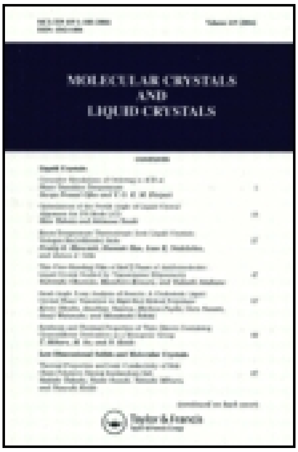

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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To cite this article: Toshihide Kamata , Toshio Fukaya , Takehito Kodzasa , Hiroo Matsuda & Fujio Mizukami (1995): Alloying of Linear Metal Chains in the One-Dimensional Metal Complexes and Their THG Property, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 267:1, 117-122

To link to this article: http://dx.doi.org/10.1080/10587259508033982

Mol. Cryst. Liq. Cryst. 1995, Vol. 267, pp. 117–122
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ALLOYING OF LINEAR METAL CHAINS IN THE ONE-DIMENSIONAL METAL COMPLEXES AND THEIR THG PROPERTY

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Abstract Alloying of metals forming linear chains in the one-dimensional metal complexes was performed by use of vacuum evaporation technique. Mixture of two different metal complexes with dimethylglyoxime could be fabricated into a thin film with optical quality. They showed a strong *d-p* transition band in the visible region, and their peak wavelengths subsequently varied in proportion to the mixing ratio of metal complexes. Their third-order nonlinear optical property was also investigated by third-harmonic generation measurements.

INTRODUCTION

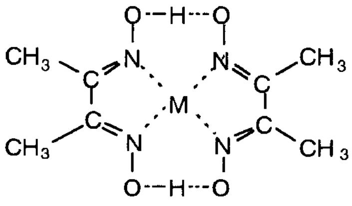
It has been known that the nickel, palladium and platinum complexes with dionedioxime have square planar configuration and form one-dimensional structure consisting of linear metal chains.[1] They have considerable interests in optoelectronic applications owing to their delocalized electrons in the one-dimensional backbone. While they have been investigated mainly for the purpose of developing new electron conductors, we have suggested that these one-dimensional metal complexes can be a good candidate for the third-order nonlinear optical material.[2]

Third-order nonlinear optical effect is one of the most promising properties for development of future optoelectronics, and many research efforts have been devoted to the search for new nonlinear optical materials with excellent properties. In order to obtain effective nonlinearity, light absorption of the materials, that is resulted in optical signal loss, should be reduced as possible. Magruder et al.[3] have demonstrated that the wavelength of the surface plasmon resonance band of nanosize metal particles, those are known to show large nonlinear optical property, can be tuned by the alloying of gold and copper ions in silica matrices. This wavelength tuning seems to be an effective technique to optimize the nonlinear optical effects.

On the other hand, metal-dionedioxime complexes show a strong absorption band due to the *d-p* transition in the visible region. Their optical nonlinearity was revealed to be enhanced by the three-photon resonance at the *d-p* transition band. However, such a large absorption band leads the optical signal loss and prevents to show effective properties. As the *d-p* transition band originates in the metal-metal interaction in the linear metal chains, introduction of hetero-atoms into metal chain is likely effective to change the absorption wavelength. Basu et al.[4] reported that true binary mixed crystal of nickel, palladium and platinum complexes with dimethylglyoxime could be obtained by crystallization from the solution of their mixture. In this study, we examined to make a thin film of one-dimensional metal complexes in which hetero metals are incorporated into the linear metal chain and tune the *d-p* transition wavelength for optimization of the optical condition. Their third-order nonlinear optical property was investigated by third-harmonic generation (THG) measurements. The nonlinear optical efficiency was discussed in relation to the effect of alloying of linear metal chains.

EXPERIMENTAL

Chemical structure of bis(dimethylglyoximato)metal(II) ($M(dmg)_2$: M=Ni, Pd, Pt) is shown in Figure 1. $M(dmg)_2$ was prepared by mixing the hot aqueous-ethanol solution containing stoichiometric amounts of dimethylglyoxime and metal salts. High purity nickel acetylacetonate, palladium chloride and potassium chloroplatinate were used without further purification. The obtained precipitates were collected by filtration, washed with hot-water and ethanol, and dried under vacuo. The final products were purified by repeated recrystallization from the dimethylformamide solution. Thin films were prepared by conventional vacuum-evaporation onto a fused silica glass substrate at room temperature. Calculated amounts of $Pt(dmg)_2$ and $Pd(dmg)_2$ or $Ni(dmg)_2$ were mechanically mixed and reduced into powder in a mortar. Mixture was put into a heating boat and simultaneously evaporated onto a solid substrate. Heating temperature was ca. 200 °C at 10^{-4} Pa. The film thicknesses, measured with a Tencor Alpha-step 300 surface profilometer, were from 0.1 to 0.2 μm. X-ray diffraction patterns were obtained by a Mac Science MXP-18 diffractometer with the use of Cu-Kα radiation. Absorption spectra of sample films were recorded on a Shimadzu UV-3100 spectrophotometer in the wavelength range 200-2500 nm.



M = Ni, Pd, Pt

FIGURE 1 Chemical structure of $M(dmg)_2$.

Third-order nonlinear optical properties were estimated by the THG Maker-fringe technique.[2] THG measurements were carried out between 1.5 and 1.8 μm of the fundamental wavelength with wavemixing of a Q-switched Nd:YAG laser and a tunable dye laser. Third-order nonlinear susceptibility $\chi^{(3)}$ was calculated by the same procedure with that reported elsewhere.[2] The value of $\chi_s^{(3)} = 2.8 \times 10^{-14}$ esu for fused silica glass was used as the standard reference.[5]

RESULTS AND DISCUSSION

Vacuum evaporation of mixture of $Pd(dmg)_2$ and $Pt(dmg)_2$ gave thin films with optical quality. Color of them altered depending on the mixing ratios. X-ray diffraction patterns were measured for respective sample films. Sharp diffraction lines were observed at 2θ = 9.90, 19.86 and 30.02° for a pure $Pd(dmg)_2$ film, and at 9.88, 19.85 and 29.98° for a pure $Pt(dmg)_2$ film. It has been known that $Ni(dmg)_2$, $Pd(dmg)_2$ and $Pt(dmg)_2$ crystallize in the orthorhombic system with almost same unit cell constants (Table I). Obtained diffraction lines were composed of (110), (220) and (330) reflections for both $M(dmg)_2$, respectively. It indicated that the $M(dmg)_2$ molecules were highly ordered in the film and mainly arranged as the stacking axis (*c*-axis) was parallel to the substrate surface. Almost same diffraction patterns were obtained for evaporated films of mixture with any mixing ratios. Each (nn0) reflection appeared as a sharp and strong line. This means that the mixture was well ordered in the film and their crystal structures were almost same with that of original $M(dmg)_2$.

TABLE I Unit cell constants of $Ni(dmg)_2$, $Pd(dmg)_2$ and $Pt(dmg)_2$.

	[A] $Ni(dmg)_2$	[B] $Pd(dmg)_2$	[B] $Pt(dmg)_2$
a (Å)	16.68	16.76	16.82
b (Å)	10.44	10.50	10.56
c (Å)	6.49	6.50	6.51
M-M (Å)	3.25	3.25	3.25

[A]: ref 7, [B]: ref 8.

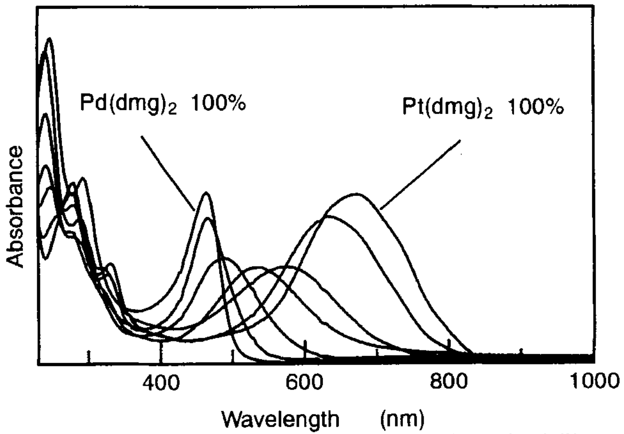


FIGURE 2 Absorption spectra of the deposited film of mixture of $Pd(dmg)_2$ and $Pt(dmg)_2$ with different mixing ratios.

Figure 2 shows absorption spectra of the evaporated films of Pd(dmg)$_2$ and Pt(dmg)$_2$ mixture with different mixing ratios. A strong absorption band appeared in the visible region for respective samples. Its peak wavelength varied between 465 and 680 nm in proportion to the mixing ratio. On the other hand, 248, 280, 292 and 408 nm bands appeared in the UV region. While their peak wavelengths were almost independent of the metal mixing ratio, their intensities showed dependency on the mixing ratio. The 248 and 292 nm bands increased their intensities with increase of the palladium ratio, and the 280 and 408 nm bands increased their intensities with increase of the platinum ratio. It has been known that Pd(dmg)$_2$ has strong absorption bands at 250, 290 and 465 nm, those are assigned to the π–π^* transition of ligands, the metal-ligand charge transfer transition and the *d-p* transition of metals, respectively, and Pt(dmg)$_2$ has corresponding bands at 280, 410 and 680 nm.[6] Therefore, it can be known that the wavelength of intermolecular transition was sensitive to the metal-complexes mixing, but intramolecular transition hardly occur the wavelength shifts by the metal mixing.

As reference, a Pt(dmg)$_2$ film and a Pd(dmg)$_2$ film were alternatively deposited on a glass substrate. Figure 3 shows an absorption spectrum of the alternatively deposited film. Strong absorption bands appeared at 467 and 676 nm independently. These peak wavelengths were well coincident with those of the *d-p* transition band of pure Pd(dmg)$_2$ and Pt(dmg)$_2$, respectively. It indicates that the 465 and 680 nm bands should appear in the spectrum independently if both metal complexes are completely separated in the deposited film. The *d-p* transition band is known to originate in the metal-metal interaction.[6] If the molecules are completely isolated in the film without metal-metal interaction, the *d-p* transition band should not appear in the spectrum. Therefor, the appearance of a strong absorption band in the visible region, of which wavelength differed from that of pure M(dmg)$_2$, indicated that some types of metal-metal interaction occurred in the deposited film.

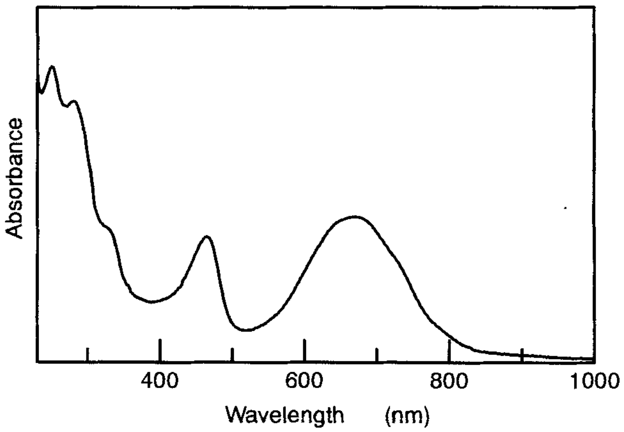


FIGURE 3 Absorption spectrum of the alternatively deposited film of Pt(dmg)$_2$ and Pt(dmg)$_2$.

From the X-ray diffraction and absorption spectroscopic analysis, it can be concluded that linear chains of metal-complexes were formed by mixture of palladium and platinum ions and palladium-platinum interactions occurred in the metal chains. It made possible to tune the *d-p* transition wavelength subsequently in proportion to the mixing ratio. Similar wavelength tunability was observed for the mixture of Ni(dmg)$_2$ and Pt(dmg)$_2$. In Figure 4, the *d-p* transition wavelength was plotted against the platinum ratio in the deposited film with nickel and palladium complexes.

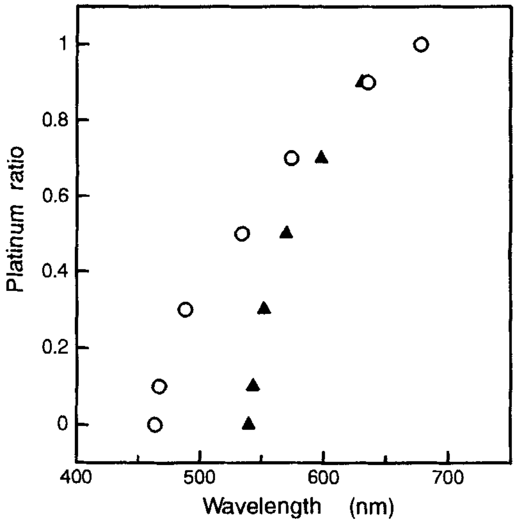


FIGURE 4 Dependence of peak wavelength on the platinum constituent ratios in the film. Circle: Pd(dmg)$_2$ and Pt(dmg)$_2$ mixture. Triangle: Ni(dmg)$_2$ and Pt(dmg)$_2$ mixture.

It has been demonstrated that alloying of metals forming linear chains in a deposited film is easily achieved by vacuum evaporation of mixture of two different metal complexes. Although the lengths of *a* and *b* axis are slightly different, nickel, palladium and platinum complexes crystallize with almost same unit cell constants as shown in Table I. This may be a reason why central metals consisting linear metal chains can be easily replaced by another metal and the complexes form alloyed linear metal chains.

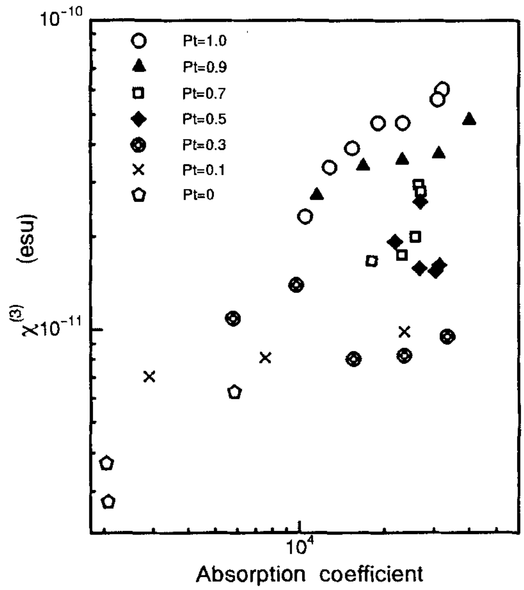


FIGURE 5 The $\chi^{(3)}$values plotted against α at the corresponding third harmonic wavelength for mixture of Pd(dmg)$_2$ and Pt(dmg)$_2$ with different mixing ratios.

Third-order nonlinear optical property of the evaporated thin films consisting of alloyed linear metal chains has been investigated by THG measurements. The wavelength dependence of the $\chi^{(3)}$ value was investigated for each sample film. They had strong metal-metal interaction and showed an absorption band due to the *d-p* transition in the visible region. The $\chi^{(3)}$ values were getting larger with increase of the *d-p* transition absorption intensity for respective samples. The largest $\chi^{(3)}$ value was observed at near absorption peak wavelength. These were attributed to the three-photon resonance effect. In order to compare the nonlinear optical activity under the resonance condition among the sample films, the $\chi^{(3)}$ values are plotted against linear absorption coefficients α in Figure 5. The $\chi^{(3)}$ values are usually dependent on the α. However, the film with higher platinum ratio tended to show larger $\chi^{(3)}$ values at the same α value. The remarkable difference of the molecular orientation could not be observed for respective sample films according to the X-ray diffraction analysis. Thus, it can be said that such a difference of $\chi^{(3)}$ values was caused by nonlinear optical activity of samples. In a previous paper,[2] we have suggested that platinum complexes have higher nonlinear optical activity than nickel and palladium complexes. Therefor, the mixing of metal with poor nonlinear activity into the metal chains induced the reduction of the nonlinear activity of the sample.

CONCLUSION

It has been demonstrated that simultaneous vacuum evaporation of mechanically mixed two different metal complexes with dimethylglyoxime gave a thin film of mixture in which linear metal chains were alloyed with hetero metal ions. Alloying the metal chain brought tunability of the strong *d-p* transition wavelength between those of pure metal complexes. The third-order nonlinear optical property of them was also investigated by THG measurements. The $\chi^{(3)}$ values were enhanced by three-photon resonance at the *d-p* transition band. However, the activity of the optical nonlinearity was dependent upon the mixing ratios. The more platinum ions were incorporated in a film, the higher optical nonlinearity could be obtained. Although alloying of linear metal chains are useful to optimize the nonlinear optical conditions with less absorption, they don't always show high nonlinear optical efficiency. Further investigations are required to improve this point.

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