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Photochemical Studies of Isolated Phenanthroline Adduct of Bis(4,4,6-trimethyl-1,3,2-dioxaphosphorinane-2-thione-2-thiolato) Nickel(II), its Formation under Photo-irradiation and Formation of β and γ-Picoline Adducts of Bis(4,4,6-trimethyl-1,3,2-dioxaphosphorinane-2-thione-2-thiolato) Nickel(II) under Photoirradiation. Part-IV

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On irradiation with visible light six coordinated octahedral phenanthroline adduct of nickel(II) bis(O,O-hexylene dithiophosphate)‡ is converted into five coordinated trigonal-bipyramidal complex. Four coordinated nickel(II) bis(O,O-hexylene dithiophosphate) on reaction with phenanthroline under photo-irradiation forms five-coordinated complex again. In contrast to the above, four-coordinated bis(O,O-hexylene dithiophosphate) nickel(II) on reaction with β and γ-picolines under photo-irradiation forms six-coordinated complexes.

Key Words: Photochemical, Phenanthroline, Adducts, Picolines, Nickel(II).

INTRODUCTION

The studies of photochemical reactions are restricted to photoisomerization and photoracemization[1–3], except some recent studies on multimetallic and macromolecular inorganic photochemistry[4]. The flexible geometry in a few examples of transition metal complexes of alkylene dithiophosphates[5, 6] prompted us to investigate the photochemical reactions of hexylene dithiophosphates. In continuation of our earlier photochemical studies of alkylene dithiophosphates of nickel(II) containing mono and bidentate nitrogen donor ligands[7–10], we report hereby the photochemical studies of six-coordinated phenanthroline adduct of bis(O,O-hexylene dithiophosphate) of nickel(II) and its formation under photo-irradiation by the reaction of four-coordinated nickel(II) bis(O,O-hexylene dithiophosphate) with 1,10-phenanthroline and its comparison with β and γ-picoline adducts formation, by the reaction of nickel(II) bis(O,O-hexylene dithiophosphate), under photo-irradiation.

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‡To avoid the cumbrous IUPAC name of the complex, trivial name nickel(II) bis(O,O-hexylene dithiophosphate) has been used throughout the script.

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EXPERIMENTAL

Nickel(II) bis(O,O-hexylene dithiophosphate) and its adduct with phenanthroline were prepared by the reported method[11–13]. 1,10-Phenanthroline from *E.* Merk was used as received without further purification. 0.01 M solution of the phenanthroline adduct of nickel(II) bis(O,O-hexylene dithiophosphate) was prepared in $CHCl_3$ in a 100 mL volumetric flask, which was kept as such under irradiation to check the evaporation. For the reaction under photo-irradiation 0.01 M solution of bis(O,O-hexylene dithiophosphate) and 0.01 M solution of phenanthroline, after irradiation for 30 min separately, were mixed together. The solution turned violet to green which indicates the formation of phenanthroline adduct. For the formation of β and γ-picoline adducts of bis(O,O-hexylene dithiophosphate) of nickel(II) under photo-irradiation, β and γ-picolines (in excess) in $CHCl_3$ and 0.01 M solution of bis(O,O-hexylene dithiophosphate) of nickel(II) were mixed after irradiating them separately for 30 min.

Irradiation was done from a Philips halogen tube of 500 watt. To remove the thermal radiations light was passed through a water jar, kept between light source and the sample. IR spectra in the range 4000–400 cm^{-1} were recorded on a Perkin-Elmer Spectrum GX, FT-IR spectrometer. Electronic spectra were recorded on a Cary-17-D model and with Systronics UV/Vis spectrophotometer-118. ^{31}P NMR spectra were recorded on Jeol-FX-2-100 spectrometer.

RESULTS AND DISCUSSION

Six-coordinated octahedral phenanthroline adduct is converted into five-coordinated trigonal-bipyramidal complex, on irradiation with visible light. Before exposure to the visible light the electronic spectrum of octahedral complex shows two bands at 1100 nm and 630 nm which are very near to the values reported earlier[13]. To observe the change in geometry the band at 630 nm was taken as a standard. After 2 h of exposure the band at 630 nm was shifted towards a higher wavelength at 635 nm and 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 430 nm. After exposure for 10 h the band at 670 nm was shifted to 680 nm and another band which appeared at 430 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 680 and 430 nm indicates the presence of five-coordinated species only[6, 14, 15]. Even addition of some extra phenanthroline solution (after irradiation) also doesn't 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 the five-coordinated complex increases by increasing the light intensity. The observations have been depicted in Fig. 2.

The photochemical formation of five-coordinated compound is further established by starting from four-coordinated square-planar nickel(II) bis(O,O-

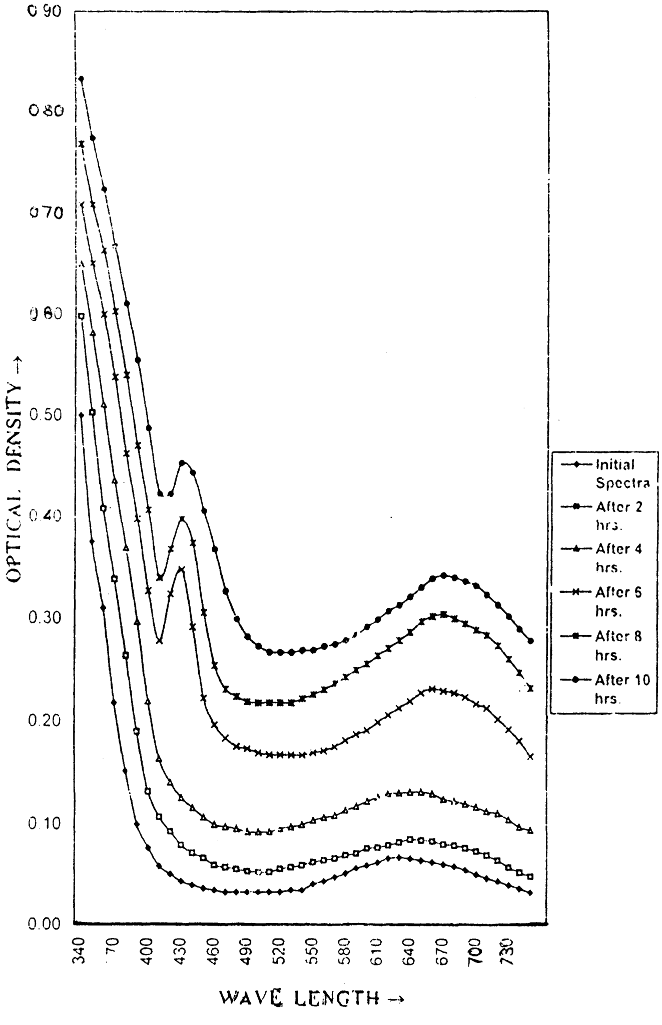


Fig. 1. Wavelength *vs.* O.D. with respect to time

hexylene dithiophosphate). The initial spectrum of square planar complex shows three bands at 696, 528, 394 nm, which are very near to the values reported earlier[11, 12]. 0.01 M solution of phenanthroline (which was already exposed for 30 min) was added to the 0.01 M irradiated (for 30 min) solution of square-planar complex in equal volume. After addition mixed solutions were irradiated for 2 h. After 2 h of exposure the band at 696 nm in the original spectrum was shifted to 685 nm and the band at 528 nm was shifted to 510 nm; the band at 394 nm in the original spectrum disappeared and a new band at 440 nm appeared. A band which appeared at 440 nm after 2 h was shifted to 430 nm. The spectrum does not show any change after further exposure and the presence of only two bands at 680 and 430 nm confirms the presence of five-coordinated Ni(II) complex.

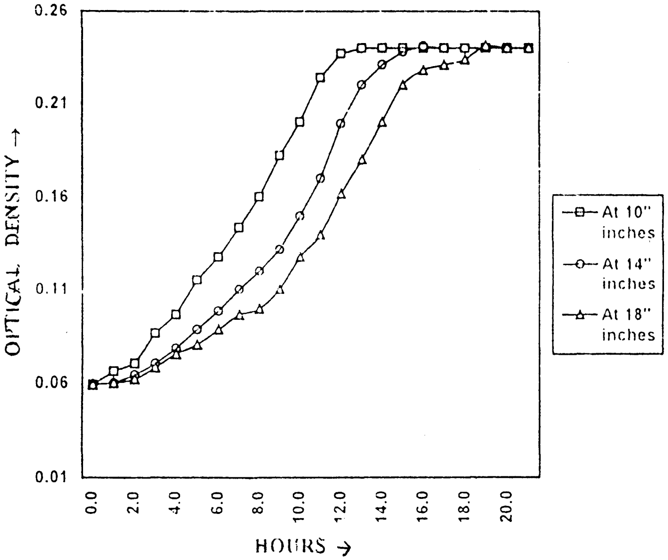


Fig. 2. Effect of light intensity

Formation of five-coordinated complex under irradiation of visible light has also been confirmed by IR and ^{31}P NMR. In IR spectra, in addition to the absorption at 670 cm^{-1}, a new strong band appears at 715 cm^{-1} also appears in free hexylene dithiophosphoric acid and their salt[16], confirming the presence of >P =S moiety. The presence of this band is only possible in five-coordinated compound.

The ^{31}P NMR spectrum of the above adduct shows only one peak at 107 ppm, which is very near to the value reported earlier[13]. 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[5]. In view of the above fact the ^{31}P NMR spectrum of the adduct was recorded at low temperature. At –40°C the presence of two different peaks, one at 106 and another at 110 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 as well as, on the basis of its analogous 2,9-dimethyl-

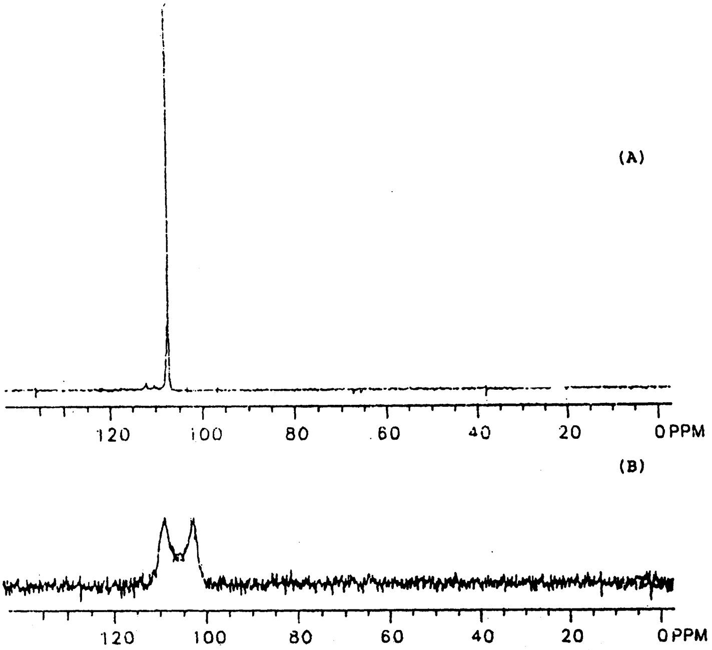
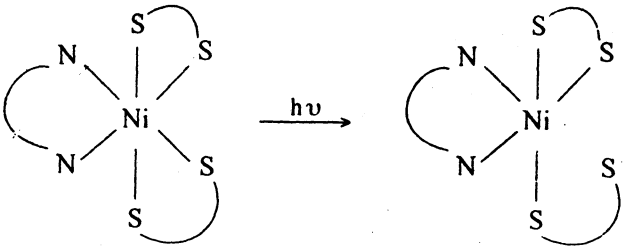


Fig. 3. ^{31}P NMR spectra of phenanthroline adduct of bis(O,O-hexylene dithiophosphato) nickel(II) (A) at room temperature (B) At –40°C

1,10-phenanthroline adduct of bis(4,4,5,5-tetramethyl-1,3,2-dioxaphospholane-2-thione-2-thiolato) nickel(II).[6] Out of the four sulphur atoms of two dithiophophate 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 γ-picoline adduct of nickel(II) bis(O,O-hexylene dithiophosphate) was investigated photochemically. Photochemical study of isolated γ-picoline adduct of nickel(II) complex was not possible as it dissociated immediately into halohydrocarbons ($CHCl_3/CH_2Cl_2$).

To observe the effect of light on the geometry of the complexes, 0.01 M solution of bis(O,O-hexylene dithiophosphate) was irradiated for 30 min. Excess picoline in $CHCl_3$ 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 earlier[11, 12]. After exposure for 1 h the spectra does not show any change. Excess γ-picoline in $CHCl_3$ was irradiated for 30 min. Both the above solutions after mixing were irradiated for further 2 h. After 2 h of exposure the band of 690 nm was shifted to 680 nm and another band at 430 nm appeared. After 4 h of exposure the band at 680 nm was shifted towards 670 nm and the band at 430 nm remains as such. After irradiation of 6 and 8 h the bands shifted to 665 nm and 645 nm respectively and the band at 430 nm disappeared. After exposure of 10 h the band at 645 nm shifted to 630 nm and after exposure for 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[11, 12].

An attempt has been made to compare the formation of β-picoline adduct under the same conditions. 0.01 M solution of bis(O,O-hexylene dithiophosphate) was irradiated for 30 min. Excess β-picoline in $CHCl_3$ 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 695, 520 and 390 nm which are very near to the values reported earlier[11, 12]. After exposure for 1 h the spectrum does not show any change. Excess β-picoline (than required) in $CHCl_3$ was irradiated for 30 min. Both the above solutions after mixing were irradiated for further 2 h. After 2 h of exposure the band of 690 nm was shifted to 680 nm and another band at 430 nm appeared. After 4 h of exposure the band at 680 nm 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 and 650 nm respectivly and the band at 430 nm disappeared. After exposure of 10 h the band at 650 nm was shifted to 640 nm and after 12 h the band at 640 nm shifted to 630 nm. After exposure for a further 2 h the presence of only one band at 630 nm indicates the presence of six-coordinated species only[5, 6].

The above observations confirm that complexes containing bidentate nitrogen donor ligands lead to the formation of five-coordinated complex under photo-irradiation. However, identical observations of β and γ-picoline adducts, containing monodentate nitrogen donor ligands, reflect the formation of six coordinated species only under photo-irradiation.

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