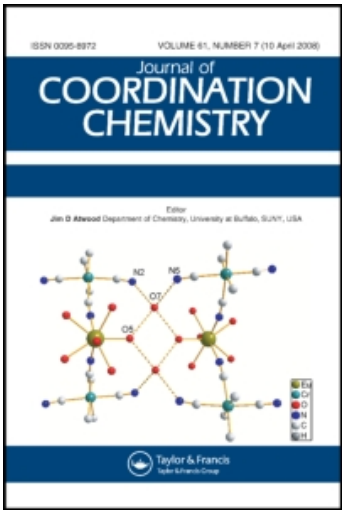

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Change in the Color of Luminescence Accompanied by Dehydration of The Solid K_4 [Pt_2 ($P_2O_5H_2$)$_4$]·$2H_2O$

Tadashi Yamaguchi[a]; Yoichi Sasaki[a]; Takeshi Ikeyama[ab]; Tohru Azumi[a]; Tasuku Ito[a]
[a] Department of Chemistry, Faculty of Science, Tohoku University, Aramaki, Sendai, Japan [b] Miyagi University of Education, Aramaki, Sendai, Japan

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CHANGE IN THE COLOR OF LUMINESCENCE ACCOMPANIED BY DEHYDRATION OF THE SOLID $K_4[Pt_2(P_2O_5H_2)_4]\cdot 2H_2O$

TADASHI YAMAGUCHI, YOICHI SASAKI, TAKESHI IKEYAMA,†
TOHRU AZUMI, AND TASUKU ITO
Department of Chemistry, Faculty of Science, Tohoku University, Aoba, Aramaki, Sendai 980, Japan
†Miyagi University of Education, Aoba, Aramaki, Sendai 980, Japan

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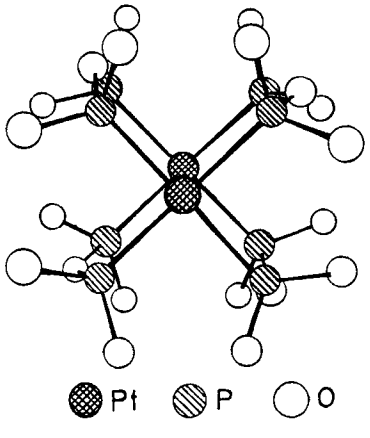
Abstract Some crystals of the titled complex undergo the change in the color of luminescence from green to orange in solid state upon dehydration.

Keywords: Luminescence, dehydration, crystals

INTRODUCTION

Binuclear platinum(II) pyrophosphite complex, $K_4[Pt_2(P_2O_5H_2)_4]\cdot 2H_2O$, is interesting, since it shows intence green luminescence both in solid and in aqueous solution even at room temperature.[1] We found some crystals of potassium salt undergo drastic change in color of luminescence to orange, on keeping in *vacuo* or heating. Crystals (A-type) showing such behavior look more yellowish, while those (B-type) lacking in such property appear more greenish. We would like to discuss here on the difference in the two types of the potassium salt and the nature of the orange luminescent species.



$[Pt_2(P_2O_5H_2)_4]^{4-}$
(H-atoms are omitted)

DIFFERENCE IN THE TWO TYPES OF THE CRYSTALS

Systematic preparation method of each type of the crystals was not found. Both types of the crystals show almost identical electronic absorption spectrum in aqueous solution, and identical crystal and molecular structures (bond distances and bond angles). There are, however, some obvious differences as follows. 1) Reflectance spectra: Only B-type has a peak in the longer wavelength region (at *ca.* 580 nm). 2) Thermal analysis (TG, DSC): A-type begins to loss its water of crystallization below 60°C, while B-type does at 140°C (Figure 1). 3) Emission spectra (solid): The peak in the A-type (518 nm) appears slightly longer wavelength as compared with the B-type (*ca.*513 nm). 4) ^{31}P-CPMAS NMR spectra: The signal at $\delta = 71.5$ ppm is singlet for the A-type, but split into two for the B-type (Figure 2). The two types of the crystals are crystallographically almost identical, but the B-type may contain small amount of oxidized species.[2] Water of crystallization in the A-type may form only weakly bonded hydrogenbond network, which may be destroyed in the B-type by the oxidized species and the water molecules are localized by stronger hydrogenbonds.

ORANGE LUMINESCENT SPECIES

From the thermogravimetry, mass loss in the dehydration process is about 4.5 %, which is equivalent to three water molecules per dimer. Since the crystals have only two waters of crystallization per dimer, intermolecular dehydration condensation should take place. ^{31}P-CPMAS NMR spectra of the dehydrated species show two peaks (δ = 77.2, 64.3 ppm). Orange emission (Figule 3) is characterized as follows. 1) Three emission peaks (or shoulders) are observed at 520, 570, and 670 nm. The peak intensity ratios change by the dehydration method (drying in *vacuo* or heating at 120°C). 2) The life time at the three peaks are different, which are < 1 μs, 2 μs and 6 μs, respectively from the higher energy region (excitation wavelength is 337.1 nm). 3) The pattern of the emission spectra

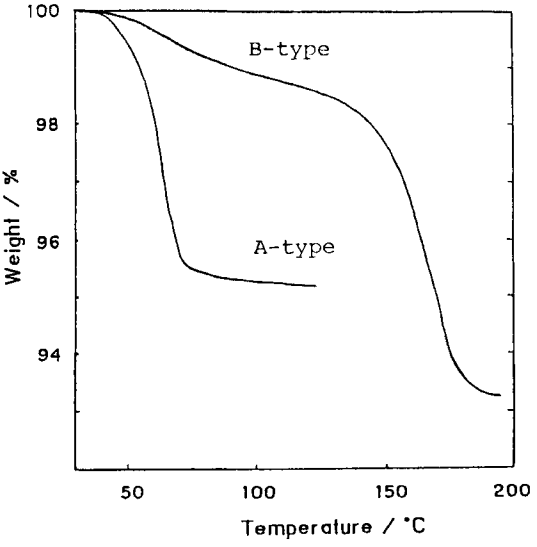


FIGURE 1 TG curves for the two types of crystals of $K_4[Pt_2(P_2O_5H_2)_4]\cdot 2H_2O$.

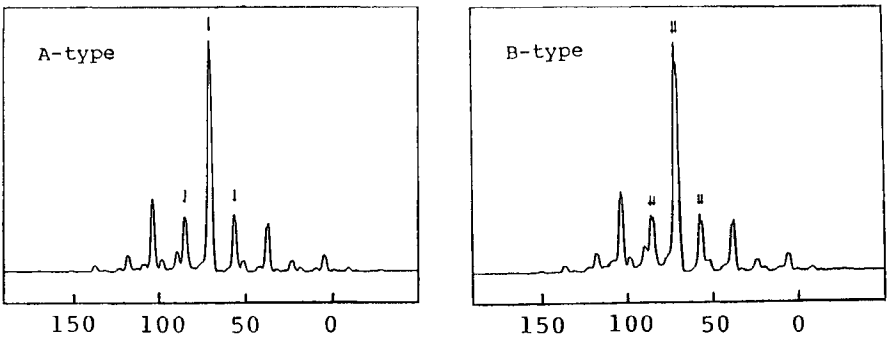


FIGURE 2 ^{31}P-CPMAS NMR spectra of the two types of crystals of $K_4[Pt_2(P_2O_5H_2)_4]\cdot 2H_2O$ (main peaks are indicated by arrows).

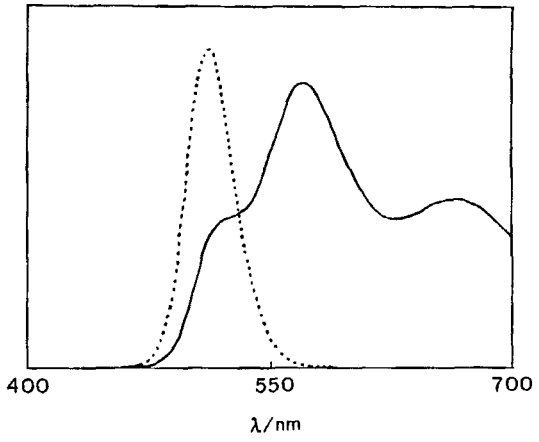


FIGURE 3 Emission spectrum of dehydrated species (——) and original species (----).

depends on the excitation wavelength and temperature. The observed behaviors of the orange luminescence indicate that the dehydrated species should be a mixture of variously condensed species. The solid slowly dissolved in water to give only the original green emission.

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