*Journal of Thermal Analysis, Vol. 35 (1989) 849–855*

# THERMAL BEHAVIOUR OF TRANSITION METAL COMPLEXES OF DITHIOCARBAZIC ESTERS. II

*L. Suber*[+], *F. Tarli, G. Chiozzini, M. Zugarini* and *C. Riccucci*

ISTITUTO DI TEORIA E STRUTTURA ELETTRONICA E COMPORTAMENTO
SPETTROCHIMICO DEI COMPOSTI DI COORDINAZIONE DEL C.N.R.,
00016 MONTEROTONDO STAZIONE, ITALY

(Received March 2, 1988)

A thermal study (simultaneous TG and DTA measurements) was carried out on the dithiocarbazic ester complexes $M[N^3CH_2R_1N^2C^1(S)SCH_3]_2$, where $M$ = Ni, Pt; $R_1 = C_6H_5$. The following disproportionation reaction occurs in the solid state:

$$\begin{array}{ccccc} 2\,M[NCH_2R_1NC(S)SCH_3]_2 & \rightarrow & M[N{=}CHR_1NC(S)SCH_3]_2 & + & M[NHCH_2R_1NC(S)SCH_3]_2 \\ \mathrm{I} & & \mathrm{II} & & \mathrm{III} \end{array}$$

II is formed through deprotonation of the $CH_2$ group bound to $N^3$, whereas III is formed through protonation of $N^3$.

The influence of inductive and/or steric effects on the mechanism of this reaction is discussed, taking into account the electrochemical and X-ray data on the complexes $Pt[NRNC(S)SR']_2$ with different $R$ substituents: $R$ = H, Ph, $CH_2Ph$, $CH_2C_5H_{11}$, $CH(CH_3)_2$, $C(CH_3)_3$; $R' = CH_3$, $CH_2Ph$.

These results accord with the behaviour of the same complexes in solution.

We previously provided evidence that the platinum(II) complexes of the dithiocarbazic esters, $Pt[N^3RN^2C^1(S)SR']_2$ ($R$ = H, Ph, $CH_2Ph$, $CH_2C_5H_{11}$, $CH(CH_3)_2$, $C(CH_3)_3$; $R'$ = Me, $CH_2Ph$), where the ligand coordinates through $N^3$ and the non-substituted S are members of the electron-transfer series:

$$Pt[NRNC(S)SR']_2^{+1} \underset{-1e}{\overset{+1e}{\rightleftarrows}} Pt[NRNC(S)SR']_2 \underset{-1e}{\overset{+1e}{\rightleftarrows}} Pt[NRNC(S)SR']_2^{-1} + \underset{-1e}{\overset{1e}{\rightleftarrows}} Pt[NRNC(S)SR']_2^{-2}$$

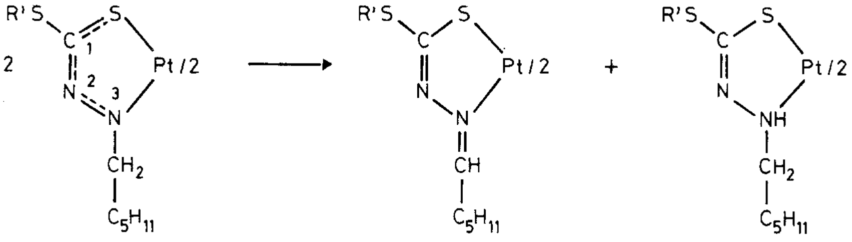
---

[+] To whom correspondence should be addressed.

*John Wiley & Sons, Limited, Chichester*
*Akadémiai Kiadó, Budapest*

The $E_p$ values showed only minor variations on change of the substituent $R$, indicating a very efficient charge delocalization over the whole system [1]. In a subsequent thermal study [2], different behaviour was found when $R$ contains a $CH_2$ group bound to $N^3$.

In these cases, apart from the melting, a decomposition process occurs and an exothermic peak is evident in the DTA curves without weight loss. This was attributed to the following disproportionation reaction, presumably promoted by the activation of the $CH_2$ group by the metal:



In this work, we report the thermal behaviour of the complexes with $R = CH_2Ph$ and $M = Ni^{2+}$ or $Pt^{2+}$ in order to monitor the effect of a different $R$ substituent and to compare the influences of the different metals.

## Experimental

### Preparation of ligands

The ligands $N{=}CHC_6H_5$ $NHC(S)SCH_3$ and $NHCH_2C_6H_5NHC(S)SCH_3$ were prepared as in Ref. 1.

### Preparation of complexes

$Ni[NHCH_2C_6H_5NC(S)SCH_3]_2$ and $(Ni[NCH_2C_6H_5NCH(S)SCH_3]_2$ were prepared as in Ref. 4.

$Ni[N{=}CHC_6H_5NC(S)SCH_3]_2$; $Ni(CH_3COO)_2$ (0.7 mmol) in water (15 $cm^3$) was added to a solution of $N{=}CHC_6H_5NHC(S)SCH_3$ (1.4 mmol) in EtOH (50 $cm^3$). The solution was stirred for 3 h. The brown product was filtered off, washed with a 1 : 1 $EtOH/H_2O$ solution and dried.

N: 12.08 (12.27⁺); C: 45.27 (45.19); H: 3.95 (4.00). $Pt[NCH_2C_6H_5NC(S)SCH_3]_2$ and $Pt(NCH_2C_6H_5NCH(S)SCH_3]_2$ were prepared as described previously [1, 3].

---

[+] The calculated values are given in parentheses.

Pt[N = $CHC_6H_5NC(S)SCH_3]_2$ : $K_2PtCl_4$ (1.3 mmol) in water (15 $cm^3$) was added to a boiling solution of N = $CHC_6H_5NHC(S)SCH_3$ (2.6 mmol). The solution was stirred for 10 min. The orange product was filtered off, washed ($EtOH/H_2O$) and dried.

N: 8.94 (9.13); C: 35.05 (35.23); H: 3.01 (2.95).

### *Physical measurements*

The simultaneous TG and DTA measurements were performed with a Stanton Redcroft STA 781 thermoanalyser, with Pt crucibles, Pt–Pt/Rh thermocouples and samples of ca. 10 mg in weight, in an air flow (50 ml $min^{-1}$) and at a heating rate of 5–10 deg $min^{-1}$. IR spectra of Nujol mulls were recorded with a perkin–Elmer 983 spectrophotometer.

## Results and discussion

Figure 1 reports the simultaneous TG and DTA curves of the complex $Ni[NCH_2C_6H_5NC(S)SCH_3]_2$. The compound shows no weight loss until ca 170°, where we observed the onset of the decomposition processes leading to the formation of NiO at 800°. In the DTA curve, two peaks are observed before 170°,

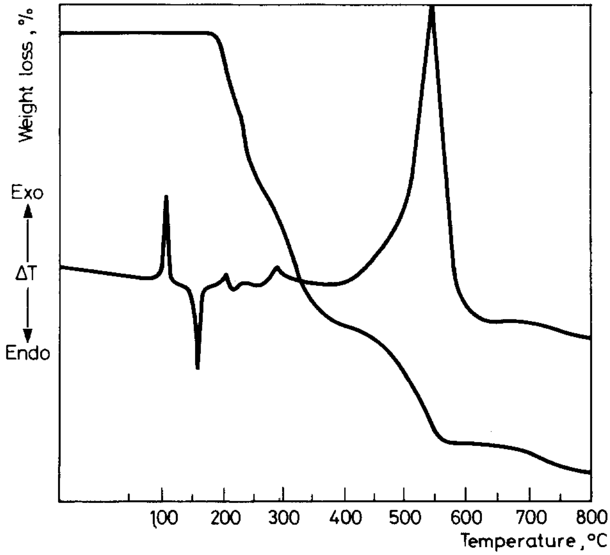


Fig. 1 Simultaneous TG and DTA curves of the complex $Ni[NCH_2C_6H_5NC(S)SCH_3]_2$

both occurring without weight loss, an exothermic one at 94° and an endothermic one at 143°.

The first peak is attributable to the disproportionation reaction:

$$2\ \underset{\text{I}}{\mathrm{Ni[NCH_2C_6H_5NC(S)SCH_3]_2}} \rightarrow \underset{\text{II}}{\mathrm{Ni[N{=}CHC_6H_5NC(S)SCH_3]_2}} + \underset{\text{III}}{\mathrm{Ni[NHCH_2C_6H_5NC(S)SCH_3]_2}}$$

Eq. (1)

The products obtained were isolated and characterized via analytical and spectroscopic measurements (Table 1). The reaction consists of a rearrangement of two hydrogen atoms per molecule (one for each ligand): one hydrogen atom is lost by the $CH_2$ group bound to $N^3$, giving the Schiff base complex II, whereas $N^3$ in III acquires a proton. Presumably, this reaction is promoted by the activation of the C—H bond by the metal.

**Table 1** Diagnostic IR frequencies ($cm^{-1}$) of platinum and nickel complexes

| Complexes | | ν(N—H) | ν(C=N) | | |
|---|---|---|---|---|---|
| $Ni[NCH_2PhNC(S)SCH_3]_2$ | *A*+*B* | 3176 | 1586 | 1565 | 1530 |
| $Ni[N{=}CHPhNC(S)SCH_3]_2$ | *A* | | 1587 | 1565 | |
| $Ni[NHCH_2PhN{=}C(S)SCH_3]_2$ | *B* | 3176 | | | 1530 |
| $Pt[NCH_2PhNC(S)SCH_3]_2$ | *C*+*D* | 3021 | 1584 | 1530 | 1480 |
| $Pt[N{=}CHPhNC(S)SCH_3]_2$ | *C* | | 1583 | | 1482 |
| $Pt[NHCH_2PhN{=}C(S)SCH_3]_2$ | *D* | 3021 | | 1532 | |

The second endothermic process is associated with a change of phase: from microscope observations and XRD powder spectra, the product turns from a microcrystalline state to an amorphous one, whereas no variations are observed in its i.r. spectrum and analysis.

Figure 2 reports the simultaneous TG and DTA curves of the complex $Pt[NCH_2C_6H_5NC(S)SCH_3]_2$. The compound melts at ca. 221°, as deduced from the sharp endothermic peak. This is immediately followed by decomposition, as indicated by the series of exothermic and endothermic peaks between 220° and 500°. At 800°, metallic platinum is the final product. Before the melting process, at 157° in the DTA curve we observe the onset of an exothermic process, which consists of two near-overlapping peaks: the one with a peak temperature of 177° occurs without weight loss, and the other, at 182°, is associated with a weight loss of ca. 0.5%.

The first process is attributable to a disproportionation reaction, as found for the

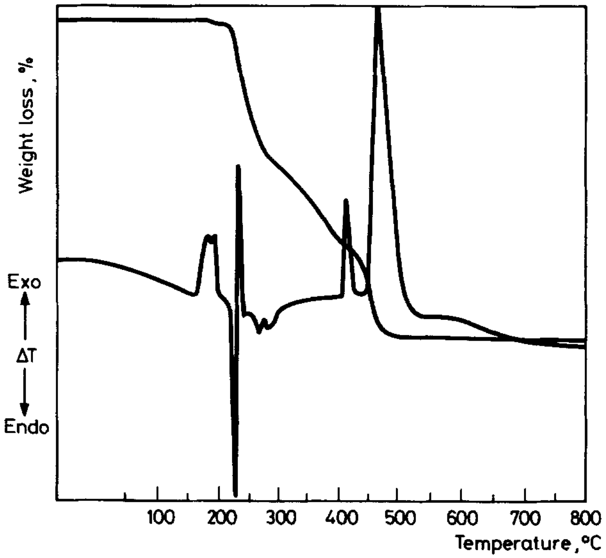


Fig. 2 Simultaneous TG and DTA curves of the complex $Pt[NCH_2C_6H_5NC(S)SCH_3]_2$

nickel complex; the activation energy for the reaction is supplied by the thermal energy. The onset temperature of ca. 150° when $M = Pt^{2+}$ and 100° when $M = Ni^{2+}$ indicates that the $Ni^{2+}$ complex has a higher reactivity than that of the $Pt^{2+}$ one, although both contain a square-planat $[MN_2S_2]$ chromophore.

The analytical and spectroscopic measurements on the product obtained after heating at 177° (the peak temperature of the first process) show that II and III are present together with unreacted I (see Eq. (1)). At 182° (i.e. corresponding to the second exothermic peak), the disproportionation reaction is virtually complete, but isolation of the mixture of II and III is not possible due to the vicinity of the decomposition processes (see Fig. 2).

Preliminary studies on the reactivity of these complexes in solution indicate that, when $R$ contains a $CH_2$ group bound to $N^3$ (e.g. when $R = CH_2C_6H_5$), in a few days the colour of the solution turns from deep-green to orange-red, due to the formation of the Schiff-base complex $Pt[N{=}CHC_6H_5NC(S)SCH_3]_2$. Thus, in solution these complexes disproportionate as in the solid state, i.e. as in Eq. (1). However, the $N^3$-protonated complex III is oxidatively unstable and reacts to give I, which disproportionates, so that the only product which can be isolated is the Schiff-base complex II.

Furthermore, although only one H atom of the $CH_2$ group bound to $N^3$ is involved in the disproportionation reaction, this reaction does not occur when $R$ contains a CH group bound to $N^3$, e.g. when $R = CH(CH_3)_2$.

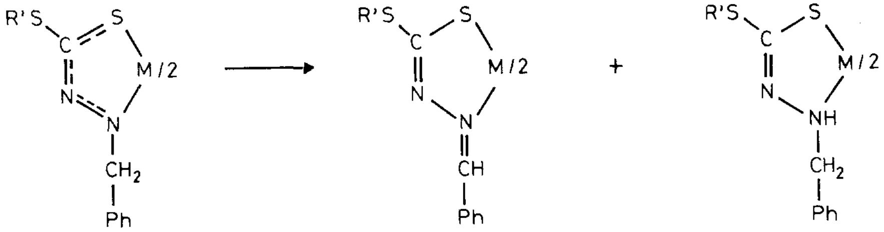
This behaviour is not readily attributable to inductive effects and/or steric effects of the *R* substituent.

Thus, comparison of the *Ep* oxidation values of the isostructural complexes Pt[NRNC(S)SR']$_2$ shows that there are no appreciable variations attributable to inductive effects when $R = CH_2Ph$, Hex$^n$ and Pr$^i$; and X-ray data on the complex with $R = CH(CH_3)_2$ are perfectly comparable with those for the complex with $R = CH_2C_6H_5$ [1, 3]. We conclude that the disproportionation reaction occurs only if a $CH_2$ group is present rather than a CH group.

## Conclusions

The thermal behaviour of the dithiocarbazic ester complexes $M[N^3RN^2C^1(S)SCH_3]_2$, where $M = $ Ni or Pt; and $R = CH_2Ph$, show an interesting process when *R* contains a $CH_2$ group linked to $N^3$.

From chemical analysis and spectroscopic methods, we attribute this process to the disproportionation reaction



This behaviour is presumably promoted by an activation of the C—H bond by the metal.

Preliminary studies on the reactivity of the complexes in solution are in agreement with the results obtained.

* * *

We thank prof. A. La Ginestra for many helpful discussions on the various aspects of this work.

## References

1 V. Fares, A. M. Giuliani, P. Imperatori, L. Suber and F. Tarli, J. Chem. Soc. Dalton Trans., 1035 (1987).

2 L. Suber, F. Tarli, G. Chiozzini and C. Riccucci, J. Thermal Anal., 31 (1988) 1073.

3 A. M. Giuliani, L. Suber and F. Tarli, to be published.

4 D. Attanasio, V. Fares, P. Imperatori, G. Mattogno and F. Tarli, J. Chem. Soc. Dalton Trans., (1988) 1217.

**Zusammenfassung** — Dithiokarbamidsäureesterkomplexe $M[N^3CH_2R_1N^2C^1(S)SCH_3]_2$ mit $M$ = Ni, Pt und $R_1$ = $C_6H_5$ wurden thermisch untersucht. Im festen Zustand spielt sich folgende Disproportionierungsreaktion ab:

$$\underset{\text{I}}{2\,M[NCH_2R_1NC(S)SCH_3]_2} \rightarrow \underset{\text{II}}{M[N=CHR_1NC(S)SCH_3]_2} + \underset{\text{III}}{M[NCH_2R_1NHC(S)SCH_3]_2}$$

II wird durch Deprotonierung der an $N^3$ gebundenen $CH_2$ Gruppe und III durch Protonierung des Atoms $N^2$ gebildet. Unter Zuhilfenahme der elektrochemischen und Röntgendaten der Komplexe $Pt[NRNC(S)SR']_2$ mit verschiedenen Substituenten $R$: $R$=H, Ph, $CH_2Ph$, $CH_2C_5H_{11}$, $CH(CH_3)_2$, $C(CH_3)_3$ und $R'=CH_3$ bzw. $CH_2Ph$ wurde der Einfluß von induktiven und/or sterischen Effekten auf den Reaktionsmechanismus diskutiert. Diese Ergebnisse stehen in Übereinstimmung mit dem Verhalten der Komplexe in Lösung.

**Резюме** — Совмещенным методом ТГ и ДТА проведено термическое исследование комплексов никеля и платины с эфиром дитиокарбазиновой кислоты общей формулы $M[N^3CH_2R_1N^2C^1(S)SCH_3]_2$, где $M$ = Ni, Pt, $R_1 = C_6H_5$. В твердом состоянии происходит реакция диспропорционирования:

$$\underset{\text{I}}{2\,M[NCH_2R_1NC(S)SCH_3]_2} \rightarrow \underset{\text{II}}{M[N=CHR_1NC(S)SCH_3]_2} + \underset{\text{III}}{M[NCH_2R_1NHC(S)SCH_3]_2}$$

Продукт II образуется путем депротонирования $CH_2$ группы, связанной с $N^3$, а продукт III-путем протонирования азота $N^2$. Влияние индукционных и (или) стерических факторов на механизм этой реакции обсуждено, исходя из электрохимических и рентгенографических данных для комплексов $Pt[NRNC(S)SR']_2$, где $R$ = различные алифатические и ароматические заместители, а $R'$ = метил и бензил. Полученные результаты согласуются с поведением этих комплексов в растворе.