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CARBODITHIOATO DERIVATIVES OF WEAK NITROGENOUS NUCLEOPHILES. III. MASS SPECTRA AND THERMAL DECOMPOSITION KINETICS OF SOME NICKEL(II) AMIDE *N*-CARBODITHIOATES

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ABSTRACT

Mass spectral and thermal studies by TG analysis of $Ni[S_2CN(COR')R]_2$ complexes ($R = Me$, *i*-Bu, Ph, Bz; $R' = Me$, Ph) in a dynamic nitrogen atmosphere have been carried out to determine their modes of decomposition. Fragmentation patterns are given and possible mechanisms are discussed. All complexes show similar TG profiles. Mass loss considerations at the main decomposition steps indicate conversion of the nickel(II) amide *N*-carbodithioates to sulphides. Reaction orders were estimated by employing the Freeman–Carroll equation, and a kinetic analysis of TG data was performed using the Coats–Redfern equation to determine the apparent activation energies and the pre-exponential factor of the Arrhenius equation.

INTRODUCTION

Recent results from our laboratory [1] have demonstrated that, on reacting Ni(II) *N*-alkyldithiocarbamates, $Ni(S_2CNHR)_2$, with acetic anhydride or benzoyl chloride in the presence of triethylamine as a deprotonating agent, an electrophilic substitution reaction occurs to give the novel nickel(II) amide *N*-carbodithioates of general type $Ni[S_2CN(COR')R]_2$. The direct synthesis of such ligands by the reaction of the corresponding weak nitrogenous base or other nucleophiles with carbon disulphide in alkaline media is difficult or even impossible, although some examples for the formation of *N*-formyl- and *N*-methyl-*N*-formyl dithiocarbamates have already been reported [2,3]. The mechanism of this electrophilic substitution reaction at the level of the frontier molecular orbital approach of chemical reactivity has been fully investigated by IEHMO calculations [1,4]. According to these

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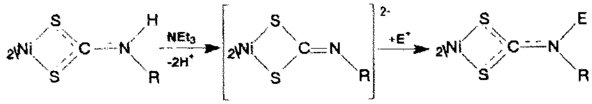


Scheme 1.

theoretical investigations, the acylation reaction of the bis(*N*-alkyldithiocarbamato)nickel(II) complexes proceeds via an S_E1 mechanism, involving $[Ni(S_2C{=}NR)_2]^{2-}$ complexes [5,6] as a transition state. Moreover, it has been demonstrated [7] that this reactivity pattern is a general synthetic route to carbodithioato derivatives of weak nitrogenous bases, such as ureas, carbamic esters and sulphonamides. Consequently, by using a wide diversity of electrophiles (E^+), new classes of carbodithioato complexes of the general formula $Ni[S_2CN(E)R]_2$, which are not available by other methods, may be synthesized according to Scheme 1.

Pursuing the thermal investigation of metal dithio-complexes [8–12], we report here results concerning mass spectral and TG studies of $Ni[S_2CN(COR')R]_2$ complexes. The interpretation and numerical analysis of the thermoanalytical data are given, as well as the evaluation of the order of reaction, the energy of activation and the pre-exponential factor, based on the differential method of Freeman and Carroll [13] and the integral method of Coats and Redfern [14].

EXPERIMENTAL

Preparation of samples

Samples of $Ni[S_2CN(COR')R]_2$ complexes (R = Me, *i*-Bu, Ph, Bz; R′ = Me, Ph) were obtained [1] from the reaction of acetone solutions of the appropriate bis(*N*-alkyldithiocarbamato)nickel(II) complex with acetic anhydride or benzoyl chloride in the presence of triethylamine (1 : 2 : 2 molar ratios). Purification was achieved by dissolving the solid in chloroform and reprecipitating with ethanol (yield: 75%). The $Ni(S_2CNHR)_2$ complexes were obtained from the reaction between nickel chloride and the appropriate dithiocarbamate salt in water–ethanol (1 : 1) solution [15]. The *N*-alkyldithiocarbamate salts were prepared and recrystallized as reported previously [16]. All the other reagents were obtained commercially.

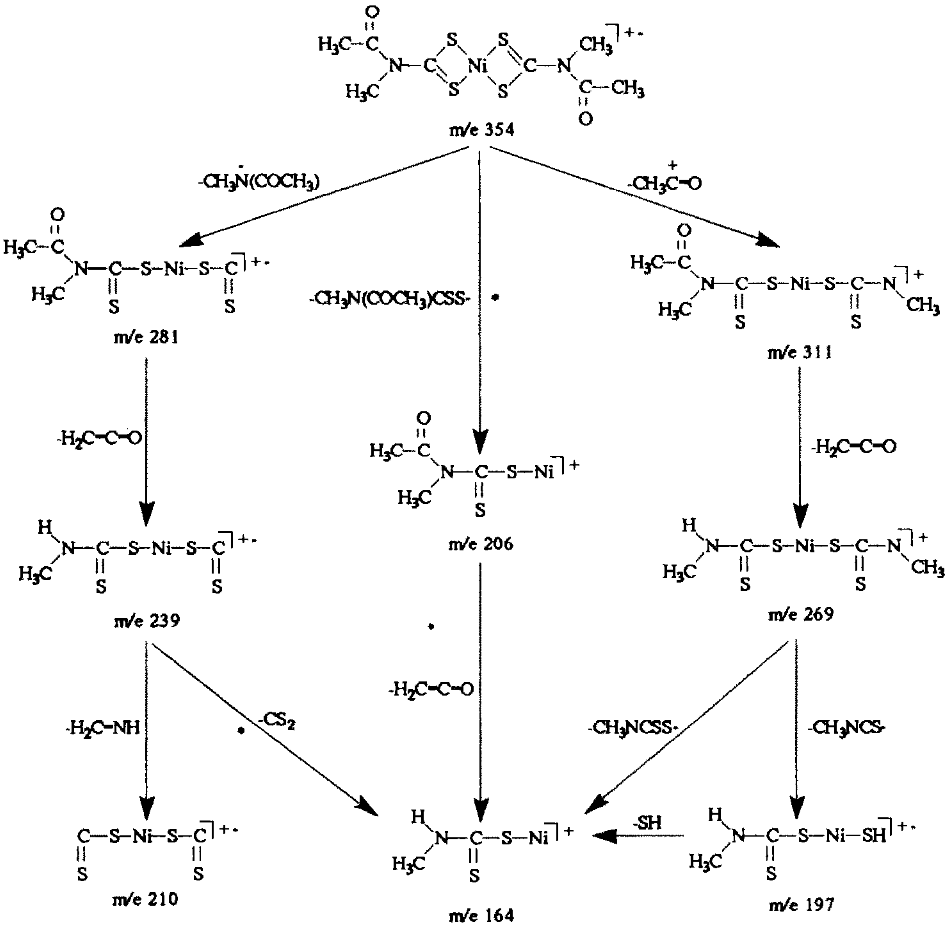
Instruments

Mass spectra were measured on an RMU-6L Hitachi Perkin–Elmer mass spectrometer with an ionization source of T-2p type operating at 70 eV. The TG curves were obtained on a Linseis L81-22 thermobalance. The measurements were performed using a dynamic nitrogen furnace atmosphere at a flow rate of 60 ml min^{-1} up to 900 °C. The heating rate was 10 °C min^{-1} and the sample sizes ranged in mass from 12 to 17 mg. The elemental analysis of carbon, nitrogen and hydrogen was performed on a Perkin–Elmer 240B microanalyser. IR spectra were recorded in the range 4000–250 cm^{-1} on a Perkin–Elmer 467 spectrophotometer, using KBr pellets.

RESULTS AND DISCUSSION

Mass spectral studies

The molecular ions of the studied compounds could not be detected in the mass spectra except in the case of the Ni[$S_2CN(COMe)Me$]$_2$ complex. The



Scheme 2.

absence of molecular ions can be attributed to decomposition, either pyrolytically in the direct inlet under the high temperature used (200–280 °C), or to electron impact. However, in all spectra the ion $[\mathrm{Ni(SC(:S)N\text{-}HR)_2}]^+$ is present, and can be regarded as a direct fragment of the molecular ion upon elimination of the two acetyl groups. This is further supported by the detection of a peak with varying relative intensity (65–100%) because of the $[\mathrm{CH_3CO}]^+$ ion. Moreover, the highest mass number ions observed for all compounds, which might be direct fragments of the molecular ion, are those of the formulae $[\mathrm{Ni(SC(:S)N(COR')R)}]^+$ and $[\mathrm{(SCS)Ni(SC(:S)N(COR')R)}]^+$. The former ion is probably due to the cleavage of one Ni–S bond and the loss of a dithiocarbamate radical. We might expect low relative abundances of these ions, considering the known thermal instability of similar compounds [17] and of organometallic compounds in general. A number of daughter ions beside the ones mentioned above were also detected. All these ions showed the characteristic mass distribution expected for the isotopic composition of nickel. The genesis of these ions is demonstrated by the fragmentation pattern shown in Scheme 2. Support for the fragmentation pathways comes from the presence of metastable peaks.

Among the most interesting and prominent peaks detected in the high mass region of the spectra of all the examined compounds are those corresponding to the ions $[\mathrm{RN(COR')C(:S)S}]^+$ and $[\mathrm{RN(COR')CS}]^+$. These ions may be partly considered as pyrolytic products because their relative intensities are affected by the temperature and the time spent in the direct inlet. Finally, in the lower mass region of the spectra, a number of the detected peaks can be satisfactorily accounted for by the fragment ion $[\mathrm{RN(COR')C(:S)S}]^+$.

Thermal behaviour

All complexes were studied by TG analysis from room temperature to 900 °C in a nitrogen atmosphere. The temperature ranges and percentage weight losses of the decomposition reactions are given in Table 1. The TG curves obtained for most of the compounds were very similar in character, showing a one-stage weight loss which corresponds to the formation of nickel sulphide. The TG curves of the compounds under study are presented in Figs. 1 and 2.

In general, decomposition begins between 130 °C and 150 °C, followed by a rapid weight loss of over 70%. It is presumed that nickel sulphide is formed as a stable residue, the calculated weight loss showing close agreement with the experimental values. This residue was also analysed for its sulphur content. Consequently, the weight loss is attributed to the evolved moieties $[\mathrm{S_2CN(COR')R + SCN(COR')R}]$, according to

$$[\mathrm{Ni(S_2CN(COR')R)_2}] \rightarrow \mathrm{NiS} + [\mathrm{R(COR')NC(:S)S}] + [\mathrm{R(COR')NCS}]$$

TABLE 1

Thermoanalytical results for nickel(II) amide *N*-carbodithioates in nitrogen atmosphere

Complex	Step	Temperature range (°C)	Weight loss (%)	Assignment	Weight loss calc. (%)
$Ni[S_2CN(COMe)Me]_2$	1	155–320	73.9	$S_2CN(COMe)Me$ $+ SCN(COMe)Me$	74.45
	residue	> 320	26.1	NiS	25.55
$Ni[S_2CN(COMe)\textit{i}\text{-}Bu]_2$	1	130–330	78.8	$S_2CN(COMe)\textit{i}\text{-}Bu$ $+ SCN(COMe)\textit{i}\text{-}Bu$	79.24
	residue	> 330	21.2	NiS	20.76
$Ni[S_2CN(COMe)Ph]_2$	1a	145–210	36.8	SCN(COMe)Ph	37.18
	b	210–310	43.1	$S_2CN(COMe)Ph$	43.88
	residue	> 310	20.1	NiS	18.94
$Ni[S_2CN(COMe)Bz]_2$	1	165–330	81.8	$S_2CN(COMe)Bz$ $+ SCN(COMe)Bz$	82.11
	residue	> 330	18.2	NiS	17.89
$Ni[S_2CN(COPh)Me]_2$	1	150–350	80.7	$S_2CN(COPh)Me$ $+ SCN(COPh)Me$	81.06
	residue	> 350	19.3	NiS	18.94
$Ni[S_2CN(COPh)Ph]_2$	1a	135–190	44.9	$S_2CN(COPh)Ph$	45.14
	b	190–340	38.9	SCN(COPh)Ph	39.82
	residue	> 340	16.2	NiS	15.04

In the case of $Ni[S_2CN(COMe)Ph]_2$ and $Ni[S_2CN(COPh)Ph]_2$, however, the decomposition of nickel(II) amide *N*-carbodithioate to metal sulphide is observed in two substeps; the first weight loss corresponds to the elimination of one dithiocarbamato group, followed by the elimination of one thiocarbamoyl group and the formation of metal sulphide after the second weight loss.

Decomposition kinetics

The decomposition curves for $Ni[S_2CN(COR')R]_2$ exhibited a well defined pattern, whereas weight loss considerations and elemental analyses indicated the final product to be NiS. For an evaluation of kinetic data from these TG traces, the Freeman–Carroll equation [13] was used in the form

$$\frac{\Delta \log(\mathrm{d}w/\mathrm{d}t)}{\Delta \log(w_\infty - w)} = \frac{(-E^*/2.303R)\Delta(T^{-1})}{\Delta \log(w_\infty - w)} + n$$

where w_∞ = mass loss at the completion of the reaction; w = mass loss up to time t; T = absolute temperature at time t; n = order of reaction; R = gas

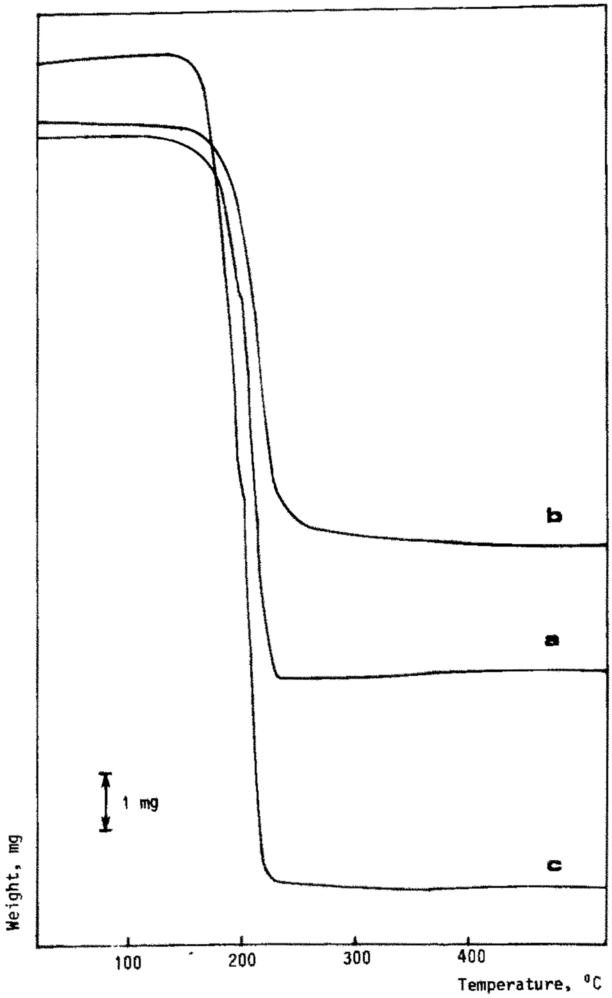


Fig. 1. TG curves of (a) $Ni[S_2CN(COMe)Me]_2$; (b) $Ni[S_2CN(COMe)i\text{-}Bu]_2$; and (c) $Ni[S_2CN(COMe)Bz]_2$ in nitrogen.

constant in kJ $deg^{-1}mol^{-1}$; and E^* = energy of activation in kJ mol^{-1}. The mass–temperature gradients (dw/dT) were obtained by making use of Stirling's central difference formula for six points [18] and were next converted into time slopes using the relation

$$dw/dt = (dw/dT)^{\Phi}$$

where Φ is the rate of heating (°C min^{-1}).

$\Delta(T^{-1})/\Delta \log(w_\infty - w)$ was plotted versus $\Delta \log(dw/dt)/\Delta \log(w_\infty - w)$ and found to be linear. The order of reaction and activation energy were obtained from the above graph. The near-unity values of the order of reaction derived from the above analysis of TG data show that first-order kinetics are applicable in all cases. Therefore, by combining [19] the usual

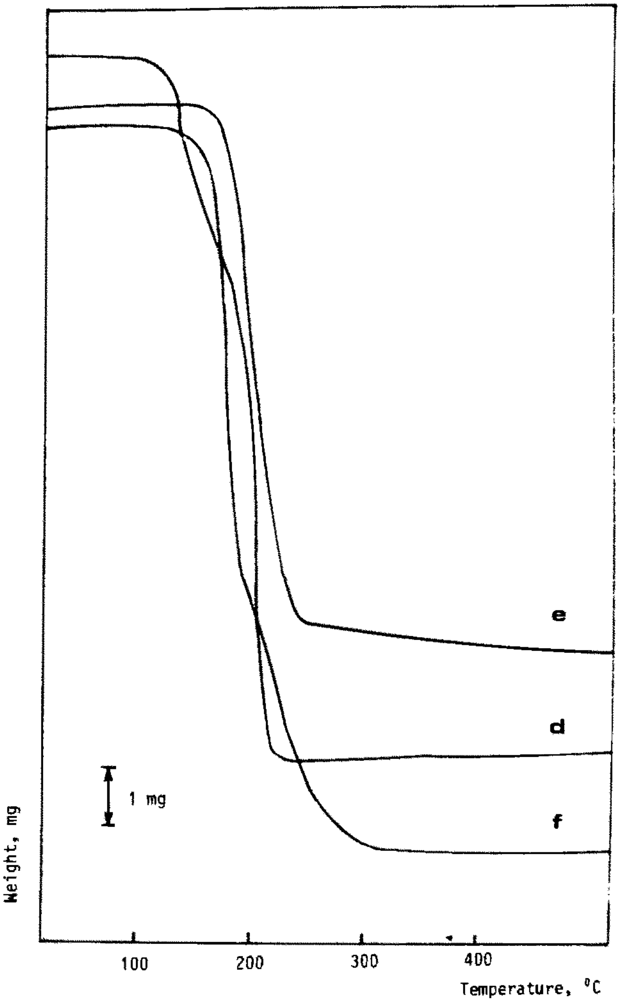


Fig. 2. TG curves of (d) $Ni[S_2CN(COMe)Ph]_2$; (e) $Ni[S_2CN(COPh)Me]_2$; and (f) $Ni[S_2CN(COPh)Ph]_2$ in nitrogen.

first-order rate law expression in terms of w and $(w_\infty - w)$ with the Arrhenius equation, we get

$$\log\left(\frac{\mathrm{d}w/\mathrm{d}t}{w_\infty - w}\right) = \frac{-E^*}{2.303RT} + \log Z$$

A plot of the left hand side expression versus T^{-1} turned out to be linear; E^* was calculated from the slope and Z from the intercept. Typical curves from the application of this equation are given in Figs. 3 and 4, and the results are summarized in Table 2. All the linear plots were evaluated by the method of least squares, and corresponding correlation coefficients (r) were calculated.

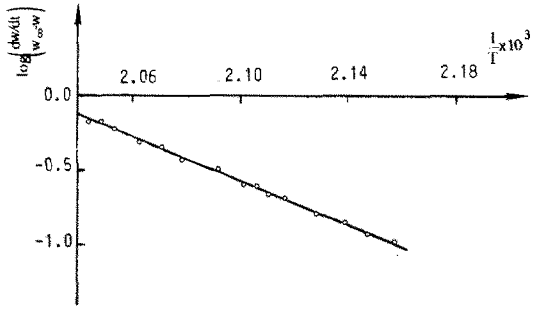


Fig. 3. Freeman–Carroll (modified) plot for Ni[$S_2CN(COMe)Bz]_2$.

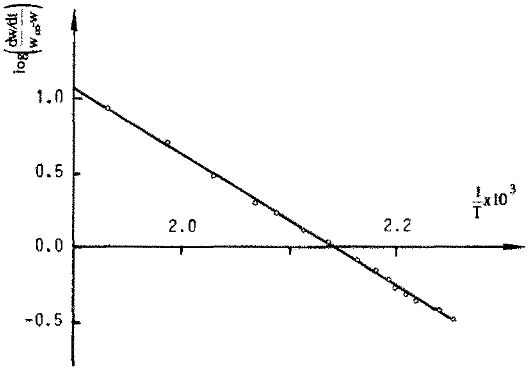


Fig. 4. Freeman–Carroll (modified) plot for Ni[$S_2CN(COPh)Ph]_2$.

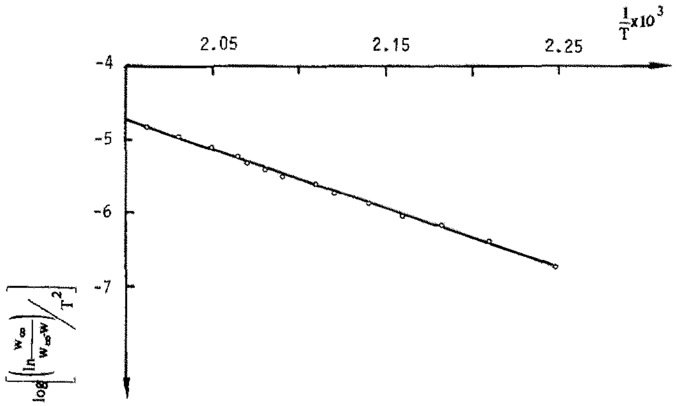


Fig. 5. Coats–Redfern plot for Ni[$S_2CN(COMe)$*i*-Bu$]_2$.

TABLE 2

Kinetic data for nickel(II) amide *N*-carbodithioates

Compound	Parameter	Value	
		From Freeman–Carroll equation	From Coats–Redfern equation
$Ni[S_2CN(COMe)Me]_2$	E^* (kJ mol^{-1})	111.0	104.6
	Z (s^{-1})	6.41×10^{10}	2.27×10^{9}
	r	0.996	0.996
$Ni[S_2CN(COMe)i\text{-}Bu]_2$	E^* (kJ mol^{-1})	161.9	155.7
	Z (s^{-1})	1.85×10^{17}	1.04×10^{15}
	r	0.997	0.995
$Ni[S_2CN(COMe)Ph]_2$	E^* (kJ mol^{-1})	94.4	110.0
	Z (s^{-1})	3.27×10^{8}	7.76×10^{9}
	r	0.990	0.992
$Ni[S_2CN(COMe)Bz]_2$	E^* (kJ mol^{-1})	139.7	146.1
	Z (s^{-1})	5.36×10^{14}	9.96×10^{13}
	r	0.995	0.993
$Ni[S_2CN(COPh)Me]_2$	E^* (kJ mol^{-1})	98.6	113.6
	Z (s^{-1})	7.93×10^{10}	2.02×10^{10}
	r	0.996	0.990
$Ni[S_2CN(COPh)Ph]_2$	E^* (kJ mol^{-1})	105.7	121.5
	Z (s^{-1})	4.66×10^{9}	3.65×10^{11}
	r	0.993	0.993

After studying the decomposition kinetics, it was considered worthwhile to try one more method mentioned in the literature [20], and for this the Coats–Redfern equation [14] was chosen. For first-order processes, this

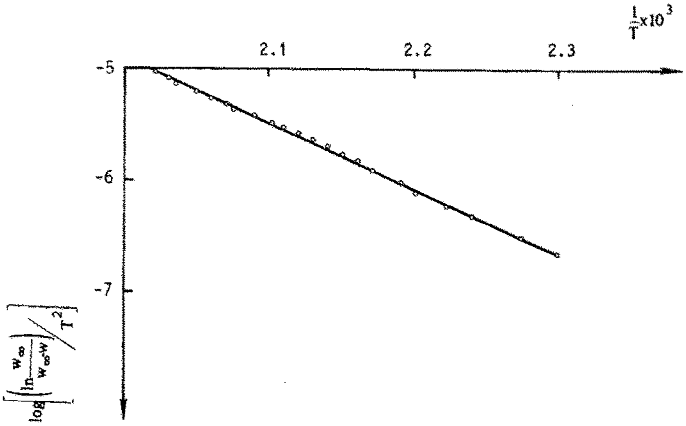


Fig. 6. Coats–Redfern plot for $Ni[S_2CN(COPh)Me]_2$.

equation may be written in the form

$$\log \frac{2.303 \log\left(\frac{w_\infty}{w_\infty - w}\right)}{T^2} = \log \frac{ZR}{\Phi E^*}\left[1 - \frac{2RT}{E^*}\right] - \frac{E^*}{2.303RT}$$

As $1-2RT/E^* \approx 1$, the left hand side expression was plotted versus T^{-1} (Figs. 5 and 6) and E^* was calculated from the slope. Using this value of E^*, Z was calculated from the intercept. The kinetic parameters obtained by this procedure are summarized in Table 2. As shown in the table, the near-unity values of correlation coefficients for the least squares refinements indicate good agreement. Moreover, the activation energies for the decomposition of nickel(II) amide *N*-carbodithioates were found to be between 104 and 155 kJ mol^{-1}, and thus comparable with the values previously reported for the square-planar d^8 metal(II) dithio-complexes [11].

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