

## THERMAL ANALYSIS OF DITHIOMALONAMIDE COMPLEXES

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### Abstract

Dithiomalonamide [ $\text{H}_2\text{A}$ ,  $\text{CH}_2(\text{CSNH}_2)_2$ ] and 2,2-dimethyldithiomalonamide [ $\text{H}_2\text{B}$ ,  $\text{C}(\text{CH}_3)_2(\text{CSNH}_2)_2$ ] can act as bidentate ligands and form stable, cationic 1:2 complexes with general formula  $\text{M}_2(\text{H}_2\text{L})_2\text{X}_2$  [ $\text{M}=\text{Ni}^{2+}$ ,  $\text{Pd}^{2+}$ ,  $\text{Pt}^{2+}$ ;  $\text{X}=\text{Cl}$ ,  $\text{Br}$ ,  $\text{I}$ ;  $\text{H}_2\text{L}=\text{H}_2\text{A}$ ,  $\text{H}_2\text{B}$ ] in strong acidic medium. An elaborate thermal study is presented, based on results from elemental analyses and vibrational studies (IR and Raman spectroscopy). The  $\text{H}_2\text{A}$  complexes start to decompose by releasing two  $\text{HX}$  molecules whereafter a stable intermediate  $\text{M}(\text{HA})_2$  is formed. The  $\text{H}_2\text{B}$  complexes degrade in a different way; the metal-sulphur bond is broken and the ligand is expelled as a whole. Influences of the metal ion and of the halogenide counterions are investigated.

**Keywords:** complexes, IR, TG

### Introduction

The physico-chemical study of amide and thioamide containing ligands has been the subject of intense research in our laboratory for several years. After the exploration of a wide variety of oxamide-based ligands and their thio-analogues from the coordination chemistry point of view [1-6], this study is now being extended to malonamide and its thioderivatives [7-8]. The introduction of a  $\text{CH}_2$  group between the two thioamide functions in dithiomalonamide creates interesting complexation possibilities as the protons of this methylene group are quite acidic and therefore can take part in the coordination process.

Transition metal complexes of this ligand have been investigated by several groups but only vague results were presented [9-11]. Recently we published on the detailed vibrational analysis of cationic complexes with  $\text{Ni}^{2+}$ ,  $\text{Pd}^{2+}$ ,  $\text{Pt}^{2+}$  and also compared the behaviour of this ligand to dithiooxamide [12]. Some thermal analysis results were mentioned. In the present paper we would like to contribute to a more elaborate study of the thermal behaviour in which a comparison is made between dithiomalonamide itself and the doubly carbon-substituted derivative 2,2-dimethyldithiomalonamide, mainly based on results from

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IR and Raman spectroscopy and elemental analyses for the identification of the products.

## Experimental

Dithiomalonamide has been prepared according to literature data [13]. For 2,2-dimethyldithiomalonamide the starting material malononitrile was doubly substituted at the methylene group using NaH and CH<sub>3</sub>I in DMSO and then was allowed to react with hydrogen sulphide gas.

The preparation of the complexes of dithiomalonamide (H<sub>2</sub>A) has already been described [12]. The complexes of 2,2-dimethyldithiomalonamide (H<sub>2</sub>B) have been synthesized in a quite similar way, using the same solvents and molar ratios. Elemental analysis of the compounds confirms the proposed general formula: M(H<sub>2</sub>L)<sub>2</sub>X<sub>2</sub> with M=Ni<sup>2+</sup>, Pd<sup>2+</sup>, Pt<sup>2+</sup>; X=Cl, Br, I; H<sub>2</sub>L=H<sub>2</sub>A (CH<sub>2</sub>(CSNH<sub>2</sub>)<sub>2</sub>) [12], H<sub>2</sub>B (C(CH<sub>3</sub>)<sub>2</sub>(CSNH<sub>2</sub>)<sub>2</sub>) (Table 1).

Table 1 Elemental analyses of M(H<sub>2</sub>B)<sub>2</sub>X<sub>2</sub>

	%C	%H	%N	%S	%M
Ni(H <sub>2</sub> B) <sub>2</sub> Cl <sub>2</sub>	27.42 (26.44)	4.70 (4.44)	12.15 (12.33)	27.07 (28.23)	10.73 (12.92)
Ni(H <sub>2</sub> B) <sub>2</sub> Br <sub>2</sub>	20.61 (22.12)	4.13 (3.71)	9.40 (10.32)	21.89 (23.62)	9.35 (10.81)
Ni(H <sub>2</sub> B) <sub>2</sub> I <sub>2</sub>	18.33 (18.85)	3.52 (3.16)	8.30 (8.80)	18.42 (20.13)	8.61 (9.12)
Pd(H <sub>2</sub> B) <sub>2</sub> Cl <sub>2</sub>	24.58 (23.93)	4.27 (4.02)	10.77 (11.16)	24.58 (25.55)	
Pt(H <sub>2</sub> B) <sub>2</sub> Cl <sub>2</sub>	21.12 (20.34)	3.55 (3.14)	9.34 (9.49)	21.16 (21.71)	

A Bruker IFS 113V Fourier Transform Spectrometer equipped with a Globar source and a liquid N<sub>2</sub> cooled MCT detector or a DTGS detector has been used for the mid IR region and for the far IR measurements respectively. The sample is pressed in KX or polyethylene. The Raman data have been collected on a Bruker IFS 66V equipped with a FRA 106 FT-Raman Accessory, a CW Nd:YAG laser source and a liquid N<sub>2</sub> cooled Ge detector. The TG and DTA curves have been recorded on a Seiko 200 TG-DTA and a DuPont 951 Thermobalance with a R90 controller (for the isothermal measurements) while simultaneous TG-MS has been performed for the identification of the compounds evolved during heating. A TGA Thermobalance model 2000 951 of TA Instruments has herefor been coupled to a quadrupole mass spectrometer model

Thermolab of VG Fisons Instruments with a mass range of 1–300 amu, using a flexible, heated silica lined steel capillary.

## Results and discussion

### A. Complexes of dithiomalonamide ( $H_2A$ )

In strong acidic medium dithiomalonamide acts as a neutral bidentate chelating ligand and cationic  $M(H_2A)_2X_2$  complexes can be isolated. From the full vibrational analysis, the u.v./vis. spectra and the magnetic measurements [12] can be derived that these compounds consist of a cationic part in which the metal ion is surrounded by four sulphur atoms in a square planar configuration and two halogenide counterions which are involved into hydrogen bonding with the free  $NH_2$  groups of the thioamide functions.

The thermal decomposition of these compounds, as shown in Fig. 1 for  $Ni(H_2A)_2Cl_2$ , passes through a series of consecutive losses of weight until metal sulphide (MS) remains. The loss of weight during the first, clearly endothermic step corresponds very accurately to the mass of two molecules of  $HX$ , qualitative tests of the evolved gases captured into an aqueous  $AgNO_3$ -solution confirm the

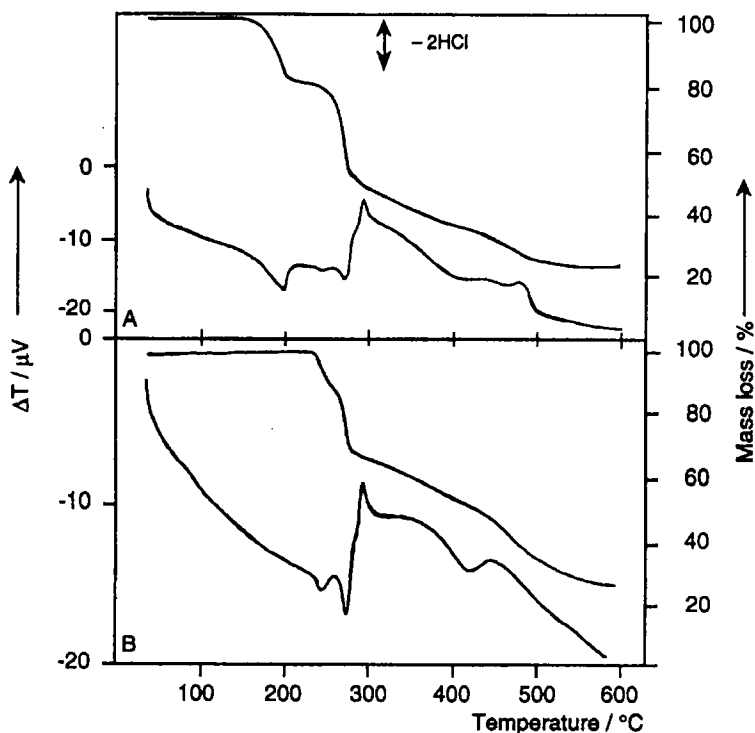


Fig. 1 TG and DTA curves and mid IR spectrum of  $Ni(H_2A)_2Cl_2$

hypothesis that the compounds have been deprotonated and 2HX are released. Undoubtedly, the strength of the interaction between the NH<sub>2</sub> groups and the counterions has a large influence on the temperature at which this reaction takes place. IR and Raman spectra provide us with a lot of information on this subject as the characteristic bands of the NH<sub>2</sub> groups are very sensitive towards intermolecular associations.

The nickel compounds containing Cl<sup>-</sup>, Br<sup>-</sup> and I<sup>-</sup> exhibit gradually weaker N-H-X<sup>-</sup> interactions as can be deduced from the upward shift of the  $\nu(\text{NH}_2)$  fundamentals in the 3500–3000 cm<sup>-1</sup> region and the shift of the NH<sub>2</sub> deformation modes towards lower wavenumbers. Also from the profiles of the bands and from the temperature effects the same conclusions can be drawn [12]. Table 2 schedules the temperature of deprotonation  $T_e$  (extrapolated onset-temperature). When  $T_e$  is compared for the three Ni(H<sub>2</sub>A)<sub>2</sub>X<sub>2</sub> complexes, we can observe that Ni(H<sub>2</sub>A)<sub>2</sub>Cl<sub>2</sub>, exhibiting the strongest interactions, is the least stable one and most easily releases two molecules of HX. The bromide and iodide analogues start to decompose at more or less the same temperature, being higher than for chloride.

**Table 2**  $T_e$  (extrapolated onset-temperature) and  $T_p$  (peak temperature in DTG) in °C for the complexes M(H<sub>2</sub>L)<sub>2</sub>X<sub>2</sub>

<i>M</i> , X=		Ni, Cl	Ni, Br	Ni, I	Pd, Cl	Pt, Cl
H <sub>2</sub> A	$T_e$	171	224	217	206	220
H <sub>2</sub> B	$T_e$	175	195	177	213	243
	$T_p$	196	206	188	256	275

Through the metal series M(H<sub>2</sub>A)<sub>2</sub>Cl<sub>2</sub> with *M*=Ni, Pd, Pt a similar comparison can be made: the  $\nu(\text{NH}_2)$  can be observed at systematically higher wavenumbers for Ni < Pd < Pt whereas the deformations show an opposite tendency [12]. Weaker interactions for platinum cause this complex to be the most stable and therefore to exhibit the highest value for  $T_e$ .

Further characterization of the decomposition pathway is possible by performing isothermal measurements at 150–155 °C in order to isolate an intermediate after deprotonation. This newly formed product has then been analysed and it has been proven to be a neutral compound with general formula M(HA)<sub>2</sub> in which the ligand is singly deprotonated at the central carbon atom in such a way as to allow for an extended electron delocalization into the chelate ring and to induce pseudo-aromaticity. This type of complexes can also be prepared in the laboratory starting from the appropriate metal salt and dithiomalonamide in a *M:L*=1:2 molar ratio under neutral conditions. Not only the vibrational analysis but also a close examination of the thermograms of Ni(H<sub>2</sub>A)<sub>2</sub>Cl<sub>2</sub> resp. Pd(H<sub>2</sub>A)<sub>2</sub>Cl<sub>2</sub> after deprotonation on one hand and of Ni(HA)<sub>2</sub> resp. Pd(HA)<sub>2</sub> on

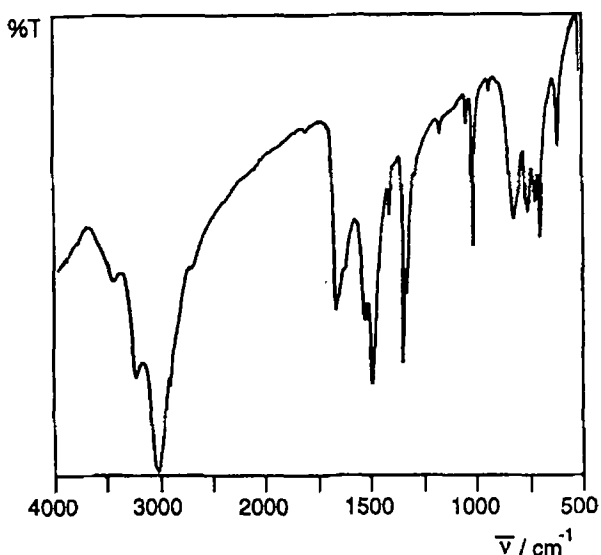
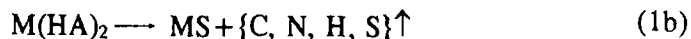
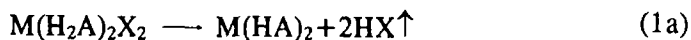


Fig. 2 TG and DTA curves of  $\text{Ni}(\text{H}_2\text{A})_2\text{Cl}_2$  and  $\text{Ni}(\text{HA})_2$

the other reveals similar thermal behaviour, as can be seen in Fig. 2 for the Ni-compounds. In the case of the other complexes ( $\text{Ni}(\text{H}_2\text{A})_2\text{Br}_2$ ,  $\text{Ni}(\text{H}_2\text{A})_2\text{I}_2$ ,  $\text{Pt}(\text{H}_2\text{A})_2\text{Cl}_2$ ) further degradation proceeds differently, due to the fact that the corresponding neutral compounds are not stable anymore at the temperature at which the deprotonation reaction is completed. This can also be derived from the IR spectra of these thermally prepared intermediates which already exhibit nitrile bands, clear signs of further decomposition.

The above results can be summarized as follows, where {C, N, H, S} represents a variety of fragments of the ligand:



#### B. Complexes of 2,2-dimethyldithiomalonamide ( $\text{H}_2\text{B}$ )

Under similar circumstances of solvents, acidity and molar ratios does 2,2-dimethyldithiomalonamide behave in a rather comparable way as previously described for the unsubstituted analogue dithiomalonamide. Stable cationic 1:2 complexes can be isolated in which the halogenides act as counterions and the metal ion is surrounded by four sulphur donor atoms in a square planar configuration. Indeed the vibrational analysis of the complexes reveals a striking analogy in coordinating abilities between  $\text{H}_2\text{A}$  and  $\text{H}_2\text{B}$  [14]. From the thermal measurements however we can deduce a completely different behaviour.

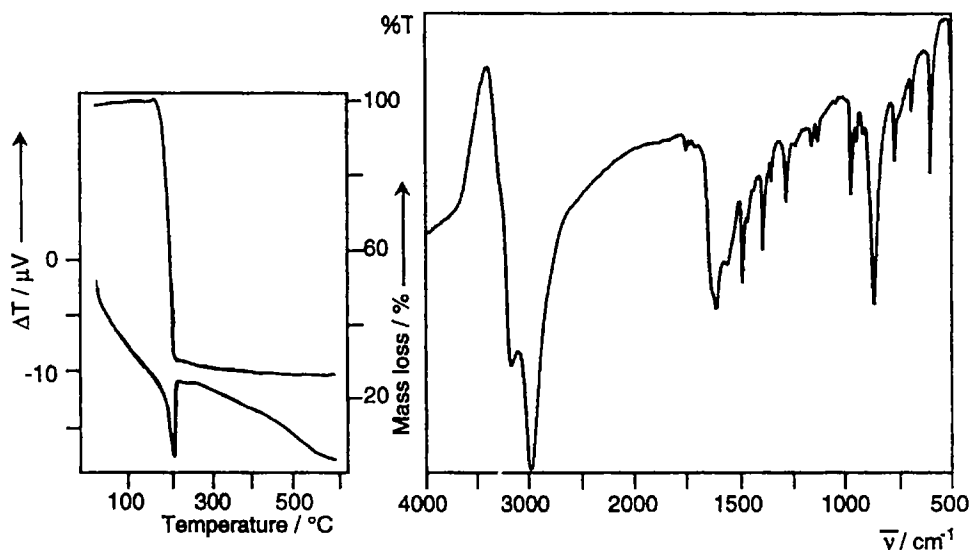


Fig. 3 TG and DTA curves and mid IR spectrum of  $\text{Ni}(\text{H}_2\text{B})_2\text{Cl}_2$

As can be observed in Fig. 3 for  $\text{Ni}(\text{H}_2\text{B})_2\text{Cl}_2$ , the  $\text{M}(\text{H}_2\text{B})_2\text{X}_2$  compounds degrade in one major step, leaving only metal sulphide (MS) behind. Some minor additional losses of weight do occur for two of the complexes but these are due to the release of associated solvent (AcOH). The presence of these solvate molecules is affirmed by the mid IR spectra, exhibiting medium weak to weak bands in the  $1750\text{--}1700\text{ cm}^{-1}$  region. The metal ion exerts a definite influence on both  $T_c$  (the temperature at which the loss of mass starts) and  $T_p$  (peak temperature at maximum weight loss in the DTG curve) as we can clearly observe an increase in stability in going from  $\text{Ni}^{2+}$  to  $\text{Pt}^{2+}$ , similar to the dithiomalonamide complexes, although the decomposition of the latter ones sets off at slightly lower temperatures. Variation of the halogenide does not seem to dramatically alter the thermal stability of the compounds (Table 2).

To get an idea about the reaction mechanism TG-MS analyses have been performed. During the degradation of the three chloride containing products  $\text{M}(\text{H}_2\text{B})_2\text{Cl}_2$ , traces of HCl,  $\text{H}_2\text{S}$ ,  $\text{CH}_3^+$  have been detected. Moreover, slight amounts of  $\text{H}_2\text{NCSC}(\text{CH}_3)_2\text{CN}$  have been deposited on the oven tube. For the  $\text{Br}^-$  and the  $\text{I}^-$  complexes no HBr or HI respectively could be observed, but no explanation is yet found for this phenomenon.

When we confine ourselves again to the chloride complexes, we can clearly see from vibrational analysis [14] that the interaction between the amide groups and the counterions is of a comparable strength through this metal series. This interaction is the determining factor in the decomposition of the complexes of dithiomalonamide. Releasing two molecules of HCl from  $\text{M}(\text{H}_2\text{A})_2\text{Cl}_2$  leads to

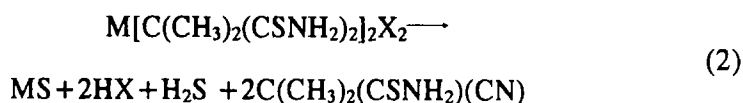
the immediate formation of the stable neutral  $M(HA)_2$  where the central C-atom is singly deprotonated. On further heating the ligand breaks down into fragments and finally metal sulphide remains. This mechanism can however not be applied to the  $H_2B$  compounds as no deprotonation can occur at the doubly substituted central carbon atom. Clearly, now the metal-sulphur bond strength is the most important parameter and the breaking of this bond probably determines the temperature at which the complexes decompose.

**Table 3**  $\nu(MS)$  vibrations ( $cm^{-1}$ ) for  $M(H_2B)_2Cl_2$

$M=$	Ni		Pd		Pt	
	IR	R	IR	R	IR	R
NCS-def.	453	456	457	460	456	464
NCS-def.	382	387	386	390	389	392
$\nu(MS)$	323	327	321	328	330	343
$\nu(MS)$	245	240	256	244	255	249
NCS-def.	226	197	230	202	231	204

The low frequency regions of the IR and Raman spectra of these compounds exhibit medium to strong bands which can be assigned to the  $\nu(M-S)$  vibrations and we can observe a shift from Ni to Pt towards higher wavenumbers (Table 3). This small increase in wavenumber indicates a large increase in force constant and thus bond strength, taking into account the downward shift expected from the mass effect, and confirms the increasing thermal stability.

These observations lead us the following representation of the decomposition process:



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## References

- 1 H. O. Desseyn, W. van Riel, L. van Haverbeke and A. Goeminne, *Trans. Metal Chem.*, 5 (1980) 88.
- 2 H. Hofmans, H. O. Desseyn and M. A. Herman, *Spectrochim. Acta*, 38A/12 (1982) 1307.
- 3 H. Hofmans and H. O. Desseyn, *Thermochim. Acta*, 85 (1985) 67.

- 4 B. Sloomakers, S. P. Perlepes and H. O. Desseyn, *Spectrosc. Int. J.*, 4 (1985) 265.
- 5 P. Geboes, E. L. Esmans and H. O. Desseyn, *Thermochim. Acta*, 124 (1988) 17.
- 6 F. Quaeys, H. O. Desseyn, B. Bracke and A. T. H. Lenstra, *J. Mol. Struct.*, 238 (1990) 139.
- 7 S. H. J. De Beukeleer and H. O. Desseyn, *Spectrochim. Acta*, 50A/14 (1994) 2291.
- 8 S. H. J. De Beukeleer, H. O. Desseyn, S. P. Perlepes and J. Mullens, *Thermochim. Acta*, 257 (1995) 149.
- 9 G. Peyronel, G. C. Pellacani, G. Benetti and G. Pollacci, *J. Chem. Soc. Dalton* (1973) 879.
- 10 A. Ray and D. N. Satharayana, *Ind. J. Chem.*, 15A (1977) 591.
- 11 L. P. Battaglia, A. B. Corradi, A. Marzotto, L. Menabue and G. C. Pellacani, *J. Cryst. Spectr. Res.*, 18/1 (1988) 101.
- 12 S. H. J. De Beukeleer and H. O. Desseyn, *Spectrochim. Acta*, 51A (1995) 1617.
- 13 H. Hlawatschek, G. Kiel and G. Gattow, *Z. Naturforsch.*, 36B (1981) 1386.
- 14 S. H. J. De Beukeleer and H. O. Desseyn, to be published.