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SOME TETRAZOLIUM SALTS AND THEIR ION-ASSOCIATION COMPLEXES WITH THE MOLYBDENUM(VI) – 4-NITROCATECHOL ANIONIC CHELATE
DTA and TGA study

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Several commercially available 2H-tetrazolium salts (TS) {2,3,5-triphenyl-2H-tetrazolium chloride (TTC), 3-(1-naphthyl)-2,5-diphenyl-2H-tetrazolium chloride (Tetrazolium Violet, TV), 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyl-2H-tetrazolium bromide (MTT), 2-(4-iodophenyl)-3-(4-nitrophenyl)-5-phenyl-2H-tetrazolium chloride (INT) and 3,3'-(3,3'-dimethoxy-4,4'-biphenylene)-bis(2,5-diphenyl-2H-tetrazolium) chloride (Tetrazolium Blue Chloride, BTC)} and their ion-associated complexes (IAC) with the Mo(VI) – 4-nitrochatechol (4-NC) anionic chelate $[MoO_2(4\text{-}NC)_2]^{2-}$ have been investigated by differential thermal analysis (DTA) and thermogravimetric analysis (TG). Some special features of the thermal behavior of the compounds have been discussed. The results show that the thermal stability of IAC depends on the factors determining the values of their association constants β: molecular mass and the presence of nitrophenyl substituent(s) in the tetrazolium ring.

Keywords: *ion-associated complexes, 4-nitrocatechol, tetrazolium salts, thermal decomposition, thermal stability*

Introduction

Tetrazolium salts (TS) are compounds possessing a five-membered ring of one carbon and four nitrogen atoms; one of these atoms bears a positive carge. The most important are trisubstituted mono- and di-TS which contain a substituent at the carbon atom (position 5 in tetrazolium ring). 2,3,5-TS have been applied as redox indicators for detection of various systems [1–6], phase-transfer catalysts [4, 7–9], photosensitive materials [4], analytical reagents [10–18], components of colorless ink for ink jet printers [19], charge-controlling agents for color toner, electro-photography etc. [20]. Some 1,4,5-TS have been found to be promising new materials for gas generating mixtures, propellants and explosives [21–23].

2,3,5-TS attracted our attention by virtue of the ability of their cations to form ion-associated complexes (IAC), which could be used for selective and sensitive determination of many elements or species involved in the anionic part of the IAC [10]. To define more precisely the areas of application of these complexes we need information about their thermal stability. However, the data reported in the literature on this subject, as well on the thermal behavior of TS itself are quite limited [4]. Patnaik *et al*. [24] have studied the thermal behavior of some 2,3,5-triphenyltetrazolium halochromates, while Boyanov *et al*. have reported data about the thermal stability of Sb(V)–2,5-diphenyl-3-(1-naphthyl)-tetrazolium IAC [25] and Mo(VI)–4-nirocatechol (4-NC)–3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyl-2H-tetrazolium 1:2:2 IAC [26].

The goal of the present work was to study and compare the thermal behavior of five widely used 2,3,5-TS (Table 1) and their IAC with the anionic Mo(VI)–4-NC chelate $[MoO_2(4\text{-}NC)_2]^{2-}$ [26, 27]. The road to reach this goal included DTA and TG investigations on 4-NC. 4-NC is a suitable ligand for the formation of stable complexes [28–30] and a well known analytical reagent [26, 27, 31–33], but no information is available in the literature about its thermal behavior.

The thermal decomposition of several molybdenum complexes with nitrogen and nitrogen–oxigen donor ligands was studied by Soliman *et al*. [34]. In present article we throw more light on the thermal stability of tetrazolium IAC and reveal the importance of association constant β value for this stability.

Experimental

TTC, TV, MTT and INT (p.a.) (Table 1) were purchased from Loba Feinchemie AG. BTC (BioChemika, for

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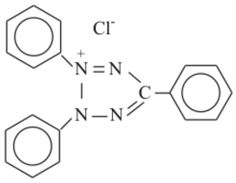
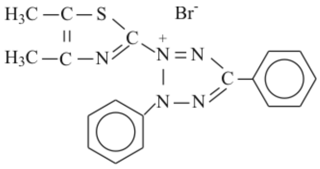
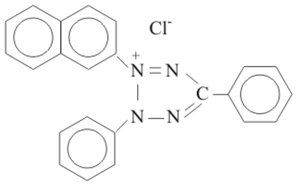
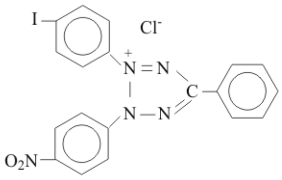
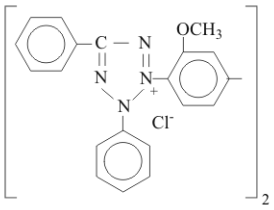
Table 1 Formulae, abbreviations and molecular masses (M_{TS}) of used tetrazolium salts and molecular masses of their cations (M_{TC})

Formula	Name and abbreviation	M_{TS}	M_{TC}
	2,3,5-triphenyl-2H-tetrazolium chloride (TTC)	334.41	298.96
	3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyl-2H-tetrazolium bromide (thiazolyl blue tetrazolium bromide, MTT)	414.31	334.41
	3-(1-naphthyl)-2,5-diphenyl-2H-tetrazolium chloride (tetrazolium violet, TV)	384.86	349.41
	2-(4-iodophenyl)-3-(4-nitrophenyl)-5-phenyl-2H-tetrazolium chloride (INT)	505.70	470.25
	3,3'-(3,3'-dimethoxy-4,4'-biphenylene)-bis(2,5-diphenyl-2H-tetrazolium) chloride (tetrazolium blue chloride, BTC)	727.66	656.76

microbiology) (Table 1), $Na_2MoO_4\cdot 2H_2O$ (p.a.) and 4-nitrochatechol (4-NC) (p.a.) were purchased from Fluka. For preparation of IAC equal volumes of aqueous solutions of Mo(VI) ($5\cdot 10^{-4}$ mol dm^{-3}), 4-NC ($1\cdot 10^{-2}$ mol dm^{-3}) and TS ($2\cdot 10^{-3}$ mol dm^{-3}) were mixed in acidic medium (pH 2.8–4.0). After homogenization the mixtures were filtered through a glass filter G4. The precipitates were washed carefully with cold water and dried up to 75–80°C.

DTA and TG were carried out with Q Derivatograph of the Hungarian company MOM at the following conditions: sensitivity of DTA, 1 mV; DTG, 1 mV; TG, 100 mg; heating rate, 10°C min^{-1}; sample mass 50 mg. Platinum crucible was used and all studies were carried out in static air medium.

The IR spectra were recorded using KBr pellets on a Perkin Elmer 1750 FT-IR spectrometer (USA).

Results and discussion

Thermal behaviour of TS

DTA and TG curves of the investigated TS are shown in Fig. 1. It can be seen that TS are stable up to 190–220°C. This fact illustrates the stability of the tetrazolium ring, which is in agreement with the literature [4]. The data from IR spectra shows that at higher temperatures the peak at about 1530 cm^{-1} (characteristic for tetrazolium ring [4]) disappears. Therefore, the tetrazolium ring does not exist at mentioned temperatures. The opening of the tetrazolium ring is accompanied with quick mass loss (Fig. 1) and intensive exothermic effect (at 190–240°C). The percentage of mass loss corresponds to the dissociation of the substituent situated at the quaternary nitrogen atom (Table 2). More special is the first dissociation step of TTC. This TS remains stable at higher temperatures (220°C) in comparison with the other TS and loses simultaneously two C_6H_5 substituents. IR spectra of the decomposition products of TTC at 245°C (Fig. 2) show that the group $C\text{-}C_6H_5$ remains unaffected at mentioned temperature. Therefore, in the interval 220–240°C TTC loses the substituents situated at two nitrogen atoms (positions 2 and 3 in tetrazolium ring), which lie (according to [4]) out of the plane of the tetrazolium ring.

It can be seen from Fig. 1 that in all samples the first intensive exothermic effect is followed by gradual mass loss. The processes of slow additional oxidation are not identical for all TS. TTC, MTT and TV are oxidized more gradually to complete mass loss than INT and BTC. The maxima of exothermic effects for the first three TS lie in the interval 520–620°C. The most continuous oxidation process (up to 780°C) is observed for TV. For MTT and TTC almost complete

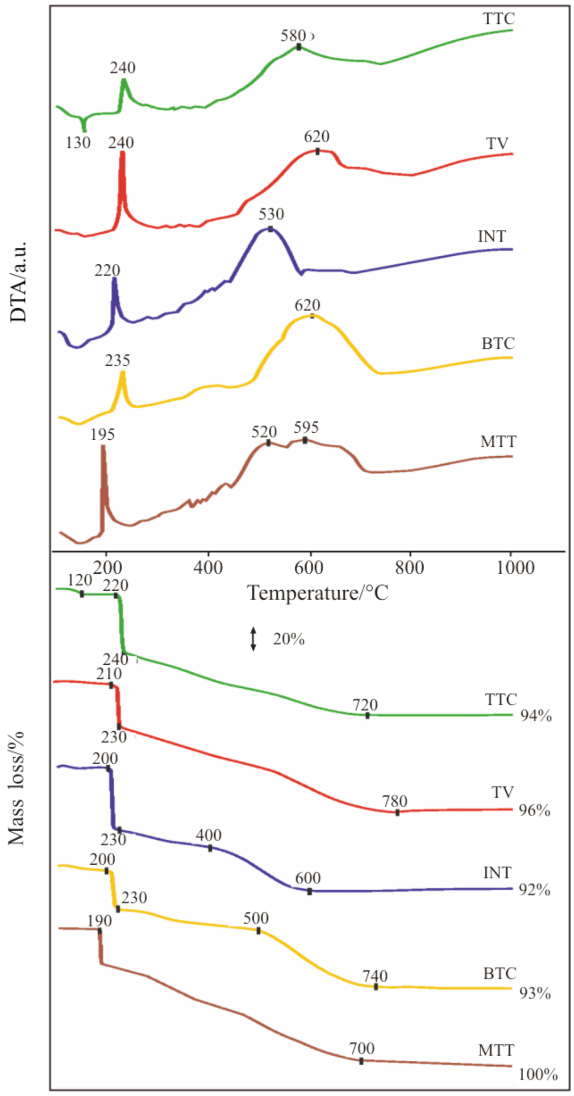


Fig. 1 DTA and TG curves of TS (TTC, MTT, TV, INT and BTC)

Table 2 Experimental and calculated first step mass loss of TS

N	TS	Temperature/°C	Expelled fragments	Experimental mass loss/%	Calculated mass loss/%
1	TTC	220–240	$2(C_6H_5)$	48.0	46.1
2	TV	210–230	$C_{10}H_7$	33.0	33.6
3	INT	200–230	C_6H_4I	40.1	42.4
4	BTC	200–230	$2(OCH_3C_6H_5)$	29.1	28.0
5	MTT	190–200	C_5H_6NS	25.6	27.1

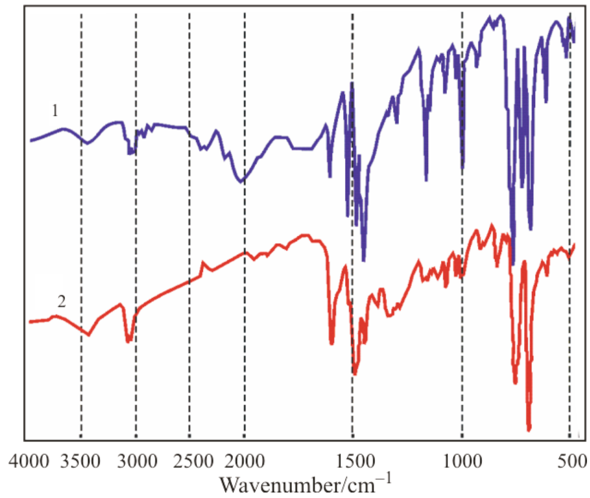


Fig. 2 IR spectra of TTC (curve 1) and its decomposition products at 245°C (curve 2)

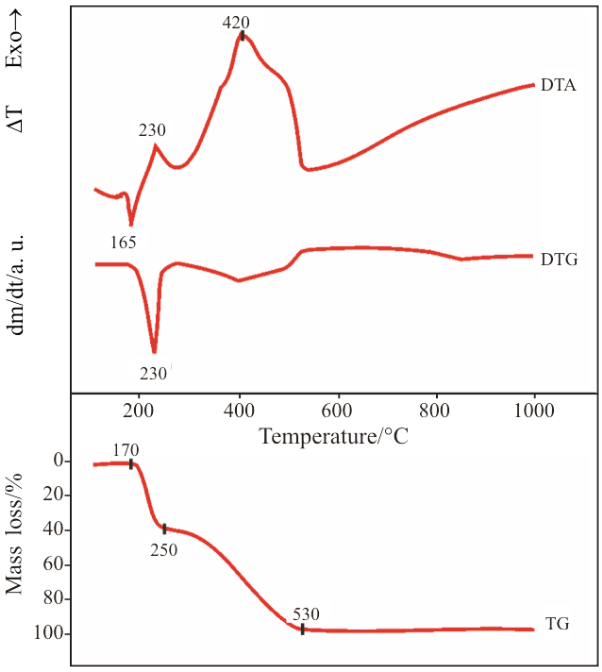


Fig. 3 TG, DTA and DTG curves of 4-NC

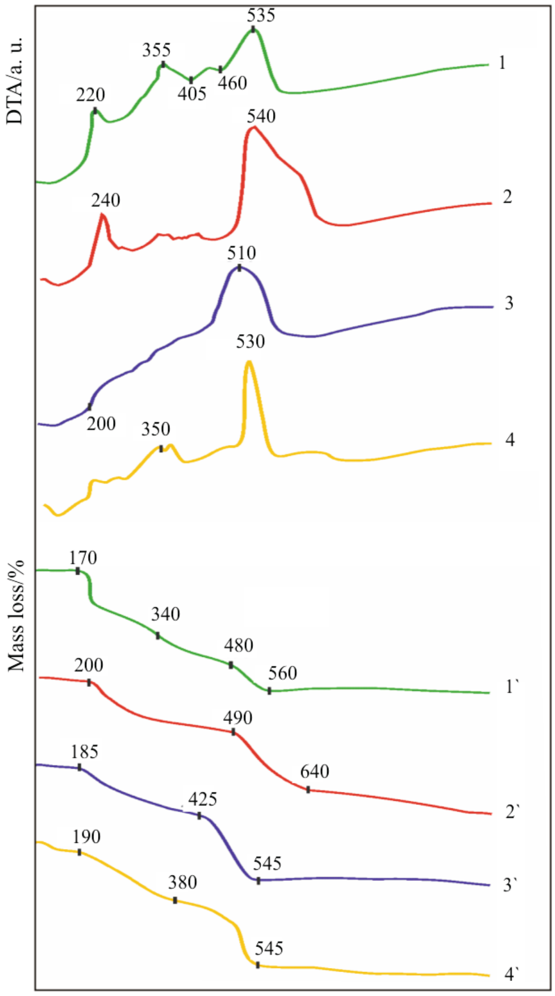


Fig. 4 1–4 – DTA and 1'–4' – TGA curves of IAC. 1,1' – $(TT)_2[MoO_2(4\text{-}NC)_2]$, 2,2' – $(TV)_2[MoO_2(4\text{-}NC)_2]$, 3,3' – $(INT)_2[MoO_2(4\text{-}NC)_2]$, 4,4' – $(BT)[MoO_2(4\text{-}NC)_2]$

mass loss occurs at 700–720°C. The additional oxidation and mass loss of the other two TS (INT and BTC) takes place at two steps. The first one finishes at about 400°C (for INT) and 500°C (for BTC), while the second one – at about 600 and 740°C respectively. The second oxidation step is characterized with more intensive mass loss. The maxima of the corresponding exothermic effects lie at 530 and 620°C.

Thermal behaviour of 4-NC

The thermal behavior of 4-NC is shown in Fig. 3. The compound is stable up to 170°C. The mass loss of the first decomposition step (170–250°C) was determined to be ~40%, which is in good agreement with the assumption that 4-NC loses simultaneously NO_2 and H_2O (calculated value 41.3%). The second, more gradual step of oxidation and mass loss finishes at 530°C. The maxima of the corresponding exothermic effects lie at 230 and 420°C. The endothermic peak at 165°C is related to the melting region of 4-NC.

Thermal behaviour of IAC

Investigated 1:2:2 (Mo:4-NC:TC^+) or 1:2:1 (Mo:4-NC:BT^{2+}) IAC are stable up to 170–200°C (Fig. 4). Note that IAC with TV^+, INT^+ and BT^{2+} are more stable than 4-NC, while the complex with TT^+ starts to decompose at the same temperature as 4-NC – 170°C. Having in mind that TTC is the most stable TS, one can conclude that there is no correlation between the thermal stability of the ternary IAC with

Table 3 Experimental and calculated first step mass loss of IAC

N	IAC	Temperature/°C)	Expelled fragments	Experimental mass loss/%	Calculated mass loss/%
1	$(TT)_2[MoO_2(4\text{-}NC)_2]$	170–230	$2NO_2+2C_6H_5$	24.0	23.8
2	$(TV)_2[MoO_2(4\text{-}NC)_2]$	200–490	$2NO_2+2C_{10}H_7+2C_6H_5$	40.0	44.2
3	$(INT)_2[MoO_2(4\text{-}NC)_2]$	185–425	$2NO_2+2C_6H_4I$	37.7	36.2
4	$(BT)[MoO_2(4\text{-}NC)_2]$	190–380	$2\{C_6H_3(OCH_3)\}+2C_6H_5+2NO_2$	40.4	42.0
5	$(MTT)_2[MoO_2(4\text{-}NC)_2]$*	180–200*	$2NO_2+2C_5H_6NS+2C_6H_5$	40.9*	42.7

* Taken from [26]

participation of 4-NC and TS from which they derive. It is known from the literature [10, 35, 36] that the formation constant β (characterizing the association process between the tetrazolium cation and the anionic chelate) depends on two factors – molecular mass and presence of nitrophenyl substituent(s) in the tetrazolium ring. The first factor influences positively, while the second factor influences negatively the value of β. The results presented in this study give us grounds to assume that the thermal stability of the monotetrazolium IAC depends on the same two factors (Fig. 5): the most stable (temperature of decomposition 200°C) is IAC with TV^+, which has higher molecular mass than TT^+ and MTT^+ and does not contain a nitrophenyl group (in contrast to INT^+).

Having in mind that the molecular mass of neotetrazolium cation (NT^{2+}) (M_{NT}=596.70) is lower than the molecular mass of BT^{2+} and that nitrobluetetrazolium cation (NBT^{2+}) and tetranitrobluetetrazolium cation ($TNBT^{2+}$) contain nitrophenyl groups we expect that uninvestigated IAC $(NT)[MoO_2(4\text{-}NC)_2]$, $(NBT)[MoO_2(4\text{-}NC)_2]$ and $(TNBT)[MoO_2(4\text{-}NC)_2]$ will be thermally more labile than $(BT)[MoO_2(4\text{-}NC)_2]$.

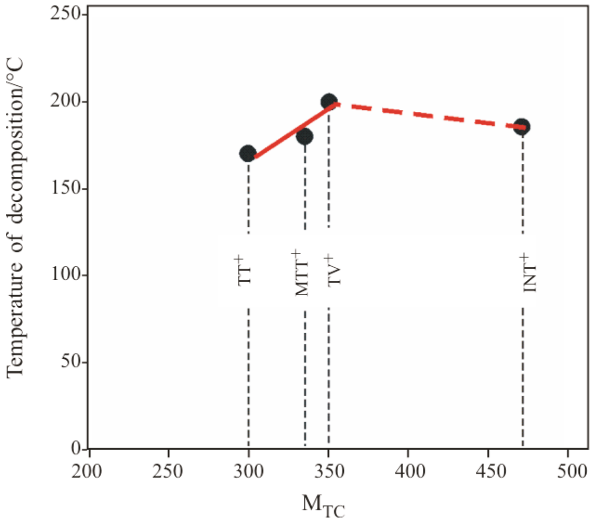


Fig. 5 Temperature of decomposition of $(TC)_2[MoO_2(4\text{-}NC)_2]$ *vs*. molecular mass of monotetrazolium cation (M_{TC}) plot. The thermal stability of IAC —– increases with increase of M_{TC} and --- – decreases if TC contain nitrophenyl group

Data for the first decomposition step of IAC are included in Table 3. The percentage of mass loss of IAC with TT^+ and INT^+ corresponds to the dissociation of the NO_2-group from 4-NC along with the substituent at the quaternary nitrogen atom in the tetrazolium ring. IAC with TV^+ and BT^{2+} remain stable at higher temperature in comparison with the IAC with TT^+ and INT^+ and lose simultaneously another substituent in tetrazolium ring (most probably C_6H_5 situated at N(3)). The same conclusion can be drawn from the data for $(MTT)_2[MoO_2(4\text{-}NC)_2]$ reported in [26].

The final product in all cases most probably is MoO_3. This compound is known to be noticeably volatile at temperatures above 600°C [37].

Conclusions

- Investigated TS (TTC, MTT, TV, INT and BTC) are stable up to 190–220°C. The first decomposition step of TS includes destroying of tetrazolium ring and expelling the substituent situated at the quaternary nitrogen atom. The most stable TS–TTC loses simultaneously two phenyl substituents.
- 4-NC is stable up to 170°C. The first decomposition step includes release of NO_2 and H_2O.
- IAC are stable up to 170–200°C. In all cases the first decomposition step is related to the release of NO_2 from 4-NC along with the substituent situated at the quaternary nitrogen atom in the tetrazolium ring. The complexes with TV^+, BT^{2+} and MTT^+ lose simultaneously another substituent in the tetrazolium ring (probably at N(3)).
- There is no correlation between the thermal stabilities of IAC and the TS, from which they derive. The thermal stability of IAC probably depends on the factors determining the value of their association constants β: molecular mass and the presence of nitrophenyl substituent(s) in the tetrazolium ring. The most stable is IAC with TV^+. The mentioned monotetrazolium cation has higher molecular mass

than TT^+ and MTT^+ and does not contain nitrophenyl substituents in its tetrazolium ring.

- IAC with ditetrazolium cation BT^{2+} is stable up to 190°C. On the basis of data mentioned in a previous point one can assume that $(BT)[MoO_2(4\text{-}NC)_2]$ is thermally more stable than uninvestigated IAC with some other well known ditetrazolium cations, such as NT^{2+}, NBT^{2+} and $TNBT^{2+}$.
- The investigated TS and their IAC with Mo and 4-NC are stable enough to be applied trouble-free in analytical chemistry and other practical areas.

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