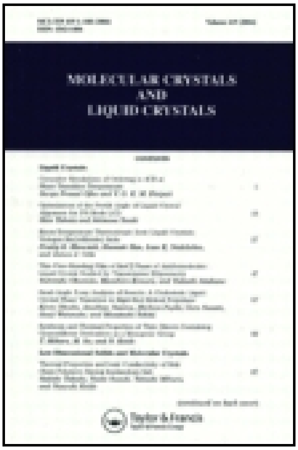

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PHOTOLUMINESCENCE OF ENANTIO-SELECTIVELY FORMED CHROMIUM(III) DOUBLE SALTS

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Abstract Chromium complex double salts of the compositions $[Cr(en)_3]$ $[Cr(ox)_3]$ and $[Cr(pn)_3][Cr(ox)_3]$ (en=ethylenediamine, pn=propylenediamine, ox=oxalate), denoted as [en][ox] and [pn][ox], respectively, were prepared from racemic and optically resolved component complexes. (+) or (-) $[Cr(en)_3]^{3+}$ selectively combines with homochiral $[Cr(ox)_3]^{3-}$ to form a chiral double salt, which has a different structure and a different low-temperature photoluminescence spectrum with respect to the racemic [en][ox] compound. The luminescence at 15 K is due to the $^2E_g \rightarrow {}^4A_{2g}$ transition of the oxalate complex. The total luminescence spectrum and the circularly polarized luminescence (CPL) spectrum of chiral [en][ox] are dominated by a progression in a 213 cm^{-1} mode with $S = 0.31$. Racemic [pn][ox] also shows a luminescence spectrum with a pronounced vibronic progression.

INTRODUCTION

Coordination compounds of chromium(III) have been subject to extensive studies of photochemical, photophysical and magnetic properties. The $^2E_g \rightarrow {}^4A_{2g}$ sharp-line luminescence of octahedral Cr^{3+} complexes serves as a probe of the molecular structures. Optical absorption and emission spectroscopy of compounds containing both a cationic and an anionic chromium complex (so-called chromium double salts) was established three decades ago.[1] The electronic absorption spectra of this type of double salts are perfect overlaps of the spectra of the component complexes, but the luminescence is originating only from the complex with the lower-energy excited state.[1,2]

In this paper, we are focussing on chiral double salts consisting of chromium complexes with the chelate ligands ethylenediamine (en) or propylenediamine (pn) on one hand and oxalate (ox) on the other hand. These complexes can have either Δ or Λ conformations, denoted as (+) and (-) in the following. By optical spectroscopy we will demonstrate the enantioselectivity in the formation of the chromium double salts and the fundamental difference between samples prepared from racemic and chiral starting material.

EXPERIMENTAL RESULTS

Formation of Double Salts

The racemic chromium(III) complex compounds $[Cr(pn)_3]Cl_3$, $[Cr(en)_3]Cl_3$ and $K_3[Cr(ox)_3]$ were synthesized and the conformational enantiomers of the two latter ones were subsequently separated by standard procedures. By slowly mixing diluted aqueous solutions of a cationic and an anionic complex, the double salts were formed as a precipitate. They were purified by successive washing with water. In the case of $[Cr(en)_3][Cr(ox)_3]$ (hereafter denoted as [en][ox]) there are in principle nine possible combinations of the (+) and (-) enantiomeric and racemic component complexes. However, only two different stereoisomeric types of the [en][ox] double salt were found. If racemic $[Cr(en)_3]^{3+}$ was used as a starting material the "racemic" type of double salt was obtained, and with either (+) or (-) $[Cr(en)_3]^{3+}$ the "chiral" type was formed. These two types of [en][ox] compounds showed completely different powder X-ray patterns and, as we will demonstrate in the next section, different photoluminescence spectra. The original chirality of the $[Cr(ox)_3]^{3-}$ component complexes seemed to be of no importance for the formation of the double salts.

If a solution of (+) $[Cr(en)_3]^{3+}$ was mixed with a doubly concentrated solution of racemic $[Cr(ox)_3]^{3-}$, the [en][ox] double salt of the chiral type precipitated, and the remaining oxalate complex solution was found to be of (-) chirality by circular dichroism (CD) spectroscopy. The respective CD spectra are displayed in Fig. 1. This experiment demonstrates the enantio-selective formation of the homo-chiral [en][ox] double salt.

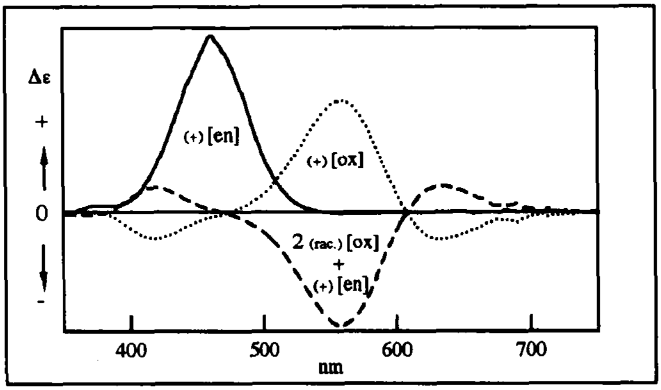

FIGURE 1 Circular dichroism spectra of chiral Cr(III) complexes in solution. Solid line: (+) $[Cr(en)_3]^{3+}$, dotted line: (+) $[Cr(ox)_3]^{3-}$, dashed line: mixture of (+) $[Cr(en)_3]^{3+}$ + 2 (rac.) $[Cr(ox)_3]^{3-}$ after precipitation of the double salt.

Luminescence Spectroscopy

In order to avoid photochemical decomposition of the chromium complex double salts, green excitation light from a filtered Hg-lamp or from a pulsed N_2-laser/dye-laser system was used instead of UV-light from standard excitation sources in all experiments. The PC-controlled spectrophotometric system consisted of a Spex 1401 double monochromator with a GaAs photomultiplier tube in combination with an SR400 two-channel gated photon counter for luminescence spectra or a TDS420 digital oscilloscope for lifetime measurements. In measurements of circularly polarized luminescence (CPL) a photoelastic modulator (50 kHz) with dynamic wavelength calibration was used, and the photon counter was set to count the left- and right-handed CPL components separately. Cooling of the samples down to 15 K was achieved by a closed-cycle He refrigerator.

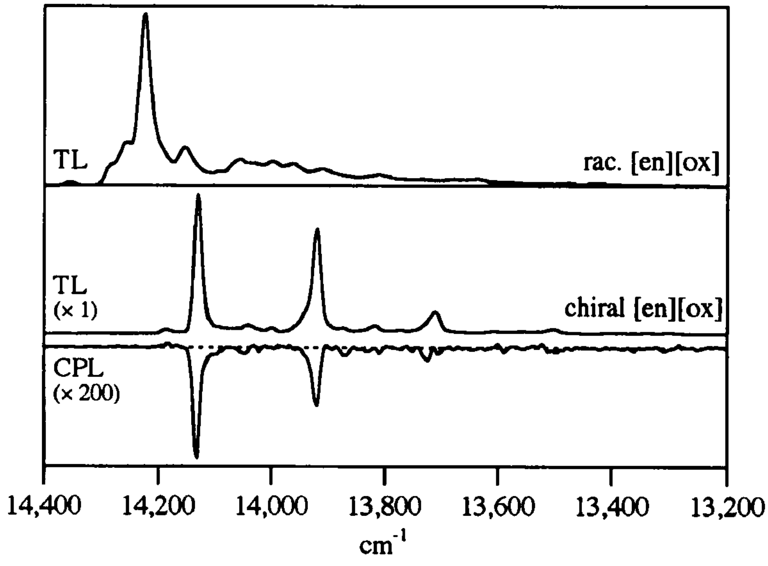

FIGURE 2 Spectra of Cr(III) complex double salt powder samples at 15 K under filtered Hg-lamp excitation (480 - 580 nm). Top: total luminescence (TL) of racemic [en][ox]. Center and bottom: TL and CPL of [en][ox] formed by the (-) and (+) enantiomers of the component complexes.

The low-temperature luminescence spectra of powder samples of the two types of [en][ox] double salts are displayed in Fig. 2. Whereas the $^2E_g \rightarrow {}^4A_{2g}$ luminescence transitions of the ethylenediamine and oxalate component complexes are lying at approximately 14,860 cm^{-1} and 14,420 cm^{-1}, respectively, the peak maxima in the double salts were found to be at lower energy, namely 14,224 cm^{-1} (racemic type) and

14,131 cm^{-1} (chiral type). The CPL spectrum of the chiral sample is also given in Fig. 2. The dissymmetry factor *g* is +/- 0.008 with the sign determined by the initial chirality of the $[Cr(en)_3]^{3+}$ component complex. The luminescence of both the racemic and chiral double salts was quenched at temperatures above 100 K.

A diluted powder sample of chiral [en][ox] was obtained by adding KBr in a ratio of 100:1 and grinding the mixed powder finely. The resulting luminescence spectrum at 15 K is shown in Fig. 3 (bottom). With respect to the undiluted sample the peaks are sharper and have a different intensity ratio. The most intense band (no. 0) is located at 14,144 cm^{-1} and has a width of approximately 8 cm^{-1}. As can also be seen in Fig. 2, most of the luminescence intensity of chiral [en][ox] is lying in the electronic origin and its equally spaced (213 cm^{-1}) vibronic sidebands. By analyzing the intensity ratios of the vibronic progression in the diluted sample, a Huang-Rhys-Factor of $S = 0.31$ was obtained. The line denoted with an asterisk, separated from peak 0 by 59 cm^{-1} was identified as a "hot" band originating from a thermally populated excited-state level.

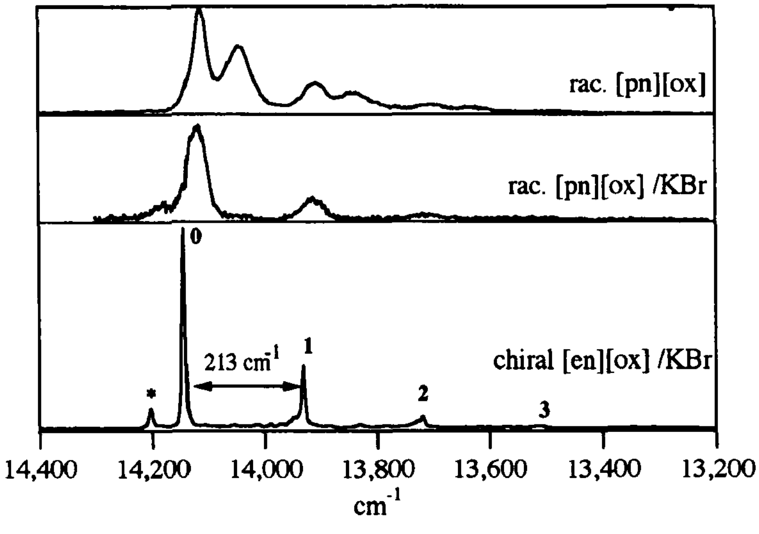

FIGURE 3 Luminescence spectra of Cr(III) complex double salts at 15 K under filtered Hg-lamp excitation (480 - 580 nm). Bottom: [en][ox] powder formed by the (-) enantiomers of the component complexes, diluted 1:100 in KBr. Top and center: racemic [pn][ox] powder samples undiluted and diluted 1:100 in KBr powder, respectively.

The luminescence decay curves of all [en][ox] samples were found to be multi-exponential due to inhomogeneities and energy-transfer processes. In racemic samples the longest-living component has a lifetime of roughly 1 ms, but in chiral samples a maximum lifetime of 200 μs was observed.

The luminescence spectra of both undiluted and diluted racemic [pn][ox] samples are given in the upper part of Fig. 3. As in chiral [en][ox] a vibronic progression is the main spectral feature. The bands show a large inhomogeneous broadening. In the undiluted sample a second set of bands with considerable intensity was observed, shifted from the main bands by 70 cm^{-1} to lower energy.

DISCUSSION

If the (+) or (-) enantiomer of $[Cr(en)_3]^{3+}$ was used as a counter ion for the anionic complex $[Cr(ox)_3]^{3-}$, a new type of the [en][ox] double salt was obtained. This "chiral" type of [en][ox] has a different crystal structure and different luminescence properties with respect to racemic [en][ox]. Although the luminescence and CPL of [en][ox] double salts are originating from the oxalate complexes, they are reflecting the chirality of the ethylenediamine complexes. Optically resolved $[Cr(en)_3]^{3+}$ complexes were found to selectively combine with $[Cr(ox)_3]^{3-}$ complexes of the same chirality, see Fig. 1. Since chromium oxalate complexes are generally known to racemize easily, the [en] complexes can always find some homochiral partners. Moreover, one can not exclude conformational changes of [ox] complexes directly induced by [en] complexes during the precipitation process. The chiral type of [en][ox] double salts is therefore assumed to contain component complexes with either (+)/(+) or (-)/(-) chirality only. A similar homochiral double salt formation was reported for bipyridine and oxalate complexes of transition metal ions, which crystallize in structures containing a three-dimensional oxalate network.[3]

The luminescence spectrum of chiral [en][ox] is dominated by a vibronic progression, as shown in Figs. 2 and 3. Whereas the zero-phonon-line does not show its full intensity in the undiluted sample due to reabsorption processes, the relative intensities of the progression members in the spectrum of the sample dispersed in KBr powder correspond to the theoretically expected Poisson distribution. One more effect of diluting the double salt powder is the sharpening of the luminescence lines by avoiding excitation-energy transfer to minority centers with slightly lower-energy emitting states. The Huang-Rhys-Factor of 0.31 is relatively large for the intraconfigurational $^2E_g \rightarrow {}^4A_{2g}$ transition, indicating some structural differences between the ground and excited state. The hot band denoted with an asterisk in Fig. 3 can be assigned to the emission from the higher-energy component of the ^2E_g excited state, which is split by low-symmetry fields. However, the observed splitting of 59 cm^{-1} is considerably larger than the typical value of 15 cm^{-1} for chromium oxalate compounds.

The luminescence spectrum of racemic [pn][ox] double salts shows the same progression as for chiral [en][ox]. The emitting oxalate units are therefore assumed to have a similar structure, although racemic $[Cr(pn)_3]^{3+}$ was used as a starting material. A striking effect of diluting the [pn][ox] sample was observed, see Fig. 3. The lower-energy set of bands present in the undiluted sample is identified to be due to a minority site acting as an acceptor of a large amount of excitation energy. The band widths of the diluted sample indicate that the [pn][ox] compound contains more structural inhomogeneities than chiral [en][ox].

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