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THERMAL ANALYSIS OF COBALT(II), NICKEL(II), COPPER(II) AND ZINC(II) BIS (3,5-DIMETHYL-1-PYRAZOLYL)DIHYDROBORATES *

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ABSTRACT

Complexes of general formula $M[H_2B(Me_2pz)_2]_2$, [where M = Co(II), Ni(II), Cu(II), and Zn(II)] are characterized by thermal analysis and complementary techniques. Mixtures of boron and metal oxides are found as final residues. Relative thermal stability (Ni > Cu > Co = Zn) and thermal behaviour are discussed. Melting and sublimation data are compared with those referred to in the literature.

INTRODUCTION

The bis(3,5-dimethyl-1-pyrazolyl)dihydroborate anion, $H_2B(Me_2pz)_2^-$, is known [1] to be a bidentate ligand which can give internal uncharged complexes with divalent metal ions (Fig. 1). When the coordination centre may exist in a tetrahedral or square planar environment, the resulting complex is monomeric and the tendency to accept additional ligand molecules (water or any other donor solvent), in order to obtain five- or six-coordination around the metal ion, is negligible. Indeed, the chelates can arrange themselves as square planar or tetrahedral conformation. In the planar complexes each $\overline{M-N-N-B-N-N}$ hexatomic ring has a pseudo-boat conformation, so that the space around the metal is screened by both the hexatomic and the pyrazolyl rings, and by the methyl substituents. As a consequence, metal pyrazolylborates are generally crystalline air-stable solids, soluble in organic solvents and volatile enough to be sublimed in vacuo and in inert atmospheres [1–3]. In this paper the thermal analyses of square planar Ni(II) and Cu(II) or tetrahedral Co(II) or Zn(II) complexes, having

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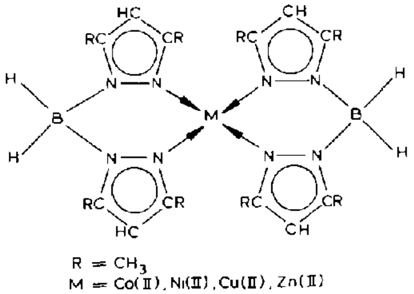

Fig. 1. The structure of bis(3,5-dimethyl-1-pyrazolyl)dihydroborate complexes with divalent metals.

general formula $M[H_2B(Me_2pz)_2]_2$ [4–6], are reported. TG, DTG and DTA have been used to check thermal stability as well as reactions induced by temperature increase in a nitrogen or oxygen stream. Other analytical techniques, such as IR and ESCA, provide additional information which is useful in order to explain the thermal behaviour of the compounds.

EXPERIMENTAL

Metal(II) bis(3,5-dimethyl-1-pyrazolyl)dihydroborates were prepared using the general procedure of mixing one equivalent of the metal ion with two equivalents of the potassium salt in solution. Products were filtered or extracted and recrystallized according to specific procedures [4,6], and checked by elemental analysis. TG and DTG curves were obtained using a DuPont model 951 thermobalance at 10°C min^{-1} with a flow rate of 100 ml min^{-1}. DTA experiments were performed in the same conditions using a DuPont 990 thermal differential analyser. IR spectra were obtained using a Perkin Elmer 177 spectrophotometer. ESCA measurements were carried out using a VG ESCA-3 photoelectron spectrometer with an Al $K\alpha_{1,2}$ source (1486.6 eV). Samples were dusted as thin films onto a gold plate.

RESULTS

Initially all the compounds were examined under a nitrogen stream to check the behaviour in an inert atmosphere. Results are shown in Fig. 2. In the TG, DTG and DTA curves a melting reaction at 235°C can be identified for the zinc compound, in agreement with the literature data [6]; and the cobalt compound shows a melting reaction at about 245°C, as reported by other authors [4], while decomposition and/or sublimation start at around 190°C. Copper and nickel compounds, on the contrary, do not allow melting

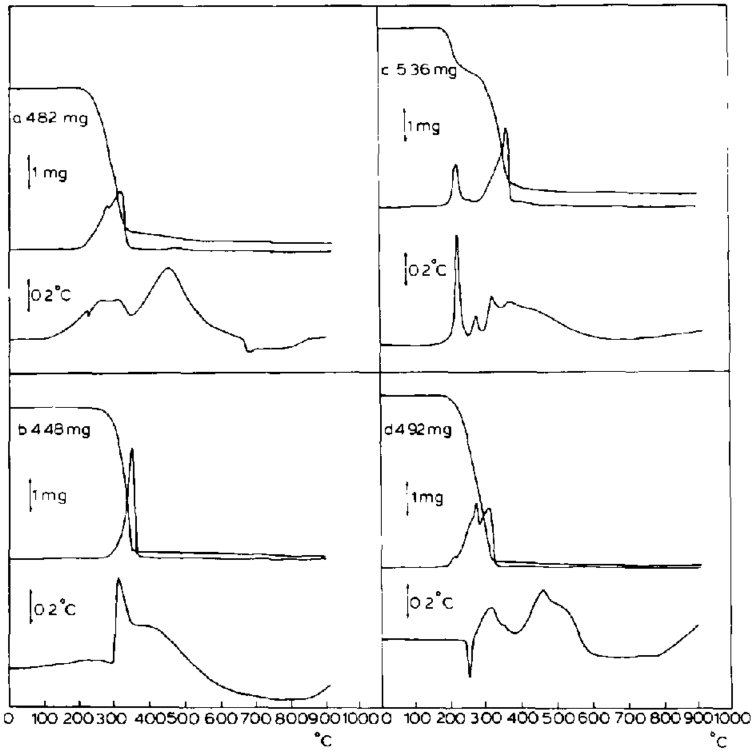

Fig. 2. TG, DTG and DTA of complexes with general formula $M[H_2B(3,5\text{-}Me_2pz)_2]_2$ carried out in a nitrogen stream (flow rate 100 ml min^{-1}) using a heating rate of 10°C min^{-1}. a, M = Co; b, M = Ni; c, M = Cu; d, M = Zn.

reactions to be identified in DTA curves owing to decomposition and/or sublimation starting at 190 and 240°C, respectively. However, in these experimental conditions the results obtained are not reproducible: the TG residues are always defective, even if considered with respect to metal amount and these residues are never the same. The behaviour of the residues, as well as the trend of TG curves, accounts for sublimation during thermal decomposition. Better results were obtained in an oxygen stream, as shown in Fig. 3, both considering the reproducibility of the curves and the definite residual weights. With the oxidant atmosphere too, melting reactions can be identified only for zinc and cobalt compounds. The other samples are thermally decomposed at a temperature lower than that reported for the melting reaction of the nickel compound, i.e. 245°C [4], and at a temperature a little higher than that reported for the first transition of the copper compound, i.e. 201°C [6]. The thermal decomposition takes place in three steps, except for the nickel compound where the first step cannot be evidenced. IR spectra of the initial compounds and of the residues formed at the end of the first step (residue at 310°C for nickel compound) are shown in

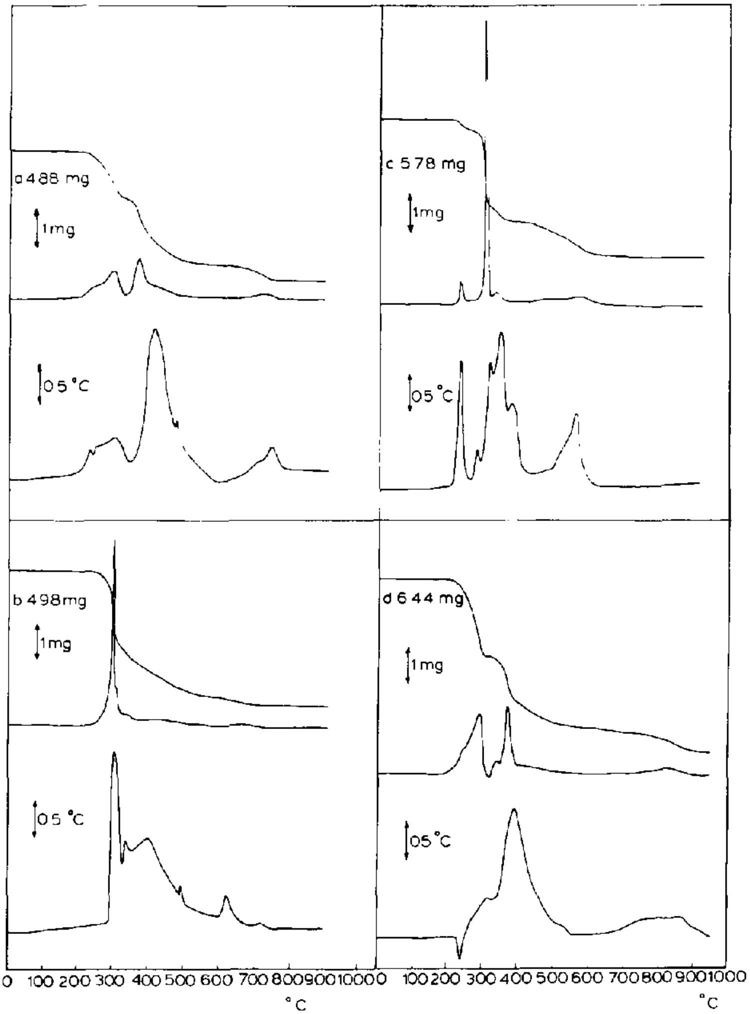

Fig. 3. TG, DTG and DTA of complexes with general formula $M[H_2B(3,5\text{-}Me_2pz)_2]_2$ carried out in an oxygen stream (flow rate 100 ml min^{-1}) using a heating rate of 10°C min^{-1}. a, M = Co; b, M = Ni; c, M = Cu; d, M = Zn.

Fig. 4. The spectra of nickel and copper complexes are in agreement with planar coordination, as well as those of cobalt or zinc with tetrahedral coordination [7]. This statement is based mainly on the pattern in the BH_2 stretching zone [7,8] (2250–2500 cm^{-1}) and on the pyrazole ring region (850–950 cm^{-1}). After the first decomposition step, BH bands can still be identified, together with those revealing the presence of organic structures. These residual structures agree with data reported in the literature describing the oxidation of the class of compounds which the complexes examined belong to. It is reported [7] that sublimation of $M[H_2B(Me_2pz)_2]_2$ complexes may be accompanied by formation of metal pyrazolates and pyrazaboles; in

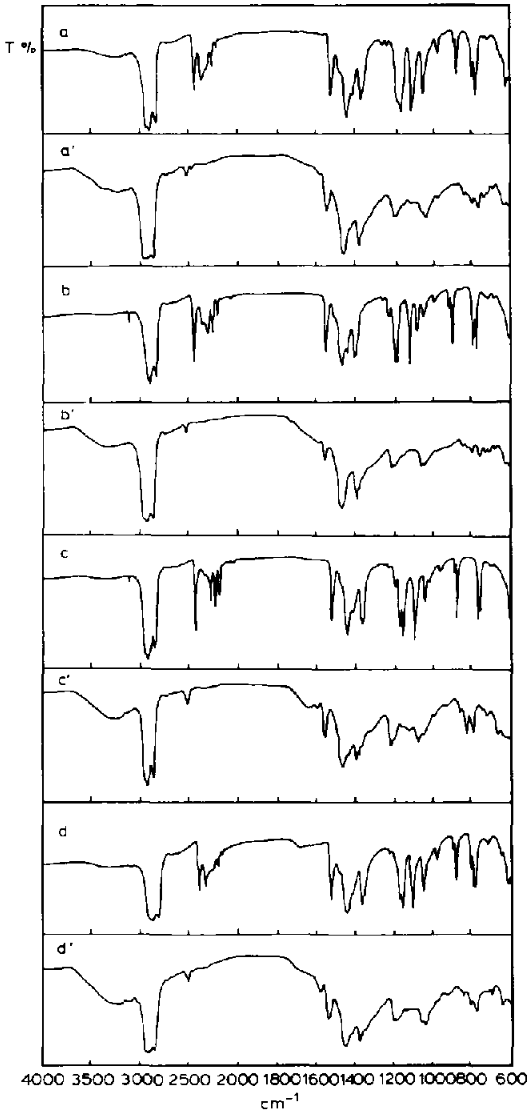

Fig. 4. IR spectra of complexes with general formula $M[H_2B(3,5\text{-}Me_2pz)_2]_2$. a, M = Co; b, M = Ni; c, M = Cu; d, M = Zn. a', b', c' and d' lines represent spectra of the residues after the first thermal decomposition in an oxygen atmosphere. Nujol was used as solvent.

this case, sublimation was accompanied by formation of the stable, sublimable and colourless 3,5-dimethylpyrazabole for which a melting temperature of 185°C was found [9]. Therefore, further thermal decomposition was expected to give mixtures of metal and boron oxides, the latter being defective with respect to the initial amount of boron. Following this assumption the residual weights at the end of the last decomposition were calculated and reported in Table 1. The known mixtures of boron and metal oxides

TABLE 1

TG of complexes with the general formula $M[H_2B(3,5\text{-}Me_2pz)_2]_2$

Results obtained in an oxygen stream (flow rate 100 ml min^{-1}) at a heating rate of 10°C min^{-1}. Weights are referred to the residue at the end of each step and are expressed as the fraction of the initial amount. Procedural decomposition temperatures (pdt) are also reported.

Metal, M	1st Step		2nd Step		3rd Step		
	Found (%)	pdt	Found (%)	pdt	Calcd. (%)	Found (%)	pdt
Co(II)	71.2	190	32.0	330	21.1	21.4	620
		300		375			720
		330		620			780
Ni(II)	67.2	230	26.0	310	21.1	20.8	580
		300		340			660
		310		580			780
Cu(II)	94.5	210	40.7	260	31.8	30.0	500
		225		300			560
		260		500			760
Zn(II)	64.6	190	29.3	330	22.2	20.7	700
		300		380			850
		330		700			930

showing better agreement with the results obtained are $B_2O_3 \cdot 3$ CoO [10], $B_2O_3 \cdot 3$ NiO [11], $B_2O_3 \cdot$ CuO [12] and $B_2O_3 \cdot 3$ ZnO [13]. ESCA measurements performed on initial compounds and on final residues account for the presence of boron and metal in the residue with a boron/metal ratio, calculated with respect to that existing in the initial compound, in agreement with the formula of the proposed mixtures of oxides. No specific reaction can be suggested for the second decomposition reaction. Carbon dioxide evolution was observed during the second and third step by bubbling the gas flowing from the furnace through barium hydroxide solution. IR spectra at the end of the second step do not show any bands, while the substance seems to be a dark solid, probably mixtures of boron and metal oxides with some carbon.

DISCUSSION

The results described in the present paper show that the melting points of the metal(II) bis (3,5-dimethyl-1-pyrazolyl)dihydroborates investigated cannot always be detected, even if they are reported in the literature. The expected melting reactions may be masked by decomposition, as in the case of nickel(II) and of copper(II), i.e. square planar complexes. However, the melting reactions are not completely masked by decomposition in the case of zinc(II) and cobalt(II), i.e. tetrahedral complexes. Probably decomposition reactions could not always be detected through visual observation. The behaviour observed here agrees with an effective saturation around the metal atoms, even if a higher number of ligands are coordinated in other cases, which is scarcely possible here owing to the bulkiness of the ligands. Very weak intermolecular bonds account for a low lattice stability [14,15] which may explain the volatility and the degree of sublimation of the compounds investigated here. The thermal stability is $Ni > Cu > Co = Zn$. This series results when the first decomposition step, under an oxygen or nitrogen atmosphere, is considered. A parallel series ($Ni > Cu > Co > Zn$) was found [1] for the $-\Delta H$ values of the enthalpies of chelation, although not all the details are known, e.g. solvent and precise experimental conditions, and if the measured values are ΔH_1, ΔH_2 or ΔH_{β_2}. The general highest thermal stability of the nickel complexes is also known and is explained in terms of a structural hypothesis [16]. It is interesting to observe that the copper complex, the second in the sequence, seems to be the only one where all the boron atoms are found in the residue ($B_2O_3 \cdot CuO$). Concerning the thermal stability sequence, it could be possible to hypothesize that the complex structure plays a main role. The higher thermal stability of the square planar complexes could probably be due to the possibility that these compounds form intermolecular bonds in the direction of the perpendicular axis. Consequently, planar Ni and Cu compounds are more stable, while decomposition (implying breaking of intermolecular bonds) takes place before a theoretical melting temperature is reached. Therefore, the previously proposed empirical model [14], ascribing the lower solid state stabilization to the solid complexes with stronger intramolecular (metal–donor) bonds, cannot be applied to this class of compounds. The possibility of intermolecular bond formation between a metal and a ligand coordinated to another metal, is so reduced that it cannot be regarded as inversely proportional to the intramolecular bond strength.

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