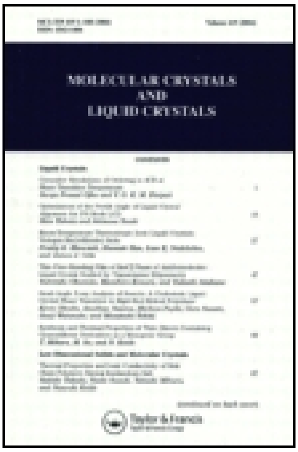

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Md. Abdus SUBHAN [a] , Takayoshi Suzuki [a] & Sumio Kaizaki [a]

[a] Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka, 560-0043, Japan

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Laser Emission in 4f-4f Transitions of Some Nd(III) Complexes

MD. ABDUS SUBHAN, TAKAYOSHI SUZUKI
and SUMIO KAIZAKI*

*Department of Chemistry, Graduate School of Science, Osaka University,
Toyonaka, Osaka, 560-0043, Japan*

The emission spectra of the [(acac)$_2$Cr(ox)Nd(HBpz$_3$)$_2$](Cr(ox)Nd) complex corresponding to both the 4f-4f emission of the Nd(III) at room temperature and the ^{2}E emission of the Cr(III) chromophore at low temperature were observed. Both the complexes [(HBpz$_3$)$_2$Nd(ox)Nd(HBpz$_3$)$_2$] (Nd(ox)Nd) and [Nd$_2$(μ-pba)$_4$(HBpz$_3$)$_2$] exhibit several 4f-4f emission bands in the NIR region.

Keywords: laser emission; 3d-4f complex; 4f-4f complex; Nd(III) complexes

INTRODUCTION

Very recently we reported the synthesis of a series of chiral 3d-4f [(acac)$_2$Cr(ox)Ln(HBpz$_3$)$_2$](Ln = La, Nd, Sm, Dy, Ho, Er, Tm and Yb) complexes[1,2] and their NIR CD and MCD corresponding to the 4f-4f transitions along with the X-ray structural analysis of Cr(ox)Ln (Ln = Sm, Ho, Er, Yb[1])[2]. Here we report the emission of [(acac)$_2$Cr(ox)Nd(HBpz$_3$)$_2$], [(HBpz$_3$)$_2$Nd(ox)Nd(HBpz$_3$)$_2$] and [Nd$_2$(pba)$_4$(HBpz$_3$)$_2$] with four pba (pba = 2- Phenyl butyrate) bridging ligand and two terminal $HBpz_3^-$ (hydrotris(pyrazol-1-yl)borate) ligands in the dinuclear Nd-Nd complex. Heterometal dinuclear 3d-4f complexes are interesting from the viewpoint of the magnetic interaction as well as energy transfer between 3d and 4f states. Tris(pyrazol-1-yl)borate Ln(III) complexes are promising to generate color in flat panel displays because of their bright and durable light emitting capability[3].

EXPERIMENTAL

Synthesis of Complexes

The complexes $[(acac)_2Cr(ox)Nd(HBpz_3)_2]$, $[(HBpz_3)_2Nd(ox)Nd(HBpz_3)_2]$ and $[Nd_2(\mu\text{-pba})_4(HBpz_3)_2]$ (which was preliminarily characterized as a tetrakis(μ-pba) dinuclear structure[6] by X-Ray analysis) were synthesized and characterized by the methods described elsewhere[1,4-6].

Measurement

Emission spectra were recorded in the powder form on a JASCO NR1800 Raman spectrophotometer at room temperature and/or at low temperatures. Variable temperature measurements were carried out by using an Oxford CF1204 cryostat.

RESULTS AND DISCUSSION

The complex Cr(ox)Nd shows three 4f-4f emission bands corresponding to the $^2H_{9/2}\rightarrow{}^4I_{9/2}$, $^4F_{5/2}\rightarrow{}^4I_{9/2}$ and $^4F_{3/2}\rightarrow{}^4I_{9/2}$ transitions from higher energy side with 514.5 nm laser excitation at room temperature as shown in the Figure 1. At 150K or below the emission bands correspon- ding to the $^2H_{9/2}\rightarrow{}^4I_{9/2}$ and $^4F_{5/2}\rightarrow{}^4I_{9/2}$ transitions disappear and an additional broad band around 12300 cm^{-1} is observed. This broad band is assigned to the emission from the ^2E state of the Cr(III) moiety in the Cr(ox)Nd complex in comparison with the emissions of Na[Cr(acac)$_2$(ox)], [(HBpz$_3$)$_2$Nd(ox)Nd(HBpz$_3$)$_2$] and [Nd$_2$(μ-pba)$_4$(HBpz$_3$)$_2$] as shown below. With the further decrease in temperature the emission bands corresponding to both the ^{2}E of Cr(III) and the $^4F_{3/2}\rightarrow{}^4I_{9/2}$ of Nd(III) become more and more intense. Five well split peaks (a-e) observed are due to the transitions from the lowest level of the $^4F_{3/2}$ excited state to five Stark levels of the $^4I_{9/2}$ ground state of Nd(III) in Cr(ox)Nd[6]. At room temperature no observation of emission (quenching of emission) from the ^{2}E state is attributable to the energy transfer from the ^{2}E to the lower lying energy level of Nd (III) ion[6].

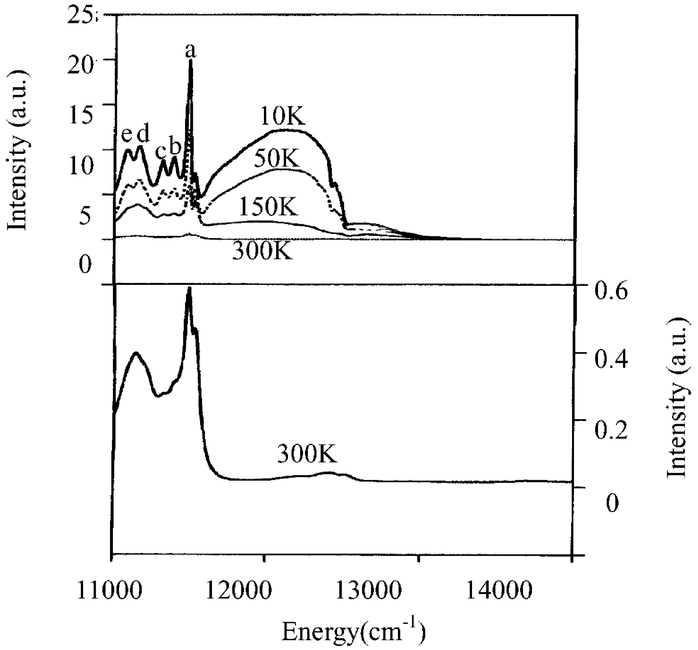

FIGURE 1 Variable temperature laser emission of (acac)2Cr(ox)Nd(HBpz$_3$)$_2$

The complex Nd(ox)Nd shows three 4f-4f emission bands corresponding to the $^2H_{9/2}\rightarrow{}^4I_{9/2}$, $^4F_{5/2}\rightarrow{}^4I_{9/2}$ and $^4F_{3/2}\rightarrow{}^4I_{9/2}$ transitions with 514.5 nm laser excitation as similarly to the Cr(ox)Nd at room temperature as shown in Figure 2.

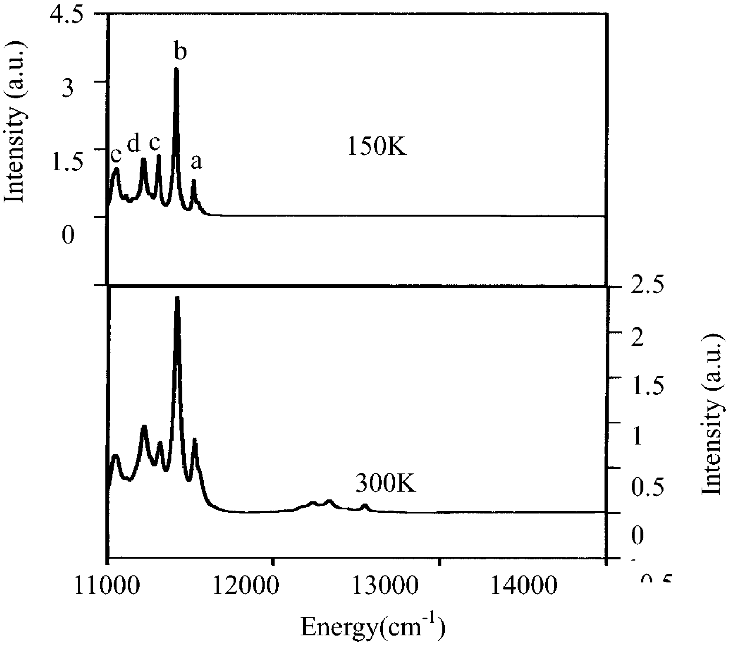

FIGURE 2 Variable temperature laser emission of $(HBpz_3)_2Nd(ox)Nd(HBpz_3)_2$

At 150K or below the higher energy $^2H_{9/2}\rightarrow{}^4I_{9/2}$ and $^4F_{5/2}\rightarrow{}^4I_{9/2}$ emissions disappear and only the $^4F_{3/2}\rightarrow{}^4I_{9/2}$ emission is observed. This is because of the depopulation of the higher energy states of excited state $^4F_{3/2}$ Kramers levels at low temperatures. For the complex Nd(ox)Nd the five well split peaks (a-e) observed are due to the transitions from the lowest level of the $^4F_{3/2}$ excited state to five Stark levels of the $^4I_{9/2}$ ground state of Nd(III)[6].

Although the complex $[Nd_2(\mu\text{-}pba)_4(HBpz_3)_2]$shows emission bands corresponding to the $^2H_{9/2}\rightarrow{}^4I_{9/2}$, $^4F_{5/2}\rightarrow{}^4I_{9/2}$ and $^4F_{3/2}\rightarrow{}^4I_{9/2}$ transitions with the 514.5 nm laser excitation at room temperature as shown in the Figure 3, at 150K or below the emission band observed corresponding to the $^4F_{3/2}\rightarrow{}^4I_{9/2}$ transitions is somewhat different from that of either the Cr(ox)Nd or Nd(ox)Nd complex. This may be attributable to the different coordination sites around the Nd moieties

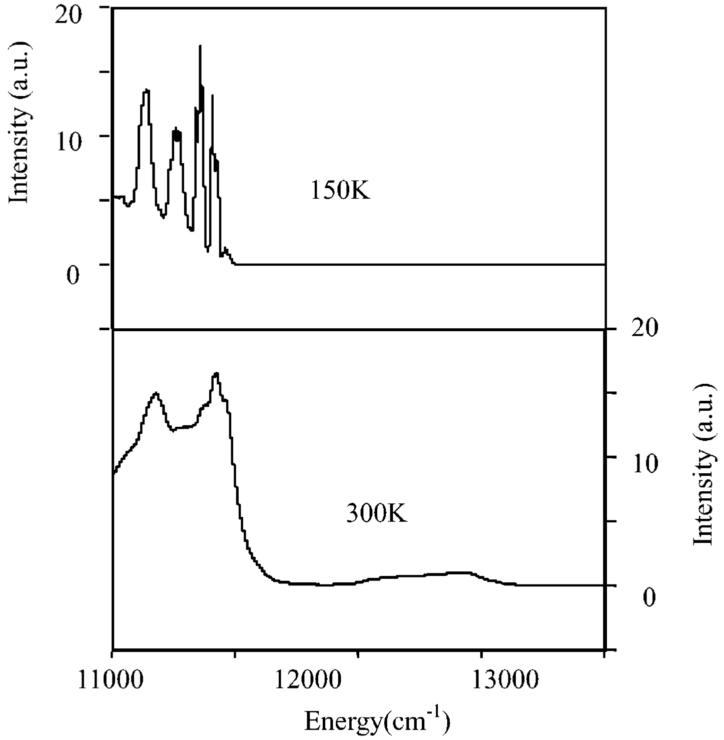

FIGURE 3 Variable temperature laser emission of $Nd(pba)_2(HBpz_3)$

and corresponding ligand field effect in these complexes[7]. In this case too, few peaks observed at low temperature is due to the transitions from the lowest level of the $^4F_{3/2}$ excited state to five Stark levels of the $^4I_{9/2}$ ground state of Nd(III).

CONCLUSIONS

A comparative study of the laser emission spectra of the 3d-4f and that of 4f-4f complexes is reported. This is the first observation of the emission of two luminescent centres in one probe; ^2E emission of the Cr(III) chromophore and 4f-4f emission of the Nd(III) and energy transfer from Cr(III) to Nd(III) in the Cr(ox)Nd assembly. Lanthanide(III) complexes with tris(pyrazol-1-yl)borate might be promising for their possible utility in the optical devices. This aspect of our work with detailed investigation of emission and photophysical properties of a series of Cr(ox)Ln complexes is developed elsewhere[6].

References

[1.] M. A. Subhan, T. Suzuki and S. Kaizaki, *J. Chem. Soc. Dalton Trans.*, 492-497(2001).

[2.] M. A. Subhan, T. Suzuki and S. Kaizaki, *The 51st Symposium on Coordination chemistry of Japan.*, Matsue, Shimane University,; Abstract 1P- F13 (September 2001).

[3.] N. Kaltsoyannis and P. Scott. , *The f elements*, Oxford Univ. Press., 29 (1999).

[4.] T. Sanada, T. Suzuki, T. Yoshida, and S. Kaizaki, *Inorg. Chem.*, **37**, 4712 (1998).

[5.] M. A. Subhan, T. Suzuki and S. Kaizaki., *J. Chem. Soc. Dalton. Trans.*, in press (2002).

[6.] (a) M. A. Subhan, S. Kaizaki and Hiroyasu Nakata, *J. Chem. Soc. Dalton. Trans.*, to be submitted (2002).; (b) M. A. Subhan, T. Suzuki and S. Kaizaki., *Manuscript in preparation.*

[7.] G. Liftane, F . Cusso, F. Jaque, J. A. Sanz-Garcia, A. Monteil, B. Varrel, G. Boulon and J. Gracia -sole, *Chem. Phys. Lett.* **176**, 5, 482(1991).