Journal of Thermal Analysis, Vol. 34 (1988) 1073–1081

THERMAL BEHAVIOUR OF TRANSITION METAL COMPLEXES OF DITHIOCARBAZIC ESTERS

Part I

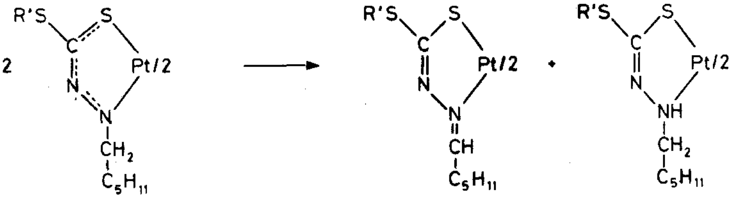
L. Suber, F. Tarli, G. Chiozzini* and *C. Riccucci*

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

(Received September 23, 1987)

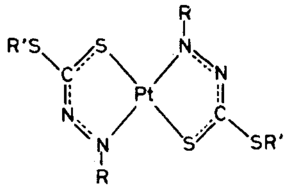
The thermal behaviour of the square-planar dithiocarbazate derivative complexes $Pt[NRNC(S)SR']_2$ (R = *n*-hexyl, R' = methyl or benzyl) has been investigated.

Simultaneous TG and DTA measurements provided evidence of the presence of an exothermic process, which proceeds without weight loss. This is attributed to the occurrence of a disproportionation reaction:



The products, which were isolated and characterized, form a 1 : 1 eutectic mixture.

Dithiocarbazic esters $N^3HRN^2HC(S)SR'$ can coordinate to metal ions in neutral or anionic deprotonated forms. In all cases, coordination takes place through N^3 and the non-substituted S atoms. We have prepared the double deprotonated complexes of Pt(II):



---

* To whom correspondence should be addressed.

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

with R = H, isopropyl, *tert*-butyl, *n*-hexyl, benzyl or phenyl, and R′ = methyl or benzyl, and studied their electrochemical behaviour [1, 2].

Cyclovoltammetric data gave evidence that they are members of the electron-transfer series:

$$\mathrm{Pt[NRNC(S)SR']_2^{+1}} \underset{-1e}{\overset{+1e}{\rightleftharpoons}} \mathrm{Pt[NRNC(S)SR']_2^{0}} \underset{-1e}{\overset{+1e}{\rightleftharpoons}}$$

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

The E_p values exhibit only minor variations on change of the substituent R, indicating a very efficient charge delocalization over the whole system.

Catalytic tests in the photolytic oxidation reactions of hydrocarbons showed that these complexes are precursors of catalytically active species which have not yet been identified [3]. To gain a deeper insight into the stabilities and reactivities of these complexes, we decided to study their thermal behaviour by means of simultaneous TG and DTA techniques.

In this work, we report on the thermal behaviour of the complexes $\mathrm{Pt[NRNC(S)SR']_2}$ (R = *n*-hexyl or benzyl, R′ = methyl or benzyl). Rather than decomposing immediately after the melting process, which is the case of all the other derivatives, these complexes exhibit an endothermic process without weight loss before the onset of decomposition. We attribute this to a disproportionation reaction involving activation of the C—H bond through the metal.

For clarity, the substituent R = *n*-hexyl is indicated as $\mathrm{CH_2R_1}$.

Experimental

Preparation of ligands

The ligands $\mathrm{NCH_2R_1HNHC(S)SR'}$ (R′ = methyl or benzyl) are prepared as in Reference [2].

Preparation of complexes

$\mathrm{Pt[NCH_2R_1NC(S)SR']_2}$: see Reference [2].

$\mathrm{Pt(NCHR_1NC(S)R']_2}$: $\mathrm{K_2[PtCl_4]}$ (6.8 mmol) in water (20 $\mathrm{cm^3}$) was added to a solution of $\mathrm{NCHR_1NHC(S)SR'}$ (13.6 mmol) in ethanol (60 $\mathrm{cm^3}$). The solution was stirred at room temperature overnight. The yellow product was filtered off, dried and crystallized from hot *n*-hexane.

$\mathrm{Pt[NCH_2R_1HNC(S)SR']_2}$: $\mathrm{K_2[PtCl_4]}$ (1.2 mmol) in water (20 $\mathrm{cm^3}$) was added to

Table 1 Analytical data of platinum complexes

Compound	Colour	Analysis, %*		
		C	H	N
$Pt[NCH_2R_1NC(S)SMe]_2$	Dark green	31.88 (31.83)	5.31 (5.34)	9.13 (9.28)
$Pt[N=CHR_1NC(S)SMe]_2$	Yellow	31.92 (31.93)	4.97 (5.02)	9.19 (9.31)
$Pt[NCH_2R_1HNC(S)SMe]_2$	Pale Green	32.11 (31.92)	5.48 (5.66)	9.26 (9.25)
$Pt[NCH_2R_1NC(S)SBz]_2$	Dark Green	44.25 (44.37)	5.07 (5.08)	7.23 (7.39)
$Pt[N=CHR_1NC(S)SBz]_2$	Yellow	44.30 (44.43)	4.98 (5.06)	7.27 (7.40)
$Pt[NCH_2R_1HNC(S)SBz]_2$	Pale green	44.25 (44.19)	5.37 (5.56)	7.23 (7.36)

* Calculated values are in parentheses.

a solution of $R_1CH_2NHNHC(S)SR'$ (2.4 mmol) in ethanol (60 cm^3). After stirring at room temperature overnight, the pale-green product was filtered off, washed with ethanol and dried over P_2O_5 in vacuum (for analytical data, see Table 1).

Physical measurements

The simultaneous TG and DTA measurements were performed by using a Stanton–Redcroft STA 781 thermoanalyser with Pt crucibles, Pt–Pt/Rh thermocouples and samples of ca 10 mg, in an air flow (50 ml min^{-1}), at heating rates of 5–10 deg min^{-1}.

IR spectra of Nujol mulls were recorded with a Perkin–Elmer 983 spectrophotometer.

Results and discussion

Figure 1 presents simultaneous TG and DTA curves of the complexes $Pt[NCH_2R_1NC(S)SR']_2$ (R' = methyl or benzyl).

At 198° (R' = methyl) and 177° (R' = benzyl), respectively, we observed the onset of the decomposition processes, leading, through the formation of isothiocyanate intermediates, to metallic platinum.

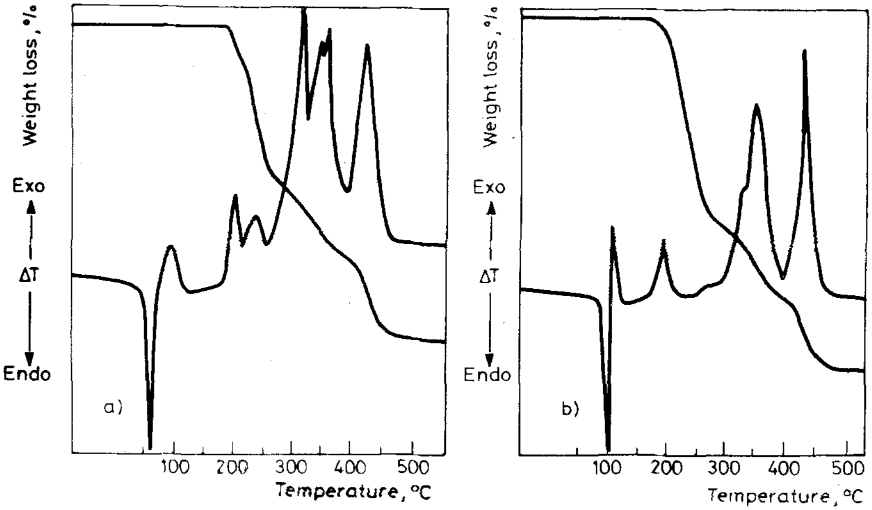


Fig. 1 Simultaneous TG and DTA curves of the complexes $Pt[NCH_2R_1NC(S)SMe]_2$ (a) and $Pt[NCH_2R_1NC(S)SBz]_2$ (b)

Before the decomposition processes, there are two peaks in the DTA curves of both complexes, which proceed without weight loss. The first one is endothermic, with peaks at 66° and 105°, attributable to the melting processes, and the second one is exothermic, with peaks at 101° and 110°. During this last process, the melt changes colour from deep-green to yellow-brown.

In both cases, the product obtained after the exothermic process led to two compounds after crystallization from diethyl ether: one is yellow and soluble the other pale-green and insoluble. Through analytical and spectroscopic measurements, they were identified as the Schiff base complexes $Pt[N=CHR_1NC(S)SR']_2$ and the N-protonated complexes $Pt[NCH_2R_1HNC(S)SR']_2$ (Figs 2–3, Tables 1–2).

Two hydrogen atoms (one for each ligand) are lost by the CH_2 moieties next to the N^3 atom, giving a Schiff base complex and an N^3-protonated complex.

The exothermic process may be attributed to the following disproportionation reaction:

$$2\,Pt[NCH_2R_1NC(S)SR']_2 \rightarrow Pt[N=CHR_1NC(S)SR']_2 + $$
$$+\,Pt(NCH_2R_1HNC(S)SR']_2$$

I III II

To verify this hypothesis, we prepared II and III with R′ = methyl, and performed simultaneous TG–DTA measurements of I, II and III and of mixtures of II and III in different ratios. They were heated up to 160° (a temperature at which

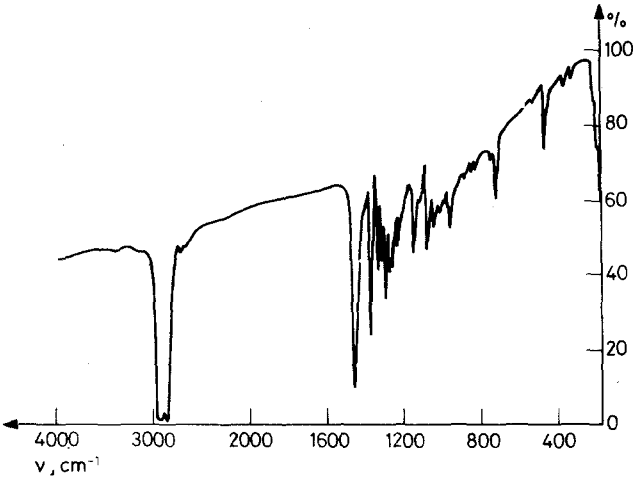


Fig. 2 IR spectrum of the complex $Pt[NCH_2R_1NC(S)SMe]_2$

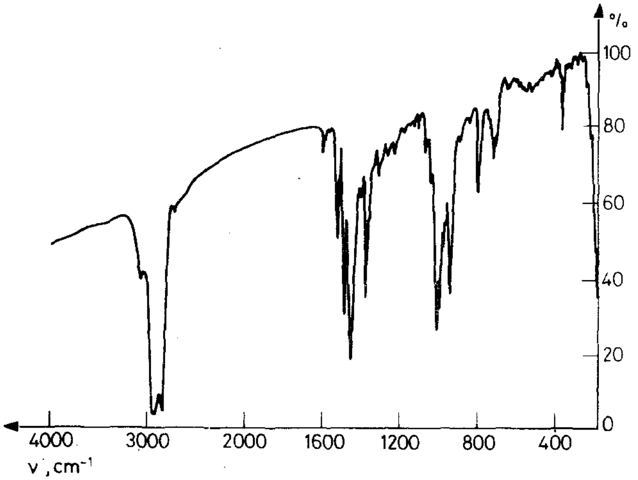


Fig. 3 IR spectrum of $Pt[NCH_2R_1NC(S)SMe]_2$ after heating to 125 °C

the disproportionation reactions are over, but the decomposition of the products has not yet begun, see Fig. 1) and then cooled down to room temperature at a controlled rate.

Surprisingly, for complex I we found only one exothermic solidification peak, which cannot be attributed to either the solidification peak of II or that of III (see Fig. 4a). To prove the existence of a eutectic mixture of II and III, we performed TG and DTA measurements on mixtures of these products in the ratios 50/50, 40/60 and 30/70. Figure 5 depicts four successive DTA cycles of the mixtures. The first cycle

Table 2 Diagnostic IR frequencies (cm^{-1}) of platinum complexes

	ν(N—H)	ν(C = N)^2	ν(C = N)^3
$Pt[NCH_2R_1NC(S)SMe]_2$		1495w	
$Pt[N=CHR_1NC(S)SMe]_2$		1489s	1601w
$Pt[NCH_2R_1HNC(S)SMe]_2$	3045s	1534s	
$Pt[NCH_2R_1NC(S)SBz]_2$		1492s	
$Pt[N=CHR_1NC(S)SBz]_2$		1492s	1604s
$Pt[NCH_2R_1HNC(S)SBz]_2$	3060s	1544s	

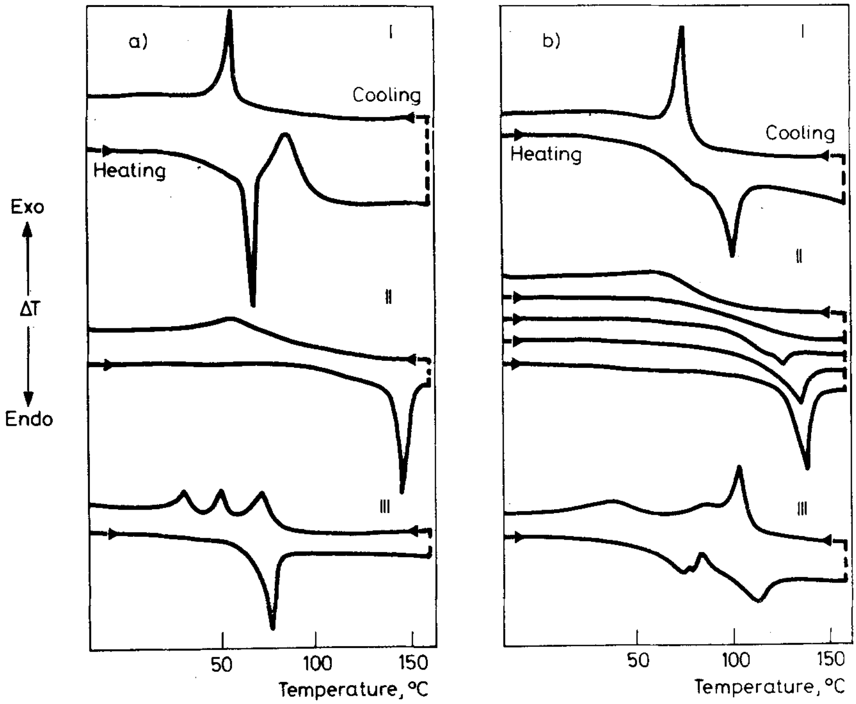


Fig. 4 a) First heating and cooling DTA cycle of complexes I, II and III. b) Successive DTA cycles of I, II and III

is, as expected, the same for all the mixtures: we observed (more or less resolved) the melting and solidification peaks of II and III (compare with Fig. 4). In the second DTA cycle, new endothermic (on heating) and new exothermic peaks (on cooling) appear for each mixture; they overlap with those found previously in the corresponding DTA cycle of compound I (see Fig. 4).

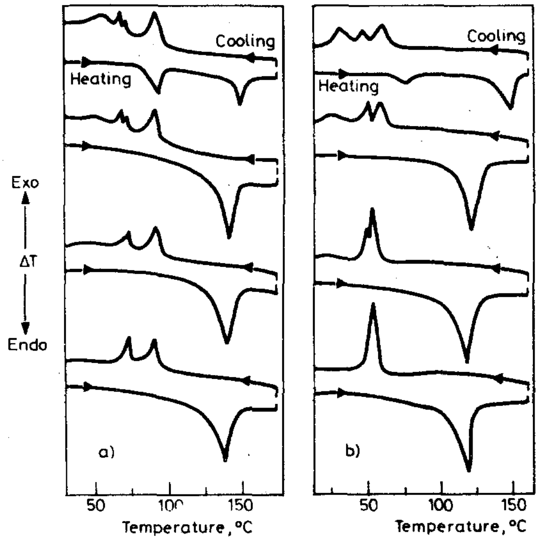


Fig. 5 Four successive DTA cycles (from above downwards) of a 50/50 mixture of II and III (a) and of a 40/60 mixture of II and III (b)

These results are in agreement with the slow formation of a eutectic mixture of complexes II and III. This mixture exhibits noteworthy thermal stability: successive DTA cycles are perfectly superimposable. By way of contrast, each single complex shows a slow tendency to decompose, as can be deduced by observing the DTA curves corresponding to the successive heat-cool cycles (see Fig. 4).

Figure 5 clearly shows that the two processes (slow formation of the eutectic mixture due to the viscosity of the melts, and decomposition of the single components) are competitive, leading to a gradual evolution of the curves, because the initial composition of the mixture is changed after several cycles. In fact, we can deduce that the thermal decomposition of complex III is faster than that of complex

Table 3 Melting, disproponation and decomposition peak-temperatures (°C) of platinum complexes

Complexes	T_{melt}	$T_{dispr.}$	$T_{dec.}$
$Pt[NCH_2R_1NC(S)SMe]_2$	66	101	198
$Pt[N{=}CHR_1NC(S)SMe]_2$	75	—	215
$Pt[NCH_2RHNC(S)SMe]_2$	145	—	175
$Pt[NCH_2R_1NC(S)SBz]_2$	105	110	177
$Pt[N{=}CHR_1NC(S)SBz]_2$	66	—	210
$Pt[NCH_2R_1HCN(S)SBz]_2$	140	—	181

II (see Fig. 4): for example, we found that, besides the eutectic melting and solidification peaks after four DTA cycles, the initial 50/50 mixture shows the peaks corresponding to II, because this complex is now in excess compared with the other one. Conversely, the 40/60 mixture attains the 1 : 1 composition after four DTA cycles, i.e. it gives only the eutectic peaks (Fig. 5).

Finally, these results are also in agreement with those obtained with the complex $Pt[NCH_2R_1NC(S)SBz]_2$, which behaves in an analogous manner (see Table 3).

Conclusions

Dithiocarbazate derivative complexes of the type $M[NRNC(S)SR']_2$, which show electron-transfer properties and are precursors of active catalytic species, exhibit interesting thermal behaviour when R contains a CH_2 group linked to N^3 (e.g. R = *n*-hexyl or benzyl). These complexes undergo an exothermic process in the range 100–110°, which occurs without weight loss. It is attributed to the following disproportion reaction:

$$\begin{aligned} 2\,Pt[NCH_2R_1NC(S)SR']_2 \rightarrow & Pt[N{=}CHR_1NC(S)SR']_2 + \\ & + Pt[NCH_2R_1HNC(S)SR']_2 \end{aligned}$$

This interpretation has been confirmed by comparison of the thermal curves of the above compounds with those of the mixtures at different ratios of the products of disproportionation. Consecutive thermal cycles permitted the different thermal stabilities to be followed as the 1 : 1 eutectic mixture of the two products is formed.

* * *

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

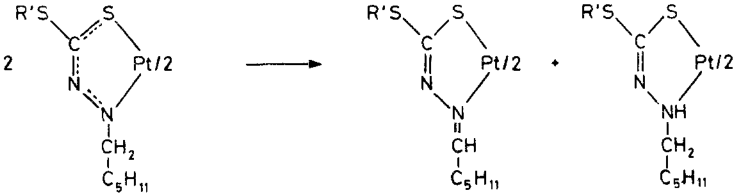
References

1 C. Battistoni, A. M. Giuliani, E. Paparazzo and F. Tarli, J. Chem. Soc. Dalton Trans., 1293 (1984).

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

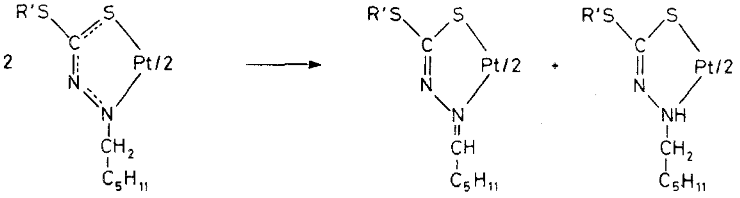
3 A. Monaci and F. Tarli, XXX ICCC (Nanchino, 1987).

Zusammenfassung — Das thermische Verhalten der rechteckig planaren Dithiokarbazatkomplexe Pt(NRNC(S)SR']$_2$ mit R = *n*-hexyl und R' = methyl bzw. benzyl wurde untersucht. Gleichzeitige TG- und DTA-Messungen bewiesen das Vorhandensein eines exothermen Vorganges ohne Masseverlust. Dies wird der Disproportionierungsreaktion



zugeschrieben. Die isolierten und beschriebenen Produkte bilden ein Eutektikum vom Verhältnis 1 : 1.

Резюме — Исследовано термическое поведение плоских квадратных комплексов платины с производными дитиокарбазина общей формулы Pt[NRNC(S)SR']$_2$, где R = *n*-гексил, R' = метил, бензил. Измерения, проведенные совмещенным методом ТГ и ДТА, показали наличие экзотермического процесса, протекающего без потери веса. Наблюдаемый эффект обусловлен реакцией диспропорционирования



Оба продукта были выделены, идентифицированы и установлено, что они образуют эвтектическую смесь состава 1 : 1.