Thermochimica Acta, 54 (1982) 237–241
Elsevier Scientific Publishing Company, Amsterdam—Printed in The Netherlands

Note

THERMOGRAVIMETRY OF SOME NOBLE AND COMMON METAL CHELATES OF 1,3,4-THIADIAZOLE-2-THIOL-5-AMINO AND *N*-ACETYLACETONE-ANTHRANILIC ACID

K.N. JOHRI and B.S. ARORA

Department of Chemistry, University of Delhi, Delhi-110007 (India)

(Received 25 November 1980)

Thermogravimetric (TG) studies of a number of metal chelates with a view to determining their thermal stability and gravimetric evaluation of a variety of metal ions have been carried out by Johri et al. [1–3]. 1,3,4-Thiadiazole-2-thiol-5-amino (HTTA), a monoprotic bidentate ligand, forms coloured, crystalline and insoluble chelates with Ru(III), Rh(III), Pd(II), Ir(III) and Pt(IV) [4]. Similarly, *N*-acetylacetone-anthranilic acid (H_2-AAA), a diprotic tridentate ligand, forms coloured insoluble, crystalline chelates with the bivalent metal ions Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Pb(II) [5,6]. In the present communication, the results of the TG analysis of these chelates are reported.

EXPERIMENTAL

Synthesis of the ligands and chelates

1,3,4-Thiadiazole-2-thiol-5-amino was prepared by the method reported by Sandstrom [7].

9.3 g of thiosemicarbazide, 12 g of carbon disulphide and 75 ml of dry pyridine were refluxed for 2 h. Excess pyridine was then removed by vacuum distillation. The residue was dissolved in 400 ml of water at 70–80°C. On cooling, long, yellow-brown, rod-shaped crystals were formed which were collected and dried. The purity of the compound was ensured by m.p. determination (found, 235°C; reported, 234°C) and by TLC in benzene–alcohol (1 : 1) solvent system.

N-Acetylacetone-anthranilic acid was prepared by the method of Mehta et al. [5].

2.6 g of anthranilic acid was added to 2.0 ml of freshly distilled acetylacetone containing 2–3 drops of piperidine, which acts as condensing agent, and the mixture was stirred thoroughly. The contents were refluxed for an hour and cooled. The crude yellow product was recrystallized from methanol and dried. The purity of the H_2-AAA was checked by IR spectra [5] comparison and TLC in alcohol–water (1 : 1).

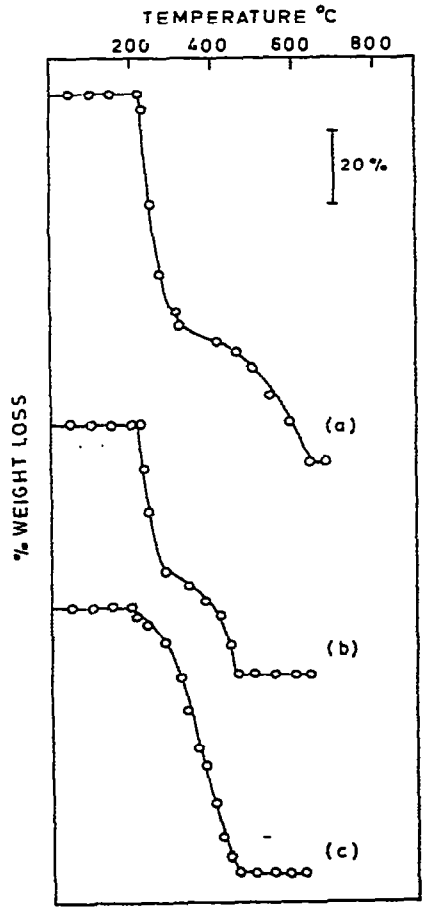
Metal chelates of HTTA. To a solution containing 15–20 μmole of the platinum

metal [Ru(III), Rh(III), Pd(II), Ir(III) and Pt(IV)] salt solution, 50–80 μmole of HTTA solution in 50% alcohol was added. The resulting precipitate was digested, separated and washed with water, alcohol and ether.

Metal chelates of H_2-AAA. Each metal salt solution (0.01 M) buffered at pH 4.0–5.0 with sodium acetate–acetic acid, was mixed with an equivalent amount of H_2-AAA solution (0.01 M). The precipitated metal complex was collected washed with water and aqueous alcohol and dried.

TG analysis. The TG of each chelate was carried out by the automatic recording thermobalance Setaram G-70, under the following conditions

Heating rate	20°C min^{-1}
Atmosphere	self-produced
Sensitivity	20° per small division
Sensitivity of balance	2 mg per small division
Furnace	0–1000°C
Sample	20–30 mg



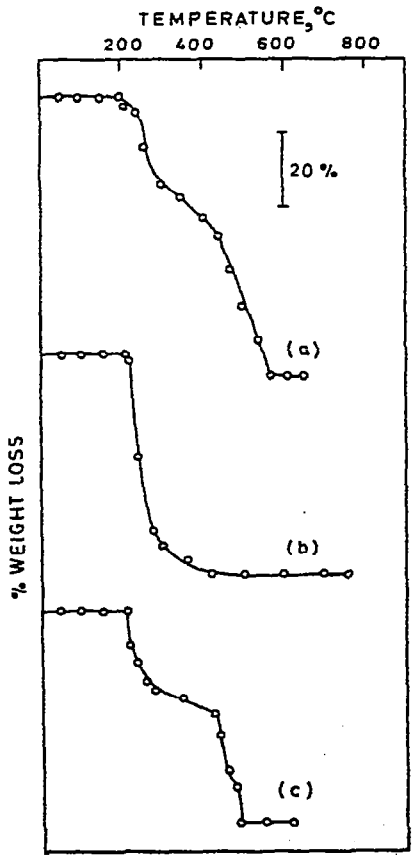


Fig. 1. TG curves of (a) HTTA, and the HTTA complexes of (b) Ru(III) and (c) Rh(III).

Fig. 2. TG curves of the HTTA complexes of (a) Pd(II), (b) Ir(III) and (c) Pt(IV).

Pre-weighed samples in a quartz crucible were heated within the furnace in contact with air and the effect of heating from room temperature to 1000°C on the mass of each solid chelate was recorded on chart paper. Thermal decomposition curves, showing loss in weight at various temperatures, were plotted (Figs. 1–4). The Coats–Redfern equation for a reaction order of $n = 1$ was ensured throughout for each sample. The activation energy values were found to fall within a narrow range. The summary of the results depicting temperatures at which significant changes occurred and also the observed/calculated yield of the respective metal oxides are summarised in Table 1.

RESULTS AND DISCUSSION

The TG curves reveal that metal–HTTA and metal–H_2-AAA chelates are stable at least up to 200°C. The general nature of all the TG curves is similar in that there

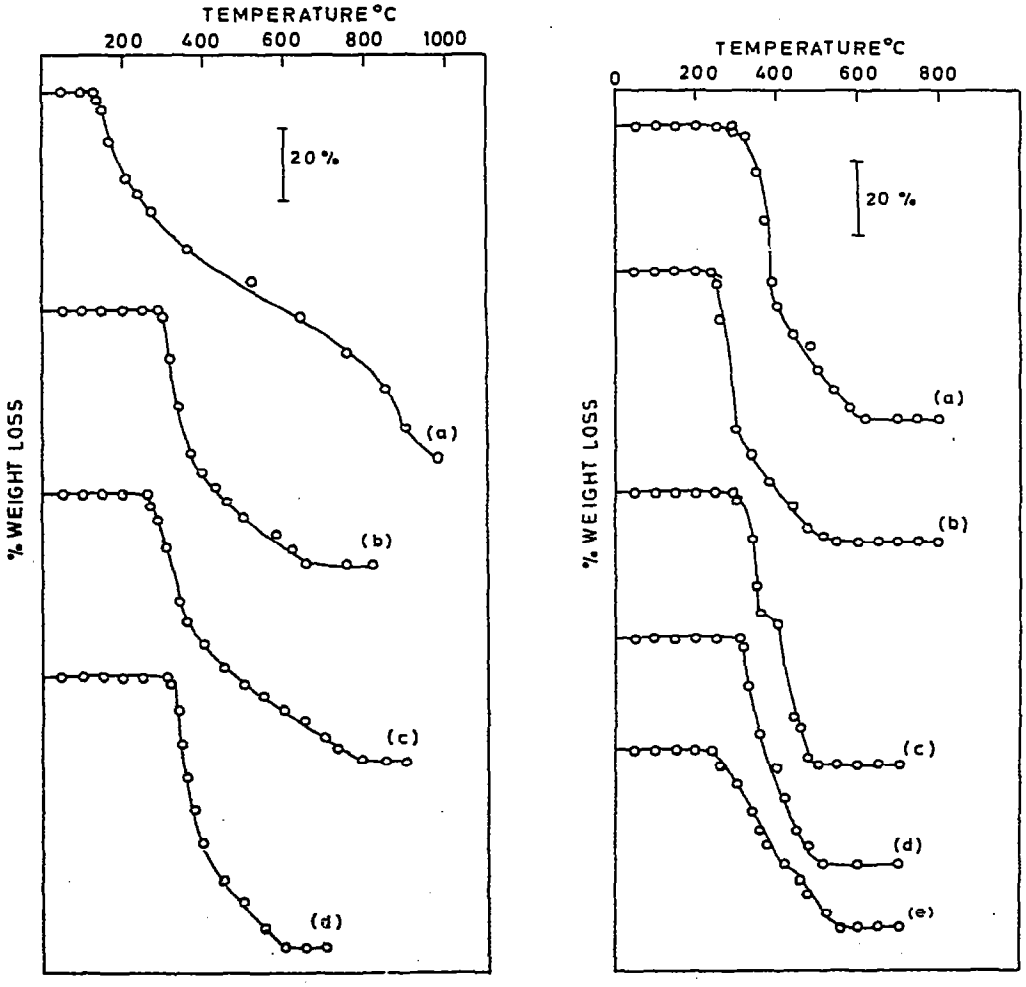


Fig. 3. TG curves of (a) H_2-AAA, and the H_2-AAA complexes of (b) Mn(II), (c) Fe(II) and (d) Co(II).

Fig. 4. TG curves of the H_2-AAA complexes of (a) Ni(II), (b) Cu(II), (c) Zn(II), (d) Cd(II) and (e) Pb(II).

TABLE 1

Thermogravimetry of metal chelates of HTTA/H_2-AAA

Compound	Decomposition temp. (°C)		Probable nature of residue	Actual weight loss [a] (%)
	Initial	Final		
$Ru(C_2H_2N_3S_2)_2Cl$	220	520	Ru	68.0 (70.0)
$Rh(C_2H_2N_3S_2)_2Cl$	210	460	Rh	71.4 (69.6)
$Pd(C_2H_2N_3S_2)_2$	210	570	Pd	76.2 (71.8)
$Ir(C_2H_2N_3S_2)_2Cl$	210	420	Ir	60.0 (55.1)
$Pt(C_2H_2N_3S_2)_2Cl_2$	210	480	Pt	57.2 (58.2)
$Mn_2C_{24}H_{22}O_6N_2$	300	660	Grey, MnO_2	69.6 (68.1)
$Fe_2C_{24}H_{22}O_6N_2$	265	780	Brown, Fe_2O_3	72.4 (70.1)
$Co_2C_{24}H_{22}O_6N_2$	320	600	Black, CoO	72.7 (78.7)
$Ni_2C_{24}H_{22}O_6N_2$	290	620	Black, NiO	80.0 (78.8)
$Cu_2C_{24}H_{22}O_6N_2$	250	550	Brown, CuO	73.3 (71.6)
$Zn_2C_{24}H_{22}O_6N_2$	300	500	White, ZnO	74.2 (71.2)
$Cd_2C_{24}H_{22}O_6N_2$	320	510	White, CdO	60.9 (61.0)
$Pb_2C_{24}H_{22}O_6N_2$	240	560	Black, PbO	47.8 (49.3)

[a] Calculated weight loss in parentheses.

is one step decomposition throughout. Rh(III)–HTTA, Cd(II)–H_2-AAA and Pb(II) –H_2-AAA chelates show uniform rates of decomposition, whereas in the case of other chelates, the rate of thermal decomposition decreases after 40–45% weight loss. This, presumably, may be due to the oxidation of metals to their oxides within the respective temperature ranges. The initial horizontal part of the curves is considered suitable for the gravimetric determination of these metal ions in the form of their respective metal–HTTA/H_2-AAA chelates. The linearity of the Coats–Redfern plot [8] for a reaction order of $n = 1$ is ensured throughout for all the products. The activation energy values vary within a narrow range.

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