Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Photophysical and Photochemical Properties of Three-Dimensional Metal-Tris-Oxalate Network Structures

Andreas Hauser [a] , Marianne E. Von Arx [a] , Rene Pellaux [b] & Silvio Decurtins [b]

[a] Institut für anorganische und physikalische Chemie, Universität Bern, Freiestrasse 3, CH-3000, Bern, 9, Switzerland

[b] Institut für Anorganische Chemie der Universität Zurich, Winterthurerstrasse 190, CH-8057, Zurich, Switzerland

Version of record first published: 04 Oct 2006.

To cite this article: Andreas Hauser , Marianne E. Von Arx , Rene Pellaux & Silvio Decurtins (1996): Photophysical and Photochemical Properties of Three-Dimensional Metal-Tris-Oxalate Network Structures, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 286:1, 225-230

To link to this article: http://dx.doi.org/10.1080/10587259608042290

Mol. Cryst. Liq. Cryst., 1996, Vol. 286, pp. 225–230
Reprints available directly from the publisher
Photocopying permitted by license only

PHOTOPHYSICAL AND PHOTOCHEMICAL PROPERTIES OF THREE-DIMENSIONAL METAL-TRIS-OXALATE NETWORK STRUCTURES

ANDREAS HAUSER*, MARIANNE E. VON ARX
Institut für anorganische und physikalische Chemie, Universität Bern, Freiestrasse 3, CH-3000 Bern 9, Switzerland

RENE PELLAUX, SILVIO DECURTINS
Institut für Anorganische Chemie der Universität Zürich, Winterthurerstrasse 190, CH-8057 Zürich, Switzerland

Abstract Chemical variation and combination of metal ions of different valencies in the oxalate backbone as well as in the tris-bpy cation of the three-dimensional network structures of the type $[M^{II}_2(ox)_3][M^{II}(bpy)_3]$ (bpy = 2,2'-bipyridine, ox = $C_2O_4^{2-}$), $[M^{I}M^{III}(ox)_3][M^{II}(bpy)_3]$ and $[M^{I}M^{III}(ox)_3][M^{III}(bpy)_3]ClO_4$ offer unique opportunities for studying a large variety of photophysical processes. Depending upon the relative energies of the excited states of the chromophores, excitation energy transfer either from the tris-bipyridine cation to the oxalate backbone or vice versa is observed, as for instance from $[Ru(bpy)_3]^{2+}$ as photo-sensitiser to $[Cr(ox)_3]^{3-}$ as energy acceptor in the combination $[NaCr(ox)_3][Ru(bpy)_3]$, or from $[Cr(ox)_3]^{3-}$ to $[Cr(bpy)_3]^{3+}$ in $[NaCr(ox)_3][Cr(bpy)_3]ClO_4$. In addition efficient energy migration within the oxalate backbone is observed. Furthermore, depending upon the excited state redox potentials, light-induced electron transfer processes may be envisaged.

INTRODUCTION

The class of chiral three-dimensional metal-tris-oxalate network structures of compositions $[M^{II}_2(ox)_3][M^{II}(bpy)_3]$ and $[M^{I}M^{III}(ox)_3][M^{II}(bpy)_3]$ (ox = $C_2O_4^{2-}$, bpy = 2,2'-bipyridine) recently synthesised by Decurtins et al. [1] have interesting structural, magnetic and photophysical properties.[2] Despite the complexity of the nuclear structure, they crystallise in the enantiomorphic space groups $P4_132/P4_332$ and $P2_13$, respectively. Each and every metal on the oxalate backbone is coordinated by three oxalate ions, and each and every oxalate ion acts as bridging ligand, resulting in a three-dimensional negatively charged network with rather large cavities. The metal-tris-bipyridine cation nicely fit into these cavities, thus actively stabilising the whole structure.

The crystallisation process is fully enantio-selective in so far as the conformations of the metal centres on both the oxalate backbone and in the tris-bipyridine cation are of the same chirality. This implies specific, chiral interactions between the negatively charged backbone and the complex cation. In fact, mechanistically the latter is thought to act as

template for the formation of the supramolecular network structure, best described as cubic 3-connected 10-gon net.[3] In the crystal lattice the molecular trigonal axis of the tris-chelate complexes is retained.

There are basically no limits to the combination of transition metal ions which can be incorporated into these structures, as long as the charges of those on the oxalate backbone add up to +4 and the one on the tris-bpy cation is +2. With the incorporation of an additional ClO_4^- ion, the latter may also take on a value of +3.[4] Of course, the relative stability constants of the constituting tris-chelate complexes determine which of the metal ions end up as tris-oxalate and which one as tris-bipyridine complexes.

The magnetic properties of the above class of compounds are mainly determined by the metal ions on the oxalate backbone. These can interact with each other via the bridging ligands as super-exchange pathway, giving rise to magnetic phenomena such as antiferro- and ferri- and ferromagnetism.[2,5] For the photophysical and photochemical properties the tris-bipyridine cation may be equally important. Indeed, the ubiquitous photosensitiser $[Ru(bpy)_3]^{2+}$ [6] will play a key role in the following discussion on excitation energy transfer and light-induced electron transfer properties of selected combinations of metal ions.

$[Ru(bpy)_3][NaM(ox)_3]$ (M = Al, Cr, Co)

The compound with the photophysically inactive Na^+ and Al^{3+} metal ions on the oxalate backbone and $[Ru(bpy)_3]^{2+}$ in the cavities shows the famous red luminescence attributed to the spin-forbidden metal-ligand charge transfer (MLCT) transition of this complex cation upon irradiation into the maximum of the corresponding ^{1}MLCT absorption band at ~22'000 cm^{-1} (see Fig. 1).

If Al^{3+} is replaced by Co^{3+} or Cr^{3+}, the $[Ru(bpy)_3]^{2+}$ luminescence is either partially (Co^{3+}) or completely (Cr^{3+}) quenched. In the latter case, the sharp luminescence bands characteristic for the zero-field components of the $^2E \rightarrow {}^4A_2$ transition of octahedrally coordinated and trigonally distorted Cr^{3+} [7] are observed at 14'400 cm^{-1} (see Fig. 1). This is a clear indication for very efficient energy transfer from the initially excited $[Ru(bpy)_3]^{2+}$ to $[Cr(ox)_3]^{3-}$. For such a radiationless energy transfer process to be efficient, geometric proximity between donor and acceptor and non-negligible spectral overlap between donor luminescence and acceptor absorption are required. Both conditions are ideally fulfilled by the network system. Each $[Ru(bpy)_3]^{2+}$ complex is surrounded by thirty $[Cr(ox)_3]^{3-}$ chromophores within the critical distance $R_C \approx 19$ Å, where R_C has been estimated for dipole-dipole interaction according to Ref. 8, taking the spectral overlap between the $[Ru(bpy)_3]^{2+}$ luminescence and the $^4A_2 \rightarrow {}^4T_2$ absorption of $[Cr(ox)_3]^{3-}$ into account.

In the Co^{3+} case, the $[Ru(bpy)_3]^{2+}$ luminescence is not completely quenched and no additional luminescence is being observed. Since $[Ru(bpy)_3]^{2+}$ in the excited state is

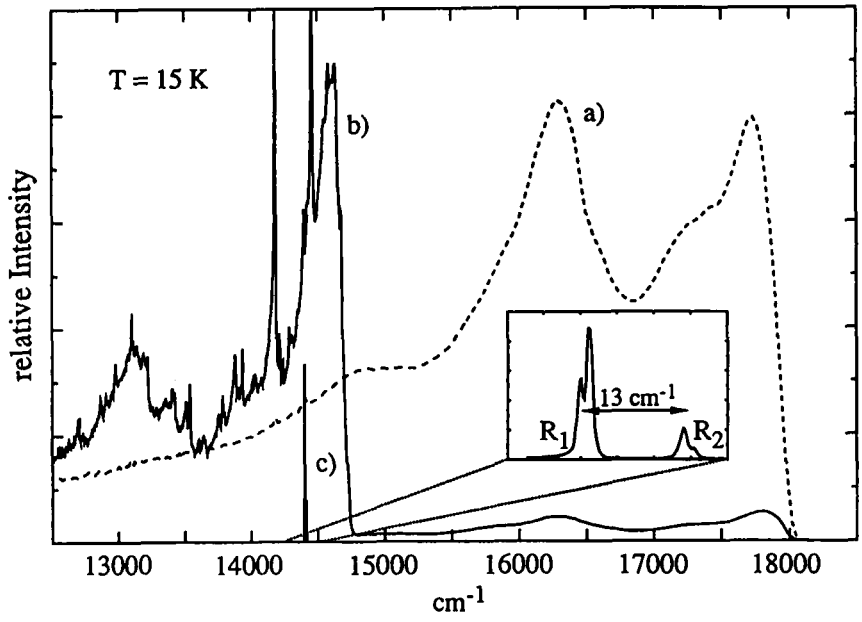

FIGURE 1 Luminescence spectra at T = 15 K of: a) $[Ru(bpy)_3][NaAl(ox)_3]$, b) $[Ru_{1-x}Os_x(bpy)_3][NaAl(ox)_3]$, x = 1%, c) $[Ru(bpy)_3][NaCr(ox)_3]$, λ_{ex} = 476 nm.

sufficiently reducing to reduce $[Co(ox)_3]^{3-}$, the quenching is thought to be due to an oxidative photo-electron transfer process.

Not only acceptors on the oxalate backbone may quench the $[Ru(bpy)_3]^{2+}$ luminescence. Replacing a fraction of the $[Ru(bpy)_3]^{2+}$ chromophores by $[Os(bpy)_3]^{2+}$ results in luminescence from $[Os(bpy)_3]^{2+}$ and a quenching of the $[Ru(bpy)_3]^{2+}$ luminescence, too. Indeed the energy transfer to $[Os(bpy)_3]^{2+}$ is even more efficient than to $[Cr(ox)_3]^{3-}$. This is due to the higher oscillator strength of the MLCT absorption on $[Os(bpy)_3]^{2+}$ as compared to the spin-allowed d-d transition on $[Cr(ox)_3]^{3-}$. In this system a critical distance R_C of approximately 40 Å is estimated.

The comparison of the total luminescence intensities and the excited state lifetimes shown as a function of temperature for diluted $[Zn_{1-x}Ru_x(bpy)_3][NaAl(ox)_3]$ (x = 0.001) and neat $[Ru(bpy)_3][NaAl(ox)_3]$ in Figs. 2a and b, proves that energy migration from $[Ru(bpy)_3]^{2+}$ to $[Ru(bpy)_3]^{2+}$ must take place. The concentration quenching in the neat compound is due to energy transfer to so-called killer traps, for instance $[Fe(bpy)_3]^{2+}$. At low enough temperatures, however, some of the energy is also trapped in shallow traps consisting of slightly disturbed $[Ru(bpy)_3]^{2+}$ chromophores at the low-energy side of the inhomogeneous distribution, having an excited state lifetime which is approximately equal to the lifetime in the diluted mixed crystal system. At temperatures above ~100 K thermal detrapping occurs, resulting in a sudden drop in the observed lifetime.

All of the above processes are schematically summarised in Fig. 3.

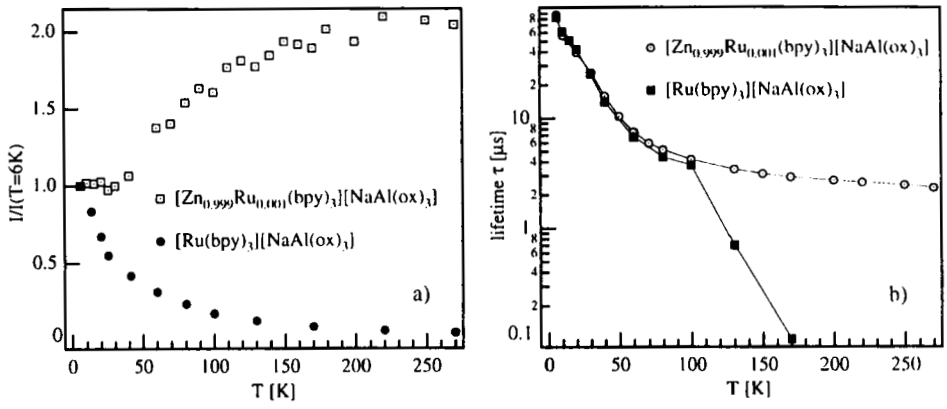

FIGURE 2 Total luminescence intensities (a) and lifetimes (b) as a function of T for $[Ru(bpy)_3][NaAl(ox)_3]$ and $[Zn_{1-x}Ru_x(bpy)_3][NaAl(ox)_3]$, x = 0.001.

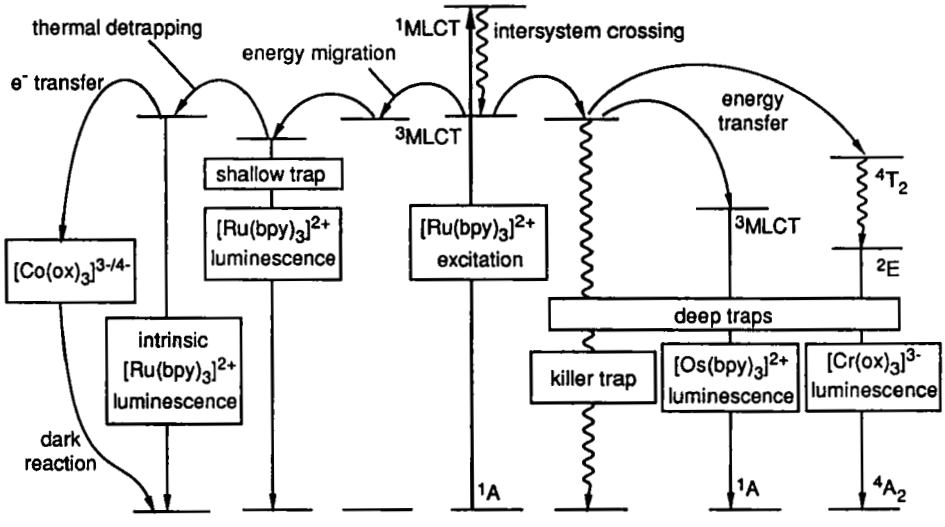

FIGURE 3 Schematic representation of the different photophysical processes observed in $[Ru_{1-x}Os_x(bpy)_3][NaAl(ox)_3]$ and $[Ru(bpy)_3][NaAl_{1-x}Cr_x(ox)_3]$.

$[M(bpy)_3][NaCr(ox)_3]ClO_4$ (M = Cr, Rh)

In Fig. 4 the single crystal absorption spectrum of $[Cr(bpy)_3][NaCr(ox)_3]ClO_4$ at 15 K is depicted. The molecular trigonal axis for both $[Cr(bpy)_3]^{3+}$ and $[Cr(ox)_3]^{3-}$ is preserved in the site symmetry of the crystal. Thus for $[Cr(bpy)_3]^{3+}$, absorption energies and zero-field splittings similar to those observed for this chromophore in other trigonal environments are to be expected. The same holds for $[Cr(ox)_3]^{3-}$. As the spectra for both $[Cr(bpy)_3]^{3+}$ [9] and $[Cr(ox)_3]^{3-}$ [10] are well known, the assignment of the bands is

straightforward. The lowest energy doublet at 13720 cm^{-1} corresponds to the R-lines of the $^4A_2 \rightarrow {}^2E$ transition of $[Cr(bpy)_3]^{3+}$ with a zero-field splitting of 15 cm^{-1}. The corresponding transition of $[Cr(ox)_3]^{3-}$, too, is easily identified as the doublet of sharp lines at 14400 cm^{-1}. The zero-field splitting in this case is 13 cm^{-1}. The shoulders on the low-energy side of this doublet may be assigned to the $^4A_2 \rightarrow {}^2T_1$ transition of $[Cr(bpy)_3]^{3+}$. The respective transition of $[Cr(ox)_3]^{3-}$ is found between 14800 and 15200 cm^{-1} together with some vibrational side bands, and the $^4A_2 \rightarrow {}^2T_2$ transition of $[Cr(ox)_3]^{3-}$ is found at 21120 cm^{-1}. As is usual for the (spin-forbidden) spin-flip transitions in Cr^{3+} complexes, they are all sharp, and as there is no centre of inversion in tris-chelate complexes, most of the (electric-dipole) intensity is in the electronic origins.

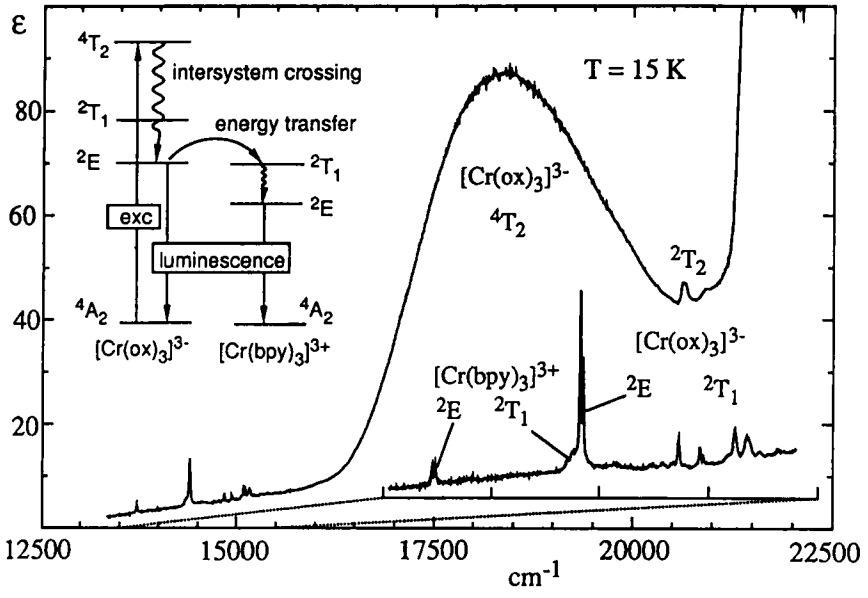

FIGURE 4 Single crystal absorption spectrum of $[Cr(bpy)_3][NaCr(ox)_3]ClO_4$ at 15 K. Inset: schematic representation of observed energy transfer processes.

When $[Cr(bpy)_3][NaCr(ox)_3]ClO_4$ is irradiated into the $^4A_2 \rightarrow {}^4T_2$ band of $[Cr(ox)_3]^{3-}$, the expected luminescence originating from the ^2E state of $[Cr(ox)_3]^{3-}$ is almost totally quenched. Despite the fact that $[Cr(bpy)_3]^{3+}$ does not absorb at the irradiation wavelength, a much stronger luminescence, clearly originating from the ^2E state of $[Cr(bpy)_3]^{3+}$, appears at lower energy. Evidently, an efficient energy transfer process from the initially excited $[Cr(ox)_3]^{3-}$ chromophore as donor to $[Cr(bpy)_3]^{3+}$ as acceptor takes place. This is not surprising: a) the spectral overlap of the $^4A_2 \rightarrow {}^2E$ band of $[Cr(ox)_3]^{3-}$ and the $^4A_2 \rightarrow {}^2T_1$ band of $[Cr(bpy)_3]^{3+}$ allows for a resonant energy transfer process, b) every $[Cr(ox)_3]^{3-}$ complex is surrounded by seven $[Cr(bpy)_3]^{3+}$ complexes at distances of less than 9 Å.

The luminescence spectrum of $[Rh(bpy)_3][NaCr(ox)_3]ClO_4$ on the other hand shows the expected luminescence from the ^2E state of $[Cr(ox)_3]^{3-}$. However there is now clear evidence for extremely efficient energy migration within the R_1-line even at liquid helium temperatures. In a resonant fluorescence line narrowing experiment,[11] it was possible to unambiguously distinguish between a resonant process[12], that is resonant within a homogeneous linewidth, and the more often observed, phonon-assisted spectral diffusion[13] into the inhomogeneous distribution. At 1.8 K the former is dominant, with increasing temperature the latter becomes more efficient.

CONCLUDING REMARKS

As the above examples show, the three-dimensional oxalate network structures are interesting from a photophysical point of view. Together with the efficient energy transfer from $[Ru(bpy)_3]^{2+}$ to $[Ru(bpy)_3]^{2+}$ in the concentrated systems and the possibility of photoelectron transfer quenching by suitable donors or acceptors, this could be significant for possible applications in heterogeneous photocatalysis.

The combination of magnetic properties[2,5] and optical properties could play an important role, for instance in the development of magneto-optical devices.

ACKNOWLEDGEMENTS

We thank the "Schweizerischer Nationalfonds" and the "Hochschulstiftung der Universität Bern" for financial assistance.

REFERENCES

1. S. Decurtins, H. W. Schmalle, P. Schneuwly, J. Ensling, P. Gütlich, J. Amer. Chem. Soc. 116, 9521 (1994).
2. S. Decurtins, R. Pellaux, A.Hauser, M. E. von Arx, to be published in NATO ASI Series, "Magnetism - a Molecular Function" (O. Kahn editor), Kluver, Dortrecht 1996.
3. A. F. Wells, Structural Inorganic Chemistry (Clarendon Press, Oxford 1984).
4. S. Decurtins, H.W. Schmalle, P.Schneuwly, R. Pellaux, A. Hauser, Inorg. Chem. in press.
5. S. Decurtins, H. W. Schmalle, P. Schneuwly, R. Pellaux, J. Ensling, Mol. Cryst. Liq. Cryst. 273, 167 (1995).
6. A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser, A. von Zelewski, Coord. Chem. Rev. 84, 85 (1988).
7. S. Sugano, Y. Tanabe, H. Kamimura, H., Pure and Applied Physics 33 (Academic Press, New York 1970).
8. G. Blasse, in NATO ASI B114 (DiBartolo, B. ed., Plenum Press, New York 1984) p. 251.
9. A. Hauser, M. Mäder, W. T. Robinson, R. Murugesan, J. Ferguson, Inorg. Chem. 26, 1331 (1987).
10. T. Schönherr, J. Spanier, H.-H. Schmidtke, J. Phys. Chem. 93, 5959 (1989).
11. A. Szabo, Phys. Rev. Lett. 27 (1971) 323.
12. A. Hauser, H. Riesen, S. Decurtins, R. Pellaux, submitted to Chem. Phys. Lett.
13. P.M. Selzer, D.L. Huber, B.B. Barnett, W.M. Yen, Phys. Rev. B17, 4979 (1978).