

## Photochemical Studies of Bipyridyl/ $\gamma$ -Picoline Adduct of bis-(4,5-Dimethyl-1,3,2-dioxaphospholane-2-thione-2-thiolato) nickel (II) under Photoirradiation, Part-III†

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On irradiation with visible light six coordinated octahedral bipyridyl adduct of nickel(II) bis-(O,O-butylene dithiophosphate) is converted into five coordinated trigonal-bipyramidal complex. Four coordinated nickel(II) bis-(O,O-butylene dithiophosphate) on reaction with bipyridyl under photo-irradiation forms five coordinated complex again. In contrast to the above, four coordinated bis-(O,O-butylene dithiophosphate) nickel(II) on reaction with  $\gamma$ -picoline under photoirradiation forms six coordinated complex.

**Key Words:** Photochemical, Bipyridyl/ $\gamma$ -picoline, Adduct, Ni(II) complex.

### INTRODUCTION

Photochemical isomerization and photoracemization of chromium, iron and cobalt complexes have been investigated intensively.<sup>1–3</sup> Literature survey reveals that the photochemical switching from one geometry to another has not been explored. The flexible geometry in few examples of transition metal complexes of alkylene dithiophosphates<sup>4,5</sup> prompted us to investigate the photochemical reactions of alkylene dithiophosphates. In continuation to our earlier work<sup>6,7</sup> we report hereby the photochemical studies of six coordinated bipyridyl adducts of bis-(O,O-butylene dithiophosphate) of nickel(II); its formation under photo-irradiation by the reaction of four coordinated nickel(II) bis-(O,O-butylene dithiophosphate) with 2,2'-bipyridyl and its comparison with  $\gamma$ -picoline adduct formation by the reaction of nickel(II) bis-(O,O-butylene dithiophosphate) and  $\gamma$ -picoline under photoirradiation.

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To avoid the cumbersome IUPAC names of the complexes, the trivial name nickel(II) bis-(O,O-butylene dithiophosphate) has been used throughout the script.

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## EXPERIMENTAL

Nickel(II) bis-(O,O-butylene dithiophosphate) and its adduct with bipyridyl were prepared by the methods reported earlier.<sup>8,9</sup> 2,2'-Bipyridyl from E. Merck was used as received without further purification. 0.001 M solution of the bipyridyl adduct of nickel(II) bis-(O,O-butylene dithiophosphate) was prepared in  $\text{CHCl}_3$  in a 100 mL volumetric flask, which was kept as such under irradiation to check the evaporation. For the reaction under photoirradiation 0.01 M solution of nickel(II) bis-(O,O-butylene dithiophosphate) and 0.01 M solution of bipyridyl, after irradiation for 30 min separately, were mixed together. The solution turned violet to green which indicates the formation of bipyridyl adduct. For the formation of  $\gamma$ -picoline adduct of bis-(O,O-butylene dithiophosphate) of nickel(II) under photoirradiation,  $\gamma$ -picoline (in excess) in  $\text{CHCl}_3$  and 0.01 M solution of bis-(O,O-butylene dithiophosphate) of nickel(II) were mixed after irradiating them separately for 30 min.

Irradiation was done from a Philips halogen tube of 500 W. To remove the thermal radiations light was passed through a water jar, kept between the light source and the sample. IR-spectra in the range  $4000\text{--}400\text{ cm}^{-1}$  were recorded on a Perkin Elmer Spectrum GX FTIR spectrometer. Electronic spectra were recorded on a Cary-17-D model and with Systronics UV/visible spectrophotometer- 118.  $^{31}\text{P}$  NMR spectra were recorded on Jeol-FX-2100 spectrometer.

## RESULTS AND DISCUSSION

On photo-irradiation with visible light the six-coordinated octahedral bipyridyl adduct is converted into five-coordinated trigonal-bipyramidal complex. Before exposure to the visible light the electronic spectrum of octahedral complex shows two bands at 1120 and 620 nm which are very near to the values reported earlier.<sup>10</sup> To observe the change in geometry the band at 620 nm was taken as a standard. After 2 h of exposure the band at 620 nm was shifted towards a higher wavelength at 630 nm and shifted to 645 nm after 4 h of irradiation. After 6 and 8 h of exposure the bands were shifted to 660 and 670 nm respectively. After 8 h a new band appeared at 435 nm. After exposure of 10 h the band at 670 nm was shifted to 675 nm and another band which appeared at 435 nm after exposure of 8 h remained as such. On further exposure for 4 h the spectrum does not indicate any change in the position of bands and the presence of only two bands at 675 nm and 435 nm indicates the presence of five coordinated species only.<sup>5, 11, 12</sup> Even addition of some extra 2,2'-bipyridyl solution (after irradiation) also does not alter the spectra on exposure for further 2 h. All the above spectra have been depicted in Fig. 1.

To observe the change in the rate of photochemical reaction by changing the intensity of light, the samples were kept at 10, 14 and 18 inches distances. It was observed that the rate of formation of five-coordinated complex increases by increasing the light intensity. The data have been depicted in Fig. 2.

The photochemical formation of five-coordinated compound is further established by starting from the four-coordinated square-planar complex of nickel(II) bis-(O,O-butylene dithiophosphate). The initial spectrum of the square-planar

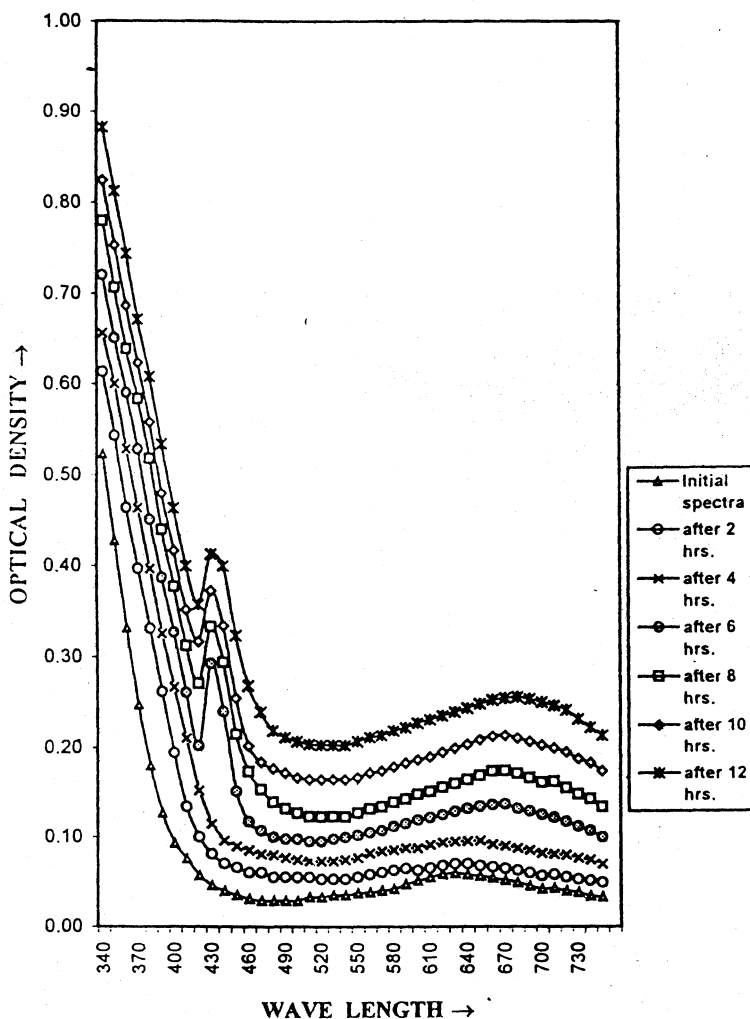


Fig. 1 Wavelength v/s O.D. with respect to time

complex shows three bands at 690, 520, 390 nm which are very near to the values reported earlier.<sup>8,9</sup> On addition of 0.01 M solution of 2,2'-bipyridyl (which was already exposed for 30 min) was added in the 0.01 M irradiated (for 30 min) solution of square-planar complex in equal volume, the solution turned violet to green indicating the formation of the adduct. After addition the mixed solutions were irradiated for 2 h. After 2 h of exposure the band at 690 nm in the original spectra were shifted to 680 nm; and the bands at 520 nm was shifted to 500 nm, the band at 390 nm in the original spectra disappeared and a new band at 430 nm appeared. After 4 h of exposure the band at 680 nm was shifted to 675 nm and the band at 500 nm disappeared. The band at 430 nm, which appeared after the exposure of 2 h was shifted to 435 nm. After further exposure the spectrum does

not exhibit any change and the presence of two bands, one at 675 nm and other at 435 nm, confirms again the presence of five-coordinated Ni(II) complex.<sup>5, 11, 12</sup>

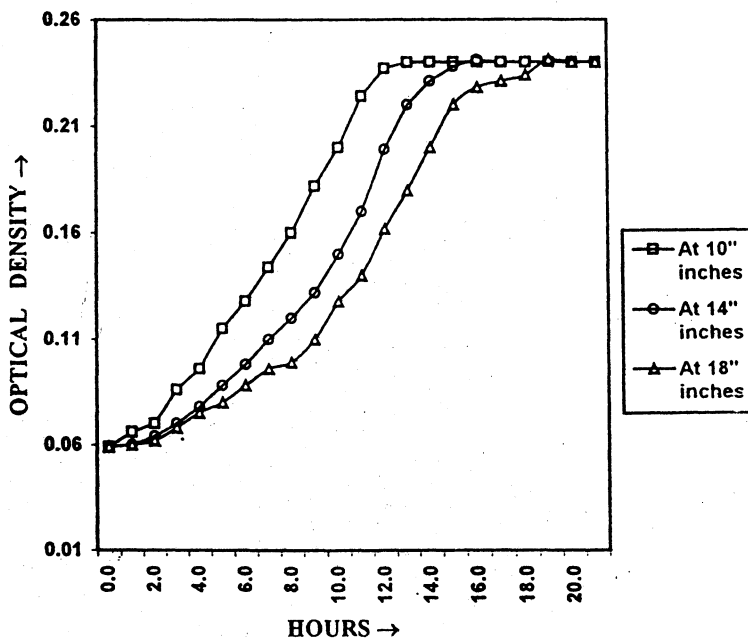


Fig. 2 Effect of light intensity

Formation of five-coordinated complex under irradiation of visible light has also been confirmed by IR and  $^{31}\text{P}$  NMR. In IR-spectra in addition to the absorption at  $670\text{ cm}^{-1}$ , a new band appears at  $720\text{ cm}^{-1}$  which also appears in free butylene dithiophosphoric acid and their salt<sup>13</sup>, which confirms the presence of  $>\text{P}=\text{S}$  moiety, which is possible only in the five-coordinated compound.

$^{31}\text{P}$  NMR spectrum of the above adduct shows only one peak at 128 ppm, which is very near to the value reported earlier.<sup>10</sup> Considering the five coordinated complex formation, after exposure of visible light, two peaks were expected, one for the phosphorus of bidentate dithiophosphate moiety and another for monodentate dithiophosphate moiety. But it has been reported earlier that due to the fast exchange between mono and bidentate dithiophosphate moieties, it is not possible to observe two different peaks at room temperature.<sup>4</sup> Considering the above fact the  $^{31}\text{P}$  NMR spectrum of the above adduct was recorded at low temperature. At  $60^\circ\text{C}$  the presence of two different peaks, one at 122 ppm and other at 130 ppm, confirms the five-coordinated complex formation after exposure of visible light (Fig. 3).

Distorted trigonal-bipyramidal geometry may be assigned on the basis of the observations made earlier<sup>6</sup> as well as on the basis of its analogous 2,9-dimethyl-1,10-phenanthroline adduct of bis-(4,4,5,5-tetramethyl-1,3,2-dioxaphospholane-2-thione-2-thiolato) nickel(II).<sup>5</sup> Out of the four sulphur atoms of two

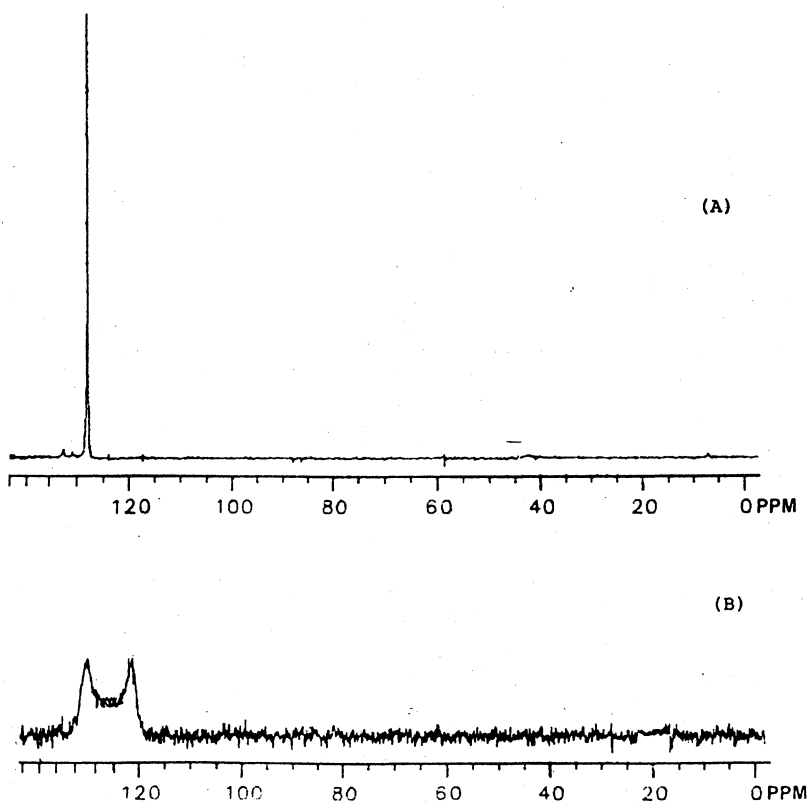
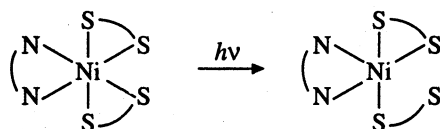


Fig. 3  $^{31}\text{P}$  NMR Spectra of bipyridyl adduct of bis-(O,O-butylene dithiophosphato) nickel(II) (A) at room temperature (B) at  $60^\circ\text{C}$

dithiophosphate moieties, three are bonded to the central nickel atom showing unidentate behaviour of one of the dithiophosphate moieties and bidentate behaviour of the other.



To compare the photochemical studies of heterocyclic ditertiary amine adducts with monodentate heterocyclic tertiary amine adducts, formation of the  $\gamma$ -picoline adduct of nickel(II) bis-(O,O-butylene dithiophosphato) was investigated photochemically. Photochemical study of isolated  $\gamma$ -picoline adduct of nickel(II) complex was not possible as it dissociates immediately in halocarbons ( $\text{CHCl}_3/\text{CH}_2\text{Cl}_2$ ).

To observe the effect of light on the geometry of the complex, 0.01 M solution

of nickel-(II) bis-(O,O-butylene dithiophosphate) was irradiated for 30 min. Excess  $\gamma$ -picoline (than required) in  $\text{CHCl}_3$  was also irradiated for 30 min. Both the solutions after mixing were further irradiated. Before exposure to the visible light the electronic spectrum of the square-planar complex shows three bands at 690, 520 and 390 nm which are very near to the values reported for four coordinated complex.<sup>8,9</sup> After exposure for 1 h the spectrum does not show any change. Excess  $\gamma$ -picoline (than required) in  $\text{CHCl}_3$  was irradiated for 30 min. Both the above solutions after mixing were irradiated further for 2 h. After 2 h of exposure the band at 690 nm was shifted to 675 nm and another band at 430 nm appeared. After 4 h of exposure the band at 675 nm was shifted towards 670 nm and the band at 430 nm remained as such. After irradiation of 6 and 8 h the bands were shifted to 660 nm and 650 nm respectively and the band at 430 nm disappeared. After exposure of 10 h the band at 650 nm was shifted to 630 nm and after exposure of further 2 h the spectrum does not indicate any change in the position of bands and the presence of only one band at 630 nm indicates the presence of six-coordinated species only.<sup>4,5</sup>

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