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Note

THERMOGRAVIMETRIC STUDIES ON THE ADDITION COMPOUNDS OF COBALT AND NICKEL DITHIOPHOSPHINATES WITH PICOLINES AND ACETYLPYRIDINES

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Magnetic and spectroscopic studies of the adducts of bis[di(2,4-dimethylphenyl)dithiophosphinato]cobalt(II) ($Co(2,4\text{-}Me_2dtpi)_2$) with pyridine type donors were reported in our earlier communication [1]. It was observed that the nature of the adducts formed with the CoS_4 core was influenced by the steric requirements of the donors. The activation energy calculations of the base decomposition process of $Co(2,4\text{-}Me_2dtpi)_2(py)$, $Co(2,4\text{-}Me_2dtpi)_2(\alpha\text{-pic})$, $Co(2,4\text{-}Me_2dtpi)_2(\beta\text{-pic})$ and $Co(2,4\text{-}Me_2dtpi)_2(\gamma\text{-pic})$ and of the addition compounds of cobalt and nickel .diphenyldithiophosphinates ($M(dtpi)_2$) with 2-, 3- and 4-acetylpyridine (2-, 3-, 4-Acpy) are discussed in this paper. In adddition, the data for the picoline adducts of cobalt are compared with the corresponding N-oxide values published elsewhere [2].

EXPERIMENTAL

The complexes were prepared as discussed earlier [1]. Thermogravimetric analysis was carried out up to 500 °C at a heating rate of 5 °C min^{-1} using a Shimadzu thermal analyser DT 30 with Al_2O_3 as reference compound.

RESULTS AND DISCUSSION

Thermal studies of addition compounds help us to understand the pattern of loss of the base molecules and aid in the determination of the activation energy required for their decomposition. From the TG curve (Fig. 1) it is observed that the decomposition of pentacoordinate adducts occurs in two steps. The base is lost first, followed by decomposition of the sulphur ligand to an unidentified black mass. In earlier studies [3,4] it was reported that the metal dialkyldithiophosphates, depending on the structure of the alkyl group and cation size, decompose thermally by an autocatalytic reaction to yield olefins, mercaptans, hydrogen sulphide and a polymeric residue.

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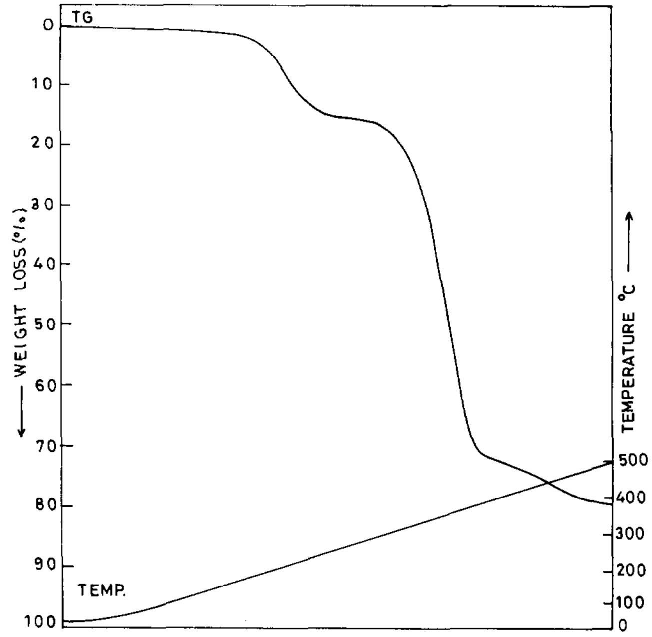

Fig. 1. TG curve of $Co(2,4\text{-}Me_2dtpi)_2(\gamma\text{-picoline})$.

From thermogravimetric data and by using the technique of Freeman and Carrol [5] the activation energy was calculated for the base decomposition process. The relationship between the weight change, temperature and activation energy is given by

$$\frac{-E^{\star}/(2.303R)\Delta T^{-1}}{\Delta \log W_r} = -x + \frac{\Delta \log(dw/dt)}{\Delta \log W_r}$$

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

The calculation of the activation energy $E^{\star}$ from the above equation consists of the following steps: (a) the weight loss w is plotted against time t and the slope of the curve gives dw/dt; (b) $\log(dw/dt)$ is plotted against $\log W_r$ at the points corresponding to curve (a) and the slope of the curve gives $[\Delta \log(dw/dt)]/\Delta \log W_r$; (c) T^{-1} is plotted against $\log W_r$ at the points corresponding to curve (a) and the slope of the curve gives $\Delta T^{-1}/\Delta \log W_r$; (d) finally, $[\Delta \log(dw/dt)]/\Delta \log W_r$ is plotted against $\Delta T^{-1}/\Delta \log W_r$ and the slope of the straight line gives $E^{\star}/2.303R$. The activation energy can then be calculated.

The values of activation energy for the first decomposition step of the compounds in this study and for the amine N-oxide complexes are given in Table 1. The difference in the activation energy values for picoline adducts indicate that the thermal stability of the complexes follows the order $Co(2,4\text{-}Me_2dtpi)_2(\gamma\text{-pic}) > Co(2,4\text{-}Me_2dtpi)_2(\beta\text{-pic}) > Co(2,4\text{-}Me_2dtpi)_2(\alpha\text{-}$

TABLE 1

Activation energy values for the complexes

Complex	Activation energy (kcal mol^{-1})
$Co(2,4\text{-}Me_2dtpi)_2(py)$	11.94
$Co(2,4\text{-}Me_2dtpi)_2(\alpha\text{-pic})$	16.71
$Co(2,4\text{-}Me_2dtpi)_2(\beta\text{-pic})$	19.13
$Co(2,4\text{-}Me_2dtpi)_2(\gamma\text{-pic})$	22.29
$Co(2,4\text{-}Me_2dtpi)_2(pyo)$ [a]	10.80
$Co(2,4\text{-}Me_2dtpi)_2(\alpha\text{-pico})$ [a]	12.87
$Co(2,4\text{-}Me_2dtpi)_2(\beta\text{-pico})$ [a]	15.42
$Co(2,4\text{-}Me_2dtpi)_2(\gamma\text{-pico})$ [a]	18.31
$Co(dtpi)_2(2\text{-Acpy})$	9.52
$Co(dtpi)_2(3\text{-Acpy})$	13.34
$Co(dtpi)_2(4\text{-Acpy})$	14.65
$Ni(dtpi)_2(2\text{-Acpy})$	2.95
$Ni(dtpi)_2(3\text{-Acpy})_2$	32.55
$Ni(dtpi)_2(4\text{-Acpy})_2$	34.44

[a] Data from ref. 2.

pic) > $Co(2,4\text{-}Me_2dtpi)_2(py)$. The basicity values of these ligands as judged by their log K values are in the order [6] pyridine (5.17) < β-picoline (5.63) < α-picoline (5.96) < γ-picoline (6.02). Although the basicity of α-picoline is greater than β-picoline, the activation energy of the α-picoline adduct is lower than that of the β-picoline adduct. This could be due to steric hindrance of the methyl group at the α-position. These complexes were found to have higher activation energies than their corresponding amine N-oxide analogues which indicates the stronger donor ability of the amines.

Activation energies have also been calculated for the adducts of cobalt and nickel diphenyldithiophosphinates with acetylpyridines. Although nickel forms 1 : 2 complexes with 3- and 4-Acpy, only one decomposition step was observed corresponding to the loss of two base molecules. The thermal stability of both cobalt and nickel compounds as given by their activation energy values follows the order 4-Acpy > 3-Acpy > 2-Acpy. This sequence may be explained by considering the basicity values of these donors which show a similar trend.

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