

FOUR EMISSION BANDS FROM A QUADRATE CHROMIUM(III) COMPLEX

W. TUSZYNSKI, E. STRAUSS

FB Physik, Universität, 2900 Oldenburg, Germany

The luminescence of solid state and dissolved trans-[Cr(cyclam)(CN)₂]ClO₄ has been studied by time-resolved spectroscopy. Four bands covering the blue to near infrared region were observed which are assigned to various d-d transitions of Cr(III). The lowest emitting states are strongly dependent on deuteration and solvation.

1. INTRODUCTION

The cyclic tetramine 1,4,8,11-tetraazacyclotetradecane (cyclam) forms complexes with several transition metal ions¹. We report about the luminescence of trans-[Cr(cyclam)(CN)₂]ClO₄. This complex is of special interest due to its excellent photochemical stability². The quantum efficiency for substitution photochemistry is smaller than 10⁻⁵.

Phosphorescence of the dissolved complex with a maximum at 720 nm has been observed². Its intensity is enhanced by deuteration of the cyclam N-H protons and totally quenched in alkaline solutions. We have paid particular attention to the emission of the solid deuterated complex, but present also some results of the dissolved and of the undeuterated complex for comparison.

2. MATERIALS AND METHODS

The complexes were synthesized according to the literature^{1,2}. Solvent was bidest. H₂O with nitric acid. The luminescence was excited with an Ar⁺ cw laser at 458 nm or a pulsed N₂ laser at 337 nm. Spectra were recorded using a $\frac{1}{4}$ m monochromator (1200 nm and 500 nm blaze) and S1 or S20 cathods photomultipliers. The spectral dependence of the detection sensitivity was not corrected for. Time-resolved spectra were obtained using an averaging transient digitizer or a boxcar unit. A closed-cycle refrigerator was used for low temperature.

3. RESULTS

The quartet absorptions arising from the transitions to the octahedral ⁴T₂ and ⁴T₁ states (see fig.1) are in the UV

due to the high ligand field strength. Their tetragonal splitting is not large enough to be seen. Below 300 nm is a charge transfer transition. The doublet absorption around 700 nm is very weak.

An intense emission band centered at 435 nm is observed on excitation at 337 nm (fig.1). It has a short decay time of less than 50 ns, indicating a spin-allowed transition. In contrast, the rather weak emission centered at 523 nm (see fig.1) has a decay time of about 25 μ s in the powder and is assigned to a spin-forbidden transition. Both emissions, the 523 nm phosphorescence and the 435 nm fluorescence, are observed in acid solutions also.

A different, much more intense phosphorescence is observed in the 700 nm to 900 nm region on excitation at 458 nm. As depicted in fig.2, it strongly depends on deuteration as well as on being crystallized or dissolved. In the deuterated solid complex, the lifetime is 19 μ s at

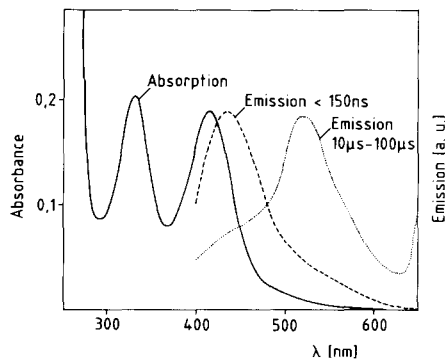


FIGURE 1
Absorption of a 5·10⁻³ M pH 7 complex solution and emission of the deuterated solid

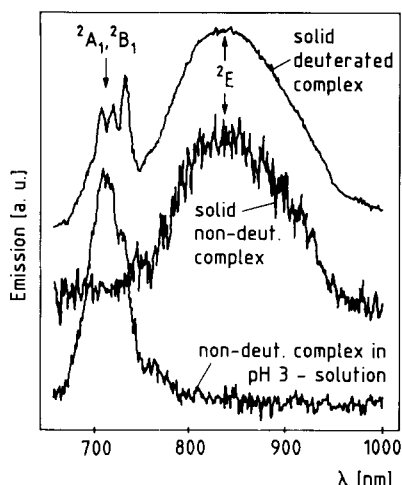


FIGURE 2

Phosphorescence in the 700 nm - 900 nm region

720 nm and 13 us at 835 nm. It is reduced by concentration quenching, as a comparison with values from 10^{-4} molar solution at pH 2 indicates, where the lifetime is 210 us in the non-deuterated and 1.2 ms in the deuterated complex.

The 720 nm emission always exhibits pronounced vibronic fine structure. For the deuterated solid, the 720 nm emission completely disappears upon cooling below 80 K. The remaining 835 nm band is very similar to the room temperature spectrum of the non-deuterated solid. This clearly shows that the states involved are in thermal equilibrium.

4. DISCUSSION

We assume all bands to arise from Cr(III) levels. The bands can be assigned by comparing their maxima with transition energies taken from the Tanabe-Sugano diagram of octahedral d^3 -complexes. With the ligand field parameter $Dq = 2350 \text{ cm}^{-1}$ (a value between those of N-coordinated and CN-ligands for Cr(III)) and the electron-electron interaction parameter $B = 620 \text{ cm}^{-1}$ (like for en-ligands) the following 0-0 transitions are calculated:

$$\begin{array}{ll} {}^2E: 13600 \text{ cm}^{-1} (735 \text{ nm}) & {}^4T_2: 23500 \text{ cm}^{-1} (426 \text{ nm}) \\ {}^2T_1: 14100 \text{ cm}^{-1} (709 \text{ nm}) & {}^4T_1: 29700 \text{ cm}^{-1} (337 \text{ nm}) \\ {}^2T_2: 20400 \text{ cm}^{-1} (490 \text{ nm}) & \end{array}$$

These octahedral transition energies describe rather well the observed bands because the tetragonal splittings are small compared to the dominant octahedral field components and the electron-electron interaction. Deviations also may be due to varying equilibrium distances in the individual states.

According to ligand field theory, the energy separation of the 2E states (${}^2A_1/{}^2B_1$) to the quadrate 4B_1 ground state is not affected by the tetragonal field, in contrast to the 2T_1 states (${}^2A_2/{}^2E$). Consequently the equilibrium distances in these states are different. The largest difference to the ground state equilibrium is expected in the quadrate 2E state and thus we assign the broad 835 nm phosphorescence band to the ${}^2E - {}^4B_1$ transition and the structured 720 nm band to ${}^2A_1/{}^2B_1 - {}^4B_1$. The large spectral changes are then explained by the altered level ordering caused by different tetragonal field strength. Apparently the non-deuterated solid has the largest strength (2E emission only) and dissolved complexes the smallest (${}^2A_1/{}^2B_1$ emission only). This assignment is in agreement with the solvent influence observed in other quadrate Cr(III) complexes³.

The intense blue fluorescence is assigned to the ${}^4E/{}^4B_2$ levels arising from 4T_2 . Either both or only one of the states may be involved. Also, the 523 nm phosphorescence may be assigned to a transition from the 2T_2 states ${}^2E/{}^2B_2$ to 4B_1 because its position agrees well with the calculated value. These assignments are supported by the observed lifetimes which indicate spin-allowed and spin-forbidden transitions respectively.

Although more experimental verification is needed, there already is convincing evidence that the Cr(III) cyclam complex is one of the rare exceptions from Kasha's rule i.e. it luminesces from states higher than the first excited state.

REFERENCES

1. C.K. Poon and M.L. Tobe, *J.Chem.Soc(A)* (1968) 1549
2. N.A. Kane-Maguire, W.S. Crippen and P.K. Miller, *Inorg.Chem.* 22 (1983) 696
3. A.F. Fucaloro, L.S. Forster, S.G. Glover and A.D.Kirk, *Inorg.Chem.* 24 (1985) 4242