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Note

THERMAL STUDIES ON THE ADDUCTS OF NICKEL(II) DITHIOPHOSPHATE AND DITHIOPHOSPHINATE WITH NITROGEN DONORS

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Spectroscopic and magnetic studies of the adducts of nickel(II) dithiophosphate and dithiophosphinate with nitrogen donors were reported earlier [1]. It was observed that the change in the substituent on the phosphorus atom of dithiophosphate and dithiophosphinate was accompanied by changes in the spectral parameters. Moreover, the nature of the adducts formed by the diamagnetic NiS_4 core was influenced by the steric requirements of the donors. Therefore it was of interest to investigate the thermal stability of the adducts of bis[di(2-methyl-5-chlorophenyl) dithiophosphinato] nickel(II), $Ni(MeCldtpi)_2$ and bis(dimethyldithiophosphato) nickel(II), $Ni(Me_2dtp)_2$, with heterocyclic nitrogen donors of different steric requirements.

EXPERIMENTAL

The dithio-ligands and the complexes were prepared as described earlier [1]. The thermograms of the complexes were recorded on a MOM derivatograph (Hungary), maintaining a heating rate of 5°C min^{-1}.

RESULTS AND DISCUSSION

From the combined TG, DTG and DTA curve of the 3-picoline diadduct (Fig. 1), it is observed that there is a stepwise loss of the nitrogen donor [the DTG curve has two well-defined minima at 120°C and 180°C for

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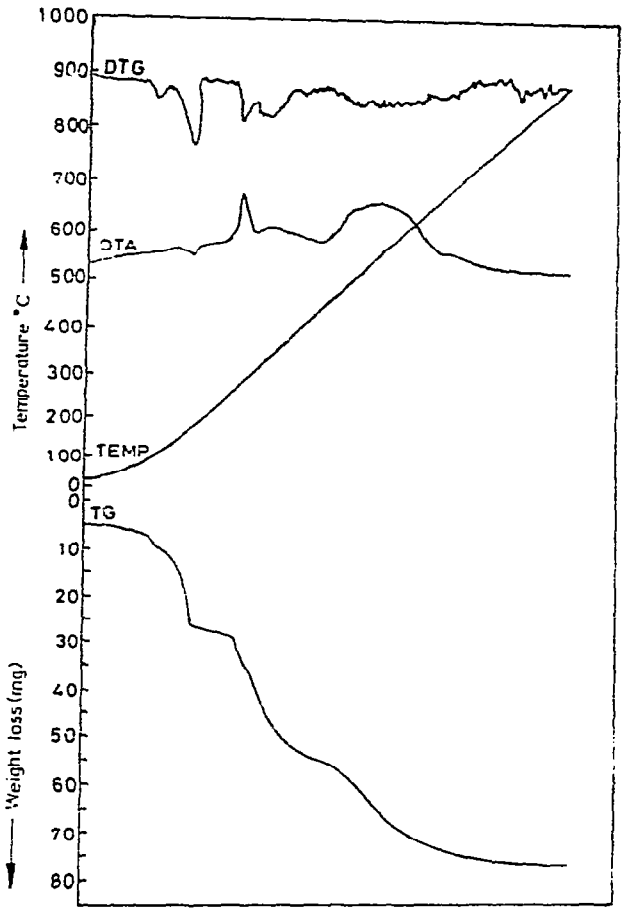

Fig. 1. TG, DTA and DTG curves of $Ni(MeCldtpi)_2(3\text{-picoline})_2$.

$Ni(Me_2dtp)_2(3\text{-pic})_2$, and at 160°C and 250°C for $Ni(MeCldtpi)_2(3\text{-pic})_2$ systems], indicating the existence of $Ni(MeCldtpi)_2(3\text{-pic})$ or $Ni(Me_2dtp)_2(3\text{-pic})$ which is unstable and decomposes rapidly to the parent complex, in agreement with the equilibrium constant studies by Carlin and Losee [2] for the $Ni(Et_2dtp)_2$ and 3-picoline system. The 2-picoline adducts showed only a one-step decomposition around 111°C, followed by decomposition of the parent complex. This lower decomposition temperature for the 2-picoline monoadducts agrees well with the reported [2] low formation constant and is due to steric hindrance by the methyl group at the 2-position of the pyridine ring.

Using the thermogravimetric data, the activation energy of decomposition of these complexes was evaluated by adopting Freeman and Carroll's technique [3]. The relationship between the weight change, temperature and

activation energy is given by

$$\frac{(-E^*/2.3\ R)\Delta(T^{-1})}{\Delta \log W_r} = X + \frac{\Delta \log dw/dt}{\Delta \log W_r}$$

where, $W_r = W_e - W$, W_e = weight at the completion of the reaction, W = total weight loss at time t, and R = gas constant (1.9872 kcal mole^{-1})

Calculation of the activation energy (E^*) from the above equation consists of the following steps:

(a) plot of weight loss (W) against time (t), the slope of which gives dw/dt;

(b) plot of $\log dw/dt$ against $\log W_r$ at the points corresponding to curve (a), the slope of which gives $(\Delta \log dw/dt)/(\Delta \log W_r)$

(c) plot of T^{-1} against $\log W_r$ at the points corresponding to curve (a), the slope of which gives $\Delta T^{-1}/\Delta \log W_r$;

(d) finally, plot of $(\Delta \log dw/dt)/(\Delta \log W_r)$ against $\Delta T^{-1}/\Delta \log W_r$, the slope of which gives $E^*/2.3\ R$ wherefrom the activation energy can be calculated.

The values of activation energy for the first and second steps of the decomposition of $Ni(MeCldtpi)_2(3\text{-pic})_2$ were 14.13 and 41.08 kcal mole^{-1}, respectively, while for $Ni(Me_2dtp)_2(3\text{-pic})_2$ the corresponding values were 11.23 and 21.93 kcal mole^{-1}, respectively. This difference in activation energy for these two systems may be an indication that dithiophosphinates form stronger adducts than dithiophosphate. X-Ray crystal structure data [4,5] also partially support this view; the Ni–N bond distances in pyridine diadducts of $Ni[(C_6H_5)_2PS_2]_2$ and $Ni[(C_6H_5O)_2PS_2]_2$ systems were found to be 2.08 and 2.11 Å, respectively. The activation energy of decomposition for the monoadducts of $Ni(MeCldtpi)_2$ and $Ni(Me_2dtp)_2$ with 2-picoline were comparatively low—of the order of 3.8 and 2.4 kcal mole^{-1}, respectively—which is not surprising, since even at room temperature these adducts decompose into the parent compounds on prolonged exposure to the atmosphere.

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