the spectral overlap decreases as function of pressure. Concomitantly, the energy transfer efficiency also decreases (Fig. 6b). At first sight, the decrease

![Fig. 3. Temporal evolution of the FLN line width following 10 µs pulsed excitation in the centre of the inhomogeneous absorption line for the 3D oxalate networks at T = 1.4 K.](image)

![Fig. 4. Persistent SHB in the R1 line of 50% deuterated NaMgAl1_xCr_x(ox)3 ·9H2O at T = 1.4 K. x=0.2, (a) non-selectively excited luminescence spectra before and after hole burning and FLN spectrum, (b) absorption spectra before and after hole burning, (c) difference absorption and luminescence spectra (adapted from Ref. [17]).](image)
in energy transfer efficiency is considerably smaller than the decrease of a factor of around 4 in spectral overlap. However, even though the decrease in spectral overlap reduces the rate constants for both mechanisms, only the contribution to the transfer efficiency occurring on the same timescale as the intrinsic lifetime of the donor, that is, the dipole-dipole contribution, is affected. A reduction in the rate constant of the fast contribution due to super-exchange even by several orders of magnitude would not affect the quantum efficiency, as it would still be much faster than the intrinsic lifetime of the donor. Therefore, only the 1/3 contribution of the total energy transfer is expected to be reduced to 1/4 of its original intensity. This is in line with the observed reduction of the total quantum efficiency depicted in Fig. 6b.

3.4. Specific spectroscopic sites in mixed crystals

As mentioned above, specific π–π interactions between the oxalate ligand on Cr$^{3+}$ and the bpy ligand on M$^{2+}$, even though comparatively small, are important for the photophysical properties of the 3D oxalate networks under consideration. In the mixed crystal series [NaCr(ox)$_3$][Zn$_x$Ru$_y$(bpy)$_3$] they result in the creation of 5 well defined spectroscopic sites according to a Poisson distribution of Zn and Ru ions over the four nearest neighbour sites. This can be concluded from the absorption spectra depicted in Fig. 7 showing multiple pairs of R lines rather than just a continuous inhomogeneous distribution.
Experimentally, an increasing number of Zn neighbours shifts the R lines toward lower energies. Based on simple pressure arguments this is counterintuitive. As shown above, the R lines in these compounds shift to lower energies with increasing external pressure, in analogy to the R lines in ruby [23]. This has been attributed to an increase in the nephelauxetic effect as a result of the decrease of the metal-ligand bond length under external pressure. Zn has a larger ionic radius than Ru, and therefore the unit cell parameter for the former is larger than for the latter, that is a = 15.6365 Å as compared to 15.5098 Å [18]. In the more expanded structure, the Cr-O bond length is expected to be a little longer, and this alone would shift the R lines to higher energies. However, this neglects the direct influence of the second coordination sphere, that is, the direct and specific interactions of a given [Cr(ox)3]3– with its immediate environment. The analysis of the crystal structure reveals 4 nearest neighbour [M(bpy)3]2+ complexes around each [Cr(ox)3]3– having interplane separations between oxalate and bipyridine ligands of around 3.5 Å, that is, small enough for significant π–π interactions. As bipyridine can act as an acceptor for electron density from the negatively charged oxalate, this results in an additional contribution to the nephelauxetic effect. For the larger Zn ion, the interplane separation between the ligands of the two complexes is smaller than for the Ru ion, and as a result this interaction is larger for the Zn ion. Therefore, this contribution to the nephelauxetic effect is larger for the Zn lattice than for the Ru lattice, and dominates the small change solely due to the small bond length change, thus shifting the R lines to lower energy in distinct steps with increasing concentration of Zn in the mixed crystals. This is further borne out by the comparison with the R lines of the 2D network, for which this contribution is missing, and which are 40 cm−1 higher in energy with respect to the R lines of the 3D networks.

4. Conclusions

The four aspects regarding the photophysical properties of [Cr(ox)3]3– discussed above are unique and due to the molecular structure of the 2 and 3D networks. They are not generally observable for doped oxide or fluoride lattices and concentrated simple ionic systems. Furthermore, they are not independent of each other. For instance, the demonstration of the importance of π–π interactions in Section 3.4 provides a solid basis for the discussion of the, at first sight, astonishing difference in the efficiency of the spectral diffusion by changing the inert metal-ion in the tris-bipyridine complex. Nevertheless, it will be necessary to actually determine the homogeneous line widths of the R1 line at low temperatures for the different lattices in order to arrive at a coherent quantitative description of both the resonant energy transfer process resulting in the multi-line pattern as well as the spectral diffusion.

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