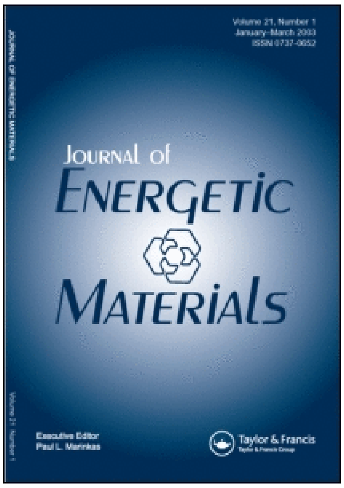

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STUDIES ON THERMAL DECOMPOSITION AND EXPLOSIVE PROPERTIES OF SOME NOVEL METAL COMPLEXES OF ARYL MERCAPTO TETRAZOLES

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ABSTRACT

Several energetic metal complexes of aryl mercapto tetrazoles have been investigated for their thermal decomposition and explosive properties. Peak decomposition temperatures and the enthalpy of decomposition data have been used to assess the thermal reactivity of the ligands and their corresponding metal complexes. Among the different ligands studied, ortho nitro phenyl mercapto tetrazole (ONPMT) is the most thermally sensitive one, thus confirming the tetrazole group to be a trigger group. Metal complexes (with metal ions from 3d transition metal ion series and heavy metal ions such as Hg (II) and Pb (II) ions)

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synthesised with ONPMT exhibit a high degree of explosive sensitivity, comparable to other primary explosives. While Ag(I)-ONPMT complex is the most sensitive, the chloro complex of Ni(II) is the most stable one. Attempts have been made to explain the thermal and explosive sensitivity characteristics of the metal-ligand complexes keeping in view the various physico-chemical factors affecting sensitivity. Some preliminary structure - property correlations could be drawn. Standard performance tests carried out on a few tetrazole-metal complexes reveal that their performance is comparable to that of lead styphnate. These complexes are, however, inferior in their initiating strength with respect to dextrinated lead azide, perhaps due to their lower bulk density.

INTRODUCTION

Recently considerable efforts are being directed towards the development of high energy inorganic coordination compounds, such as 2-(5-cyanotetrazalato)pentammine cobalt(III) perchlorate, commonly referred to as CP.[1,2] Such complexes enable us to carry out a "chemical tailoring" of the molecule such that various chemical groups which are essential for complexation to occur and result in optimum explosive sensitivity can be introduced into the molecule by a proper choice of the ligand. The present work is an attempt in this direction to synthesise metal complexes with novel and appropriate ligands and characterise the same for their structure and potential explosive properties. Tetrazoles offer interesting possibilities as ligands since various derivatives can be synthesised. These could yield metal complexes possessing properties characteristic of energetic molecules. In general, the term "energetic" will be used in this paper to refer to compounds which decompose in an exothermic manner. Sufficient data on tetrazoles is available to make structure/property correlations. Thus, it has been found that in the case of 5- susbstituted nitrotetrazoles, groups such as nitro and methyl impart high sensitivity while the effect of amine is much less.[3] It was felt that these results could aid us in choosing the chemical groups required for sensitivity. In addition, the ligand should have the necessary groups for complex formation with metal ions. Common functional groups which yield stable complexes should either be of electron donor type or contain a lone pair of electrons. A few examples of such groups are amine, carbonyl, carboxyl, thiol, etc. A literature survey has revealed that metal complexes of aryl mercapto tetrazoles have not been investigated thus far. Therefore, it was planned to prepare transition and heavy metal ion complexes of ortho nitro phenyl mercapto tetrazole.

This paper primarily deals with the investigations on the thermal and explosive properties of energetic metal complexes of aryl mercapto tetrazoles. Characterisation of their metal complexes based on metal ions from 3d series such as Cu(II), Co(II), Ni(II) and also with other metal ions like Hg(II), Pb(II) and Ag(I) has been investigated. Extensive thermal studies have been done on all ligands and metal complexes using techniques such as thermogravimetry and differential scanning calorimetry. Sensitivity tests such as friction and impact sensitivity, heat sensitivity and spark sensitivity have also been carried out on all the ligands and their metal complexes. The most sensitive ones have been chosen for explosive performance evaluation by carrying out tests like minimum value and lead plate perforation tests and performance compared with that of standard primary explosives such as lead azide and lead styphnate.

EXPERIMENTAL

A. Ligands

The ligands chosen are the following:

1. 1-(2-nitrophenyl)-5-mercapto tetrazole (ONPMT).
2. 5-anilino-1,2,3,4-thiatriazole (ATT).
3. 1-(2-nitrophenyl)-tetrazole (ONPT).
4. 1-(2-aminophenyl)-tetrazole (OAPT).

All the ligands have been synthesised adopting known procedures[4] and their structures are presented in Fig.1. These have been characterised based on physical, analytical, IR, ^{1}H NMR, ^{13}C NMR and Mass spectral data published elsewhere.[5]

B. Metal Complexes

The ligand ONPMT has been chosen for the synthesis of metal complexes. Synthesis and structural elucidation of chloro complex of Cu(II), Co(II), Ni(II) and Hg(II) ONPMT, perchlorato complexes of Cu(II), Co(II), Pb(II) ONPMT, acetato complex of Pb(II) ONPMT and Ag(I) complex of ONPMT have been carried out.[5] To a hot solution of ligand in alcohol, ethanol solution of the respective metal salt was added and refluxed for

3-5 hours and the complexes were isolated from a solution at 4-6 pH or 5-7 pH. All the complexes are coloured except silver which is white in colour and are quite stable to air and moisture and have excellent shelf-life. Their conductance value indicates them to be non-electrolytes. Coordination has been found to be through sulphur and participation of NO_2 in coordination is inferred. Based on the UV-VIS- NIR spectra, magnetic susceptibility data along with IR and ^1H NMR data, the geometries of the complexes were determined.[5] Thus it has been found that the ligand is acting as a mono basic bidentate one with S, O donor system in all cases except the chloro complex of Cu(II) where it acts as a tridentate ligand, that is the oxygens of NO_2 group on the phenyl ring participate in coordination with two Cu(II) metal ions resulting in a polymeric structure. Perchlorato complexes of Cu(II), Co(II), and Pb(II) ONPMT have the empirical formula [MLX] ($X=ClO_4$) and the chloro complex of Hg(II) is a dimer with the empirical formula $[M_2L_2X_2]_n$ (X = Cl).

The chloro complexes of Co(II), Ni(II), Ag(I) are polymers with the empirical formula $[MLXH_2O]_n$ for Co(II) and Ni(II) and $[ML]_n$ in the case of Ag(I). The chloro complex of Cu(II) is also a polymer having the empirical formula $[MLX]_n$ with bridging O, S, Cl. Proposed structures of some of the metal complexes are presented in Fig.2.

Thermal Decomposition Studies

Thermal techniques such as thermogravimetry and differential scanning calorimetry (Perkin Elmer DSC Models 1B and 2 and TGA 2) were used to evaluate the thermal stability of the compounds investigated. Both dynamic and isothermal studies were carried out in an atmosphere of nitrogen (flow rate 3.5ml/min). Peak decomposition temperatures, enthalpy values, and weight loss data have been derived from the thermal studies. Appropriate calibration standards have been used. Sample size has been varied from 0.1 - 0.4 mg for highly sensitive materials and 1-3 mg for less sensitive compounds.

Kinetics have been followed by both dynamic and isothermal techniques. For dynamic runs Ozawa method was used for the calculation of activation energy while for isothermal runs Avrami-Erofeev method was adopted.

Avrami-Erofeev Method[6]:

In this method, the fraction decomposed (x) is calculated at various intervals of time (t). A plot of

$-\log (1-x)^{1/n}$ versus time (t), should give a straight line for a correct value of n. The slope will give the rate constant. Thus at various temperatures, the rate constants have been calculated. A plot of log k versus 1/T gives a straight line with a slope of -E/2.3 R. This method utilises the following equation :

$$-\log (1-x)^{1/n} = kt + C \qquad \text{.. (5)}$$

where C is a constant.

Ozawa Method[7]:

This method states that the logarithm of the rate of heating (dT/dt), has a linear relation with the reciprocal of the absolute temperature, for a given conversion (x), regardless of the order of reaction. This method requires non-isothermal runs at different rates of heating. From the x - t curves, the absolute temperature for the given conversion (x) at different rates of heating (B) can be calculated. Plot of log (B) versus reciprocal temperature should give a straight line for a given value. At different values the plots should be parallel lines, if the activation energy remains constant.

$$\ln (B) = C - E/RT_p \qquad \text{.. (7)}$$

where T_p is the peak decomposition temperature, E is the activation energy and C is a constant.

Explosive Testing Methods

Sensitivity Tests

In this work the explosive sensitivity of the metal complexes has been evaluated by several techniques listed below. Since these are standarad techniques, details of the instruments are not given but appropriate references have been provided.

i. Impact Sensitivity Test[8]
ii. Pendulum Friction Sensitivity Test[9]
iii. Torpedo Impact and Friction Sensitivity Test
iv. Electrostatic Charge Sensitivity Test[10]
v. Ignition Temperature
vi. Heat Sensitivity Test

Performance tests

Two tests have been adopted in this work to evaluate the performance of explosives.

i) Lead Plate Perforation Test (LPT)[11]
ii) Minimum Value Evaluation - efficiency of initiatory explosives.

RESULTS AND DISCUSSION

A. Thermal decomposition studies

Dynamic DSC studies on these ligands revealed that ONPMT decomposes in two steps without melting whereas

AAT which is an isomer of ONPMT decomposes immediately following melting. ONPT and OAPT show a clear endotherm due to melting before decomposition. Fig. 3 gives the typical dynamic DSC curves of the ligands. Reduced time plots derived from fraction decomposed (x) versus time (t) curves (sigmoid in shape) indicate that the decomposition behaviour is similar at various temperatures in case of isothermal and at different heating rates in the case of non-isothermal runs (Fig. 4). All the thermal and kinetic data derived from DSC studies are presented in Table 1. Two activation energy values are given for ligands which clearly decompose in two steps. For the ligands the thermal stability based on peak decomposition temperature and activation energy values is in the following order:

ONPMT < ATT < OAPT < ONPT

TG analysis of these ligands also reveals a similar trend in stability.

Table 1 lists the thermal data obtained for the four tetrazole ligands while Table 2 gives typical isothermal data for OAPT. From the isothermal data it is evident that while the delay time for decomposition decreases with increasing temperature, the enthalpy of decomposition increases. Further, the activation energy values obtained from dynamic and isothermal DSC runs are roughly similar (compare the values given in Tables 1 and 2).

The thermal data presented in Table 1 shows clearly that while ONPMT is the most thermally sensitive, OAPT has a much higher enthalpy of decomposition compared to the former. Both are thus suitable ligands for preparing metal complexes. However, due to problems in its synthesis and low yields, this ligand was not chosen for the synthesis of metal complexes. AAT is a triazole (an isomer of ONPMT); hence this was eliminated. With regard to ONPT though it has moderately high thermal sensitivity, it has no binding sites for complexation and thus could not be chosen for the synthesis of metal complexes.

Therefore, based on the thermal sensitivity results and other criteria, ONPMT has been selected as the ligand for the preparation of metal complexes of certain 3d metal ions and heavy metal ions. Franbarger et al[2] studied the synthesis and properties of polynitrophenyl tetrazalato Cobalt (III) complexes. Lieberman[1] studied the chemistry of CP and similar explosive coordination compounds. This prompted us to synthesise and study the properties of metal complexes of ONPMT.

Thermal Studies On Metal Complexes Of ONPMT :

Dynamic and isothermal DSC runs were carried out on all the metal complexes of ONPMT. It has been observed that similar to ONPMT none of them melt but decompose (or explode) on heating. The peak decomposition temperatures of the mercapto tetrazole complexes are higher than that of the pure ligand, ONPMT. Typical thermograms are reproduced in Fig. 5. From these curves it is evident that the decomposition patterns of these complexes show considerable differences; thus a few complexes decompose in a single step while others exhibit two or three step decomposition.

Fraction decomposed (x) versus time (t) curves for dynamic and isothermal DSC of metal complexes of ONPMT indicate that the x-t curves are sigmoid in shape. From the reduced time (t/t at x = 0.5) plots for isothermal and dynamic DSC runs, it appears that the kinetic behaviour of the decomposition reaction is similar at various temperatures in the case of isothermal runs and at different heating rates for dynamic runs. Peak decomposition temperatures and enthalpy values recorded for different metal complexes are listed in Table 3. The following are the main conclusions:

* Ag(I) complex of ONPMT appears to be the most reactive among the metal complexes studied since it has the maximum enthalpy of decomposition and the decomposition occurs in a single step, although the decomposition temperature is moderately high.

* Chloro complex of Ni(II) - ONPMT is thermally the most stable complex in the mercapto tetrazole series.

* In general perchlorato complexes have been found to be more reactive than the corresponding chloro complexes.

* The enthalpy values obtained for the various complexes in isothermal runs are lower than those obtained from dynamic runs. However, in the case of the Ag(I) complex these values are fairly close to each other, again pointing to its high reactivity.

Pressure DSC studies in sealed cups have been carried out in order to examine the difference in decomposition patterns when compared to the behaviour in open cup DSC studies. Three complexes chosen for the study are the chloro complex of Hg(II) ONPMT, chloro complex of Cu(II) ONPMT and Ag(I) complex of ONPMT. Results obtained for the three complexes are given in Table 4. It is observed that for all the three complexes while the peak decomposition temperatures are nearly the same in both the runs, there is a considerable increase in the heat of decomposition values in the sealed cups. Decomposition enthalpy values in sealed cups are about 2 to 2.5 times greater than the value in open cups.

The activation energy values derived from dynamic and isothermal studies are given in Table 5. The data do not show any specific trends except that the Ni(II) complex has a large activaton energy for decomposition compared to the other complexes.

TGA analysis has been carried out for all the metal complexes of ONPMT. Only in the case of chloro complexes of Co(II) and Ni(II) ONPMT the weight loss in the first step corresponds to the loss of a water molecule. The weight loss values are 5.2% and 5.1% for Co(II) and Ni(II) complexes respectively. These are in close agreement with the theoretically calculated values of 5.40% and 5.38% for Co(II) and Ni(II) respectively. The decomposition temperatures for the various metal complexes corresponding to x=0.5 (based on weight loss) are listed in Table 6. The data is given for different heating rates. Most complexes exhibit step-wise decomposition pattern. In Ag(I)-complex and the perchlorato complex of Cu(II) the weight loss occurred in one step, whereas in perchlorato complex of Pb(II), acetato complex of Pb(II), chloro complex of Cu(II) and Hg(II), the weight loss occurred in two stages. Chloro complexes of Co(II) and Ni(II) showed weight loss in three steps and in the perchlorato complex of Co(II) the weight loss occurred in 4 steps. Therefore, it can be seen that even in TG studies the metal complexes exhibit single or multi-step decomposition as observed earlier in DSC work. Typical weight loss values recorded in TG studies for the metal complexes of ONPMT are also given in Table 6.

Explosive characteristion of metal complexes of ONPMT:

Explosive properties such as ignition temperature, heat sensitivity, friction and impact sensitivities, and electrostatic sensitivity have been measured for the various mercapto tetrazole complexes. The initiating ability of the ligand and their metal complexes has also been studied. Explosive sensitivity data for these complexes are presented in Table 7, which lists ignition temperatures, and friction, heat and electrostatic (spark) sensitivity data. It may be mentioned here that the spark sensitivity data represent 50 % initiation probability. In general, it can be stated that excepting the metal complexes of Co(II) and Ni(II), all the other complexes studied have moderate to high explosive sensitivity.

It is observed that ignition temperatures fairly match the peak decomposition temperatures recorded in dynamic DSC runs. Torpedo friction and impact sensitivity test data reveal that the chloro complex of Ni(II) is the least sensitive while the acetato complex of Pb(II) and Ag(I) ONMPT complex are found to be the most sensitive. Heat sensitivity data show that acetato complexes of Pb(II), chloro complex of Cu(II), perchlorato complex of Cu(II) and Ag(I) complex are heat sensitive and their heat sensitivity (determined by applying diffrent voltages to a fusehead in contact with the sample)is superior to the more commonly used primary explosives lead azide and lead styphnate (the corresponding values for heat sensitivity are >90 and 42 mV respectively) in detonator compositions. On the other hand, these tetrazole complexes are less hazardous due to their lower electrostatic sensitivity.

Spark sensitivity values for some of these complexes are atleast 4 - 5 times lower than those for lead styphnate (0.9 mJ). Amongst the complexes, Pb(II), Ag(I) complex of ONPMT has the maximum spark sensitivity while the chloro complexes of Co(II) and Ni(II) ONPMT were found to be the least spark sensitive.

Attempts have been made to understand the thermal and explosive sensitivity characteristics of the metal-ligand complexes keeping in view the various physico-chemical factors affecting sensitivity. Some of these factors include crystal habit, particle size, oxygen balance (fuel-oxidizer ratio), presence of trigger groups (or reactive groups) such as azide, tetrazole,etc., and electron-withdrawing groups such as chloro, nitro, perchlorato, etc., which enhance reactivtiy. Another factor which has been found to govern sensitivity, especially within a given family of explosives such as metal azides is that greater the ionisation potential of the cation, the more likely that the compound is a primary explosive.[12] The present results also enable us to draw some structure-property correlations such as:

* The high sensitivity of aryl mercapto tetrazole

confirms tetrazole group to be a trigger group.

* Metal complexes synthesised with ONPMT possess a high order of explosive sensitivity, comparable to other primary explosives.

* In general, perchlorato complexes of M(II)-ONPMT are more sensitive than the corresponding chloro complexes, an exception being the perchlorato complex of Pb(II)-ONPMT.

* The large differences in the explosive sensitivity of the acetato and perchlorato complexes of Pb(II)-ONPMT could be due to the different crystal habits of these complexes. SEM studies reveal that the acetato complex exhibits a distinctly porous and globular structure while the perchlorato complex crystallises in the form of flat crystals (Fig. 6). The role of pores in enhancing impact and friction sensitivity is well known.

* No correlation could be drawn between the second ionisation potential of the metal cation and the explosive sensitivity of the metal-tetrazole complex. In fact among the metal complexes investigated, Pb(II), Hg(II), Cu(II), and Ag(I) complexes have similar sensitivity while Co(II) and Ni(II) are less sensitive.

* The low sensitivity of the Ni(II) and Co(II)

complexes could be due to the water of crystallisation present in them.[2]

Performance tests:

Based on the above data performance tests were carried out on the ligand ONPMT and on some of its metal complexes and the results have been compared with those obtained with conventional primary explosives such as dextrinated lead azide and lead styphnate. In one such test 25 cgs of the complex is taken in a 32 mm Al or Cu coated steel shell over 30 cgs of pressed PETN (pentaerythritol tetranitrate) and pressed at a pressure of 80 kpsi (550 MPa) for Al and 120 kpsi (830 MPa) for Cu shells. The shells were then crimped with fusehead and fired over a lead plate. While in the case of Al filled detonator shells PETN did not get fully initiated , in Cu shells it was observed that PETN was initiated completely. In the case of lead azide filled shells, a 10 mm hole formed on the lead plate while with lead styphnate and Ag(II), Pb(II) & Cu(II) complexes only indentation appeared. In the case of the ligand, PETN was found to undergo only partial reaction. This test shows that the fusehead could initiate the aryl mercapto tetrazole metal complex (and also lead styphnate) and which in turn could initiate

PETN. However, unlike in the case of lead azide, with metal complexes and the styphnate , PETN has not undergone a high order detonation to result in a perforation on the lead plate. The relatively poor performance of the complexes could be due to their low bulk density and rather than due to any differences in reactivity. Thus pressed densities of the metal complexes were about 2 to 3 times lower than that of lead azide. In fact, the bulk density of metal-ONPMT complexes have been found to be in the range 0.5 to 0.8 g/cc while that of lead azide is around 1.2 g/cc. The fact that PETN got initiated completely when the filling pressure was increased in Cu shells supports this conclusion. The effect of lead azide loading pressure on detonator output performance is well known.[13]

In view of the excellent safety properties of ONPMT complexes especially compared to lead styphnate, which has a high electrostatic sensitivity it was planned to examine the feasibility of replacing the styphnate by these metal complexes. Lead styphnate is primarily used in detonators to impart flame sensitivity to lead azide, a property necessary for reliable initiation by a fusehead. Hence, lead plate perforation tests were conducted with lead azide-ONPMT metal complex in a 70:30 ratio with 15 cgs of the composition and in all cases a 9-11 mm deep hole formed on the lead plate after firing the detonator. When the above experiment was repeated with a mixture having 50:50 ratio at 15 cgs level, a 6-9 mm deep hole formed. Thus tetrazole-metal complexes evaluated in the present investigation are potential substitutes for lead styphnate and could also partially replace lead azide thereby offering excellent safety advanatages. If suitable recrystalli sation or coprecipitation methods could be adopted to enhance the bulk density of these metal complexes, it is likely that they could even match lead azide in performance.

We have employed an empirical test such as Lead plate perforation to assess the efficiency of the metal - ONPMT complexes synthesised in this work as initiatory charges. While the use of such tests is necessary, it is essential that we carry out a detailed study on the parameters controlling ignition and subsequent growth to detonation in these initiatory charges for critically evaluating their performance. We should obtain data on the peak shock pressure as well as the pressure vs. time profile since these detonation properties will determine whether or not the secondary explosive (PETN) will propagate a strong enough shock wave or produce fragments of suitable velocity for the detonator to perform effectively. These studies are planned to be carried out in the next phase of the work.

CONCLUSIONS

The primary endeavour of this work has been to synthesise metal complexes which decompose in an exothermic manner and have potential explosive properties. Thus a number of transition metal ion and heavy metal ion complexes have been prepared using different types of ligands with varying thermal reactivity properties. The ligands and their metal complexes have been studied for their thermal decomposition properties using DSC and TGA techniques. Among all the compounds, aryl mercapto tetrazole and its metal complexes have been found to be the most thermally sensitive indicating tetrazole group to be acting as a trigger group. The above ligand and its complexes have also been evaluated for their explosive properties. Silver complex is the most sensitive among all the complexes studied while the chloro complex of Ni(II) ONPMT is found to be the most stable. Attempts have been made to explain the thermal and explosive sensitivity results based on structure-property correlations. Metal- aryl mercapto tetrazole complexes were found to possess near-optimum sensitivity characteristics whereby they could find potential applications either as primary explosives or as one of the constituents in initiatory compositions. In conclusion it may be stated that coordination chemistry does indeed offer possibilities of synthesising energetic metal complexes which uniquely fulfill the requirements of specific explosive applications.

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TABLE 1. Thermal Analysis Data For Tetrazole Ligands.

Sl. No	Ligand	Melting point, K	Heat of fusion, J/g	Peak decomposition temperature(s)*, K	Heat of decomposition J/g	Activation energy for decomposition, kJ/mole
1.	1-(2-nitrophenyl) 5-mercaptotetrazole ONPMT	391	-	406, 431	1646.5	67.3, 66.4
2.	5-anilino-1,2,3,4-thiatriazole - ATT	389	10.5	425, 467	748.4	81.6, 74.4
3.	1-(2-nitrophenyl) tetrazole - ONPT	361	272.9	460	2536.0	177.0
4.	1-(2-aminophenyl) tetrazole - OAPT	356	601.1	478	5170.0	155.3

Melting points measured separately.

* Scan speed 16 deg/min.

TABLE 2. Isothermal Decomposition For O-Aminophenyl Tetrazole Ligand.

Decomposition temperature, K	Delay time, s	Heat of decomposition, J/g	Activation energy for decomposition, kJ/mole
440	360	1047.1	
445	270	1143.3	158.5
449	120	1320.4	
453	60	1450.5	

TABLE 3. Results From DSC Studies (Dynamic And Isothermal) On Mercapto tetrazole Complexes.

Sl. No	Compound	Peak decomposition temperature(s)*,K	Total heat of decomposition, (dynamic), J/g	Isothermal decomposition temperature, K and delay time (seconds)	Total heat of decomposition (isothermal), J/g
1.	Chloro complex of Hg(II) - ONPMT	429, 447	555.7 (215.5, 340.2)	420 (15)	124.9
2.	Perchlorato complex of Pb(II) - ONPMT	437	987.6	430 (15)	874.4
3.	Acetato complex of Pb(II) - ONPMT	473	706.0	475 (0)	591.4
4.	Chloro complex of Cu(II) - ONPMT	435, 494	1131.8 (374.5, 757.3)	435 (0)	338.4
5.	Perchlorato complex of Cu(II - ONPMT	493	1301.6	480 (0)	1077.5
6.	Ag(I) complex of ONPMT	501	2873.2	485 (45)	2339.1
7.	Chloro complex of Co(II) - ONPMT	505	746.4	490 (27)	588.7
8.	Perchlorato complex of Co(II) - ONPMT	510	1574.8	492 (27)	588.7
9.	Chloro complex of Ni(II) - ONPMT	533	448.9	-	-

* Scan speed 16 deg/min; typical sample mass 0.05 mg.

TABLE 4. Thermal Data From High Pressure DSC Studies On A Few Mercapto tetrazole Complexes.

Sl. No	Compound	Peak decomposition temperature(s)*,K	Total heat of decomposition, J/g
1.	Chloro complex of Hg(II) - ONPMT	435-459	1356.4
2.	Perchlorato complex of Pb(II) - ONPMT	428-478	2009.5 (628.0, 1381.5)
3.	Ag(I) complex - ONPMT	515	8289.8

* Scan speed 10 deg/min; broad exotherms for 1 and 2.

TABLE 5. Activation Energy For Decomposition Of Metal Complexes Of Mercapto tetrazole From DSC Studies.

Sl No	Compound	Activation Energy, kJ/mole Dynamic	Activation Energy, kJ/mole Isothermal
1.	Chloro complex of Hg(II) - ONPMT	143.0, 171.4	184.6
2.	Perchlorato complex of Pb(II) - ONPMT	154.8	66.3
3.	Acetato complex of Pb(II) - ONPMT	142.1	63.9
4.	Chloro complex of Cu(II) - ONPMT	167.4, 159.3	290.9, -[1]
5.	Perchlorato complex of Cu(II - ONPMT	143.2	52.8
6.	Ag(I) complex of ONPMT	153.9	66.2
7.	Chloro complex of Co(II) - ONPMT	225.1	251.7
8.	Perchlorato complex of Co(II) - ONPMT	146.7	227.7
9.	Chloro complex of Ni(II) - ONPMT	408.0	-

1: - not determined for the II exotherm.

TABLE 6. Results From Dynamic TG Studies Metal Complexes Of ONPMT.

Sl. No	Compound	Decomp. temp. for x = 0.5 at,			Percent weight loss
		10 deg/min	5 deg/min	2.5 deg/min	
1.	Chloro complex of Hg(II) - ONPMT	E	438	435	41.2
2.	Perchlorato complex of Pb(II) - ONPMT	443	435	434	42.4
3.	Acetato complex of Pb(II) - ONPMT	481	472	463	25.3
4.	Chloro complex of Cu(II) - ONPMT	E	E	481	31.2
5.	Perchlorato complex of Cu(II - ONPMT	E	E	483	47.2
6.	Ag(I) complex of ONPMT	E	E	E	-
7.	Chloro complex of Co(II) - ONPMT	507	-	-	81.9
8.	Perchlorato complex of Co(II) - ONPMT	508	-	-	66.9
9.	Chloro complex of Ni(II) - ONPMT	523	-	-	61.8

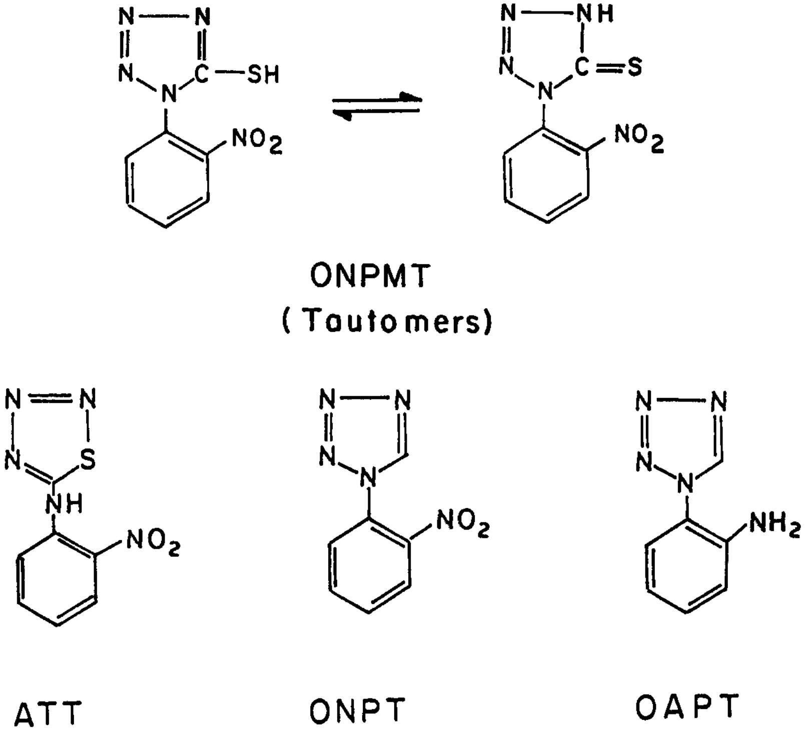
Typical sample mass: 1.0 mg, E - explosion

TABLE 7. Sensitivity Data For Metal Complexes Of Mercapto tetrazole.

Sl. No	Complex	Ignition temperature	Torp. friction & impact sensitivity, cms		Heat sensitivity, mV		Spark sensitivity, mJ
			NFL	MFL	MFL	NFL	
1.	Chloro complex of Hg(II) - ONPMT	453*	9.5	11.5	62	-	50.6
2.	Perchlorato complex of Pb(II) - ONPMT	462	21.5	-	60	-	90.0
3.	Acetato complex of Pb(II) - ONPMT	470	8.5	9.5	34	-	7.6
4.	Chloro complex of Cu(II) - ONPMT	453	16.5	21.5	34	-	90.0
5.	Perchlorato complex of Cu(II - ONPMT	496	9.5	11.5	34	-	39.9
6.	Ag(I) complex of ONPMT	508	8.5	9.5	30	-	3.2
7.	Chloro complex of Co(II) - ONPMT	518	16.5	21.5	-	90	144.0
8.	Perchlorato complex of Co(II) - ONPMT	525	11.5	16.5	-	90	38.0
9.	Chloro complex of Ni(II) - ONPMT	533	21.5	26.5	-	90	144.0

* Mass of sample 0.05 mg

NFL - No fire level; MFL - Minimum fire level.



ONPMT
(Tautomers)

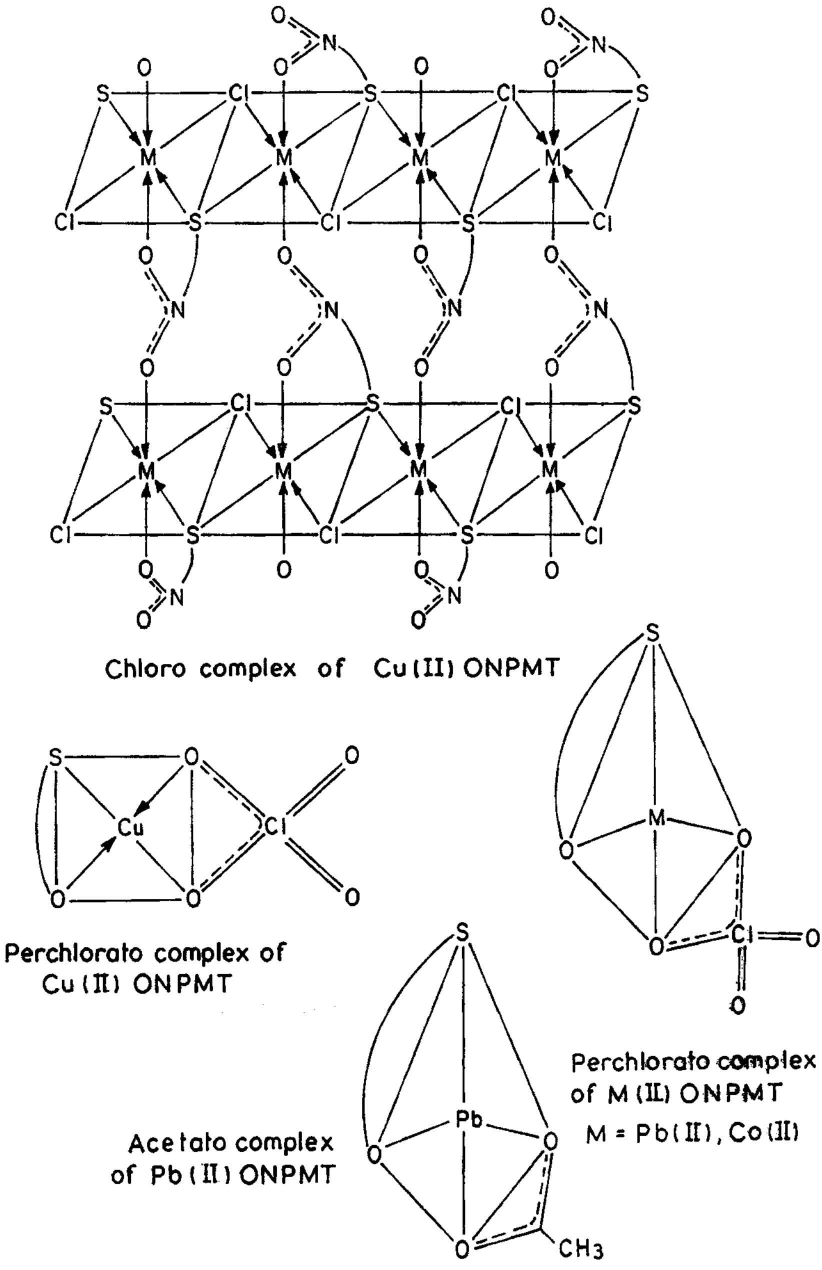
ATT

ONPT

OAPT

FIGURE 1

Chemical Structures of the Ligands chosen for this study.


Chloro complex of Cu(II) ONPMT

Perchlorato complex of Cu(II) ONPMT

Perchlorato complex of M(II) ONPMT
M = Pb(II), Co(II)

Acetato complex of Pb(II) ONPMT

FIGURE 2

Proposed structures of a few metal complexes.

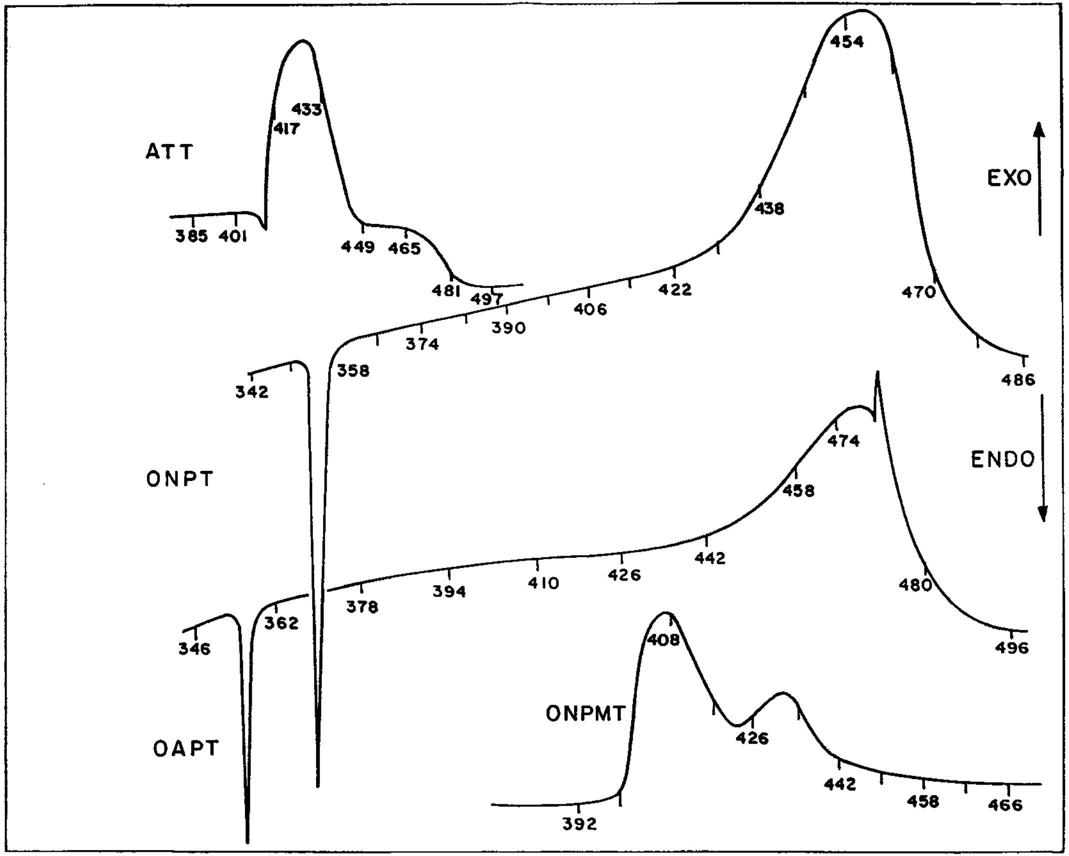


FIGURE 3

Dynamic DSC curves for different Tetrazole Ligands.

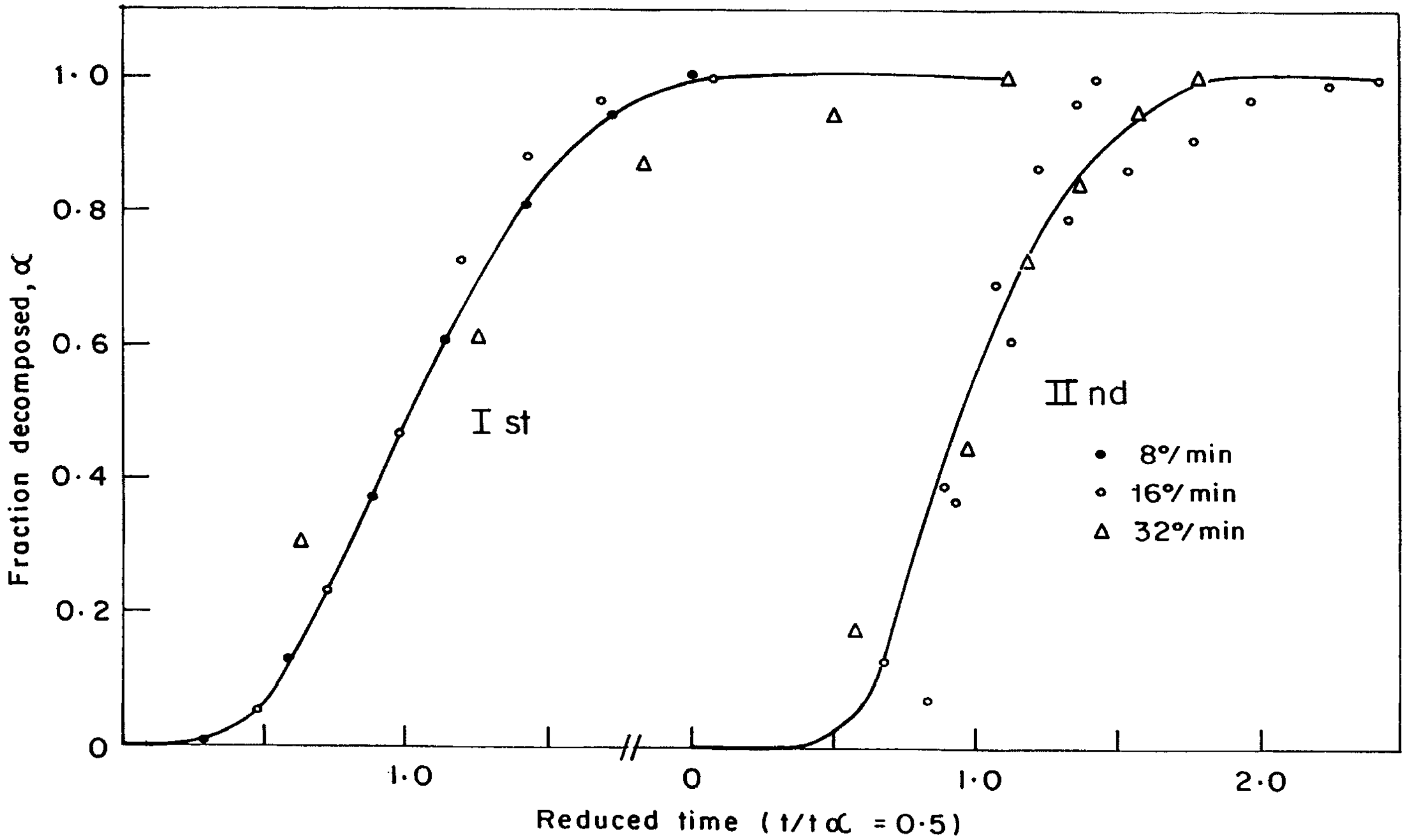


FIGURE 4

Reduced x-t plots for ONPMT.

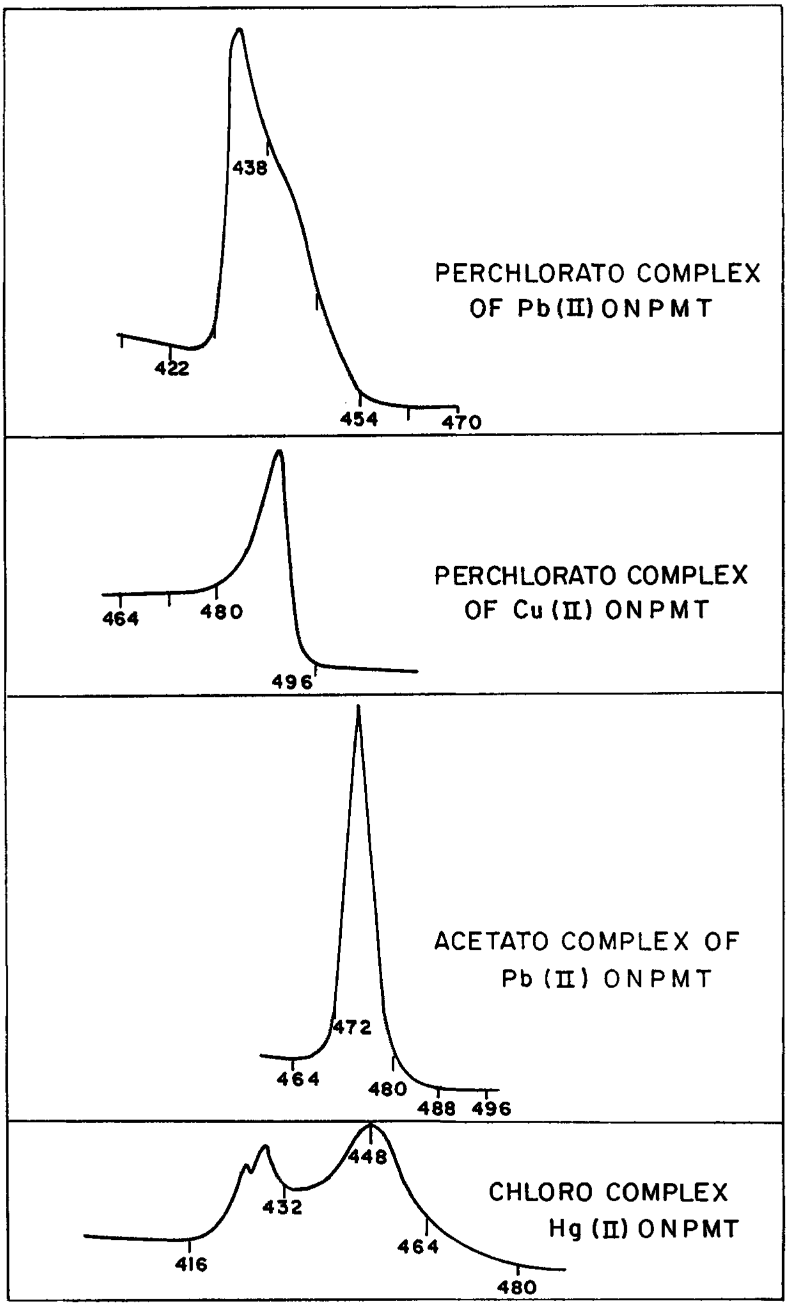


FIGURE 5

Typical dynamic DSC curves of a few Metal Complexes of ONPMT.

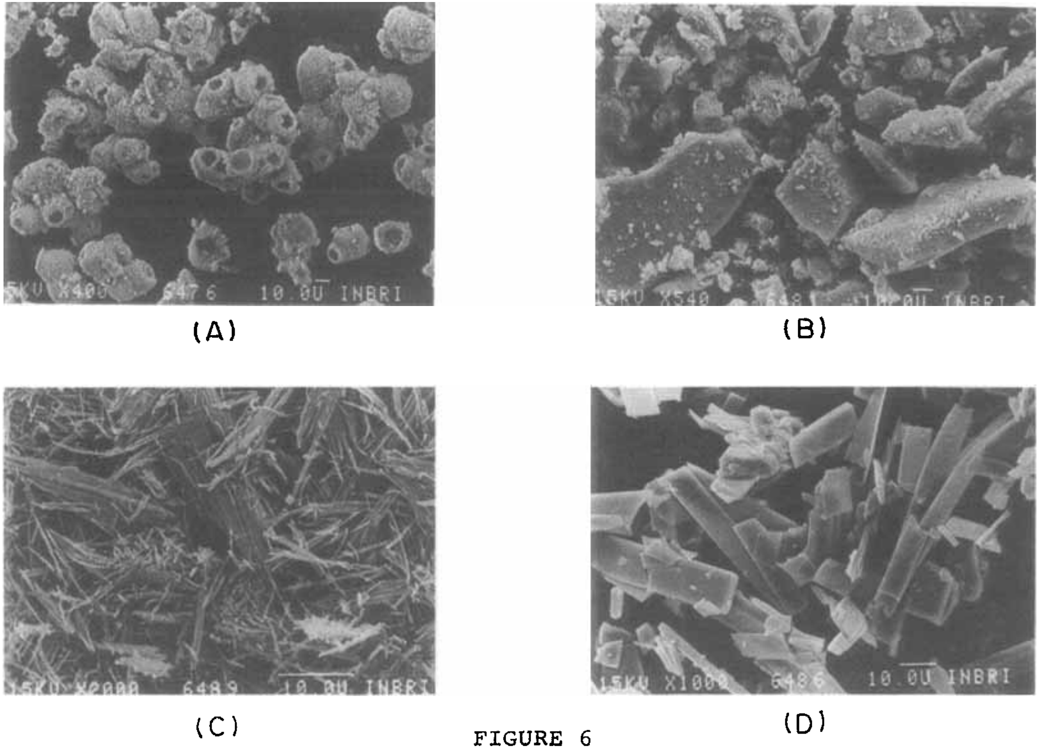


FIGURE 6

SEM photographs of a few Metal Complexes of ONPMT (A) Acetato complex of Pb(II), (B) Perchlorato complex of Pb(II), (C) Ag(I) complex and (D) Chloro complex of Hg(II).