Coordination Chemistry Reviews
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

COMPLEX COMPOUNDS OF 1,5-DISUBSTITUTED TETRAZOLES

ALEXANDER I. POPOV

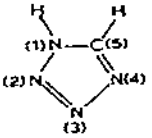
Department of Chemistry, Michigan State University, East Lansing, Michigan 48823 (U S A)

(Received April 16th, 1969)

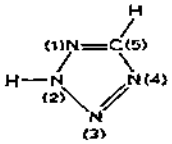
CONTENTS

A. INTRODUCTION

The parent compound of this class of ligands is the tetrazole, CN_4H_2, in which the carbon atom and the four nitrogen atoms form a five-membered ring[1,2]. The compound can exist in two tautomeric forms I and II. About 97% of the equilibrium mixture of I and II exists in form I[3].



(I)



(II)

The numbering of atoms in the ring starts with the nitrogen atom adjacent to the carbon (configuration I) and proceeds counterclockwise around the ring as shown above.

The two hydrogen atoms in positions (1) and (5) of form I can be readily replaced by aliphatic or aromatic groups giving a series of either 1-substituted, 5-substituted or 1,5-disubstituted tetrazoles.

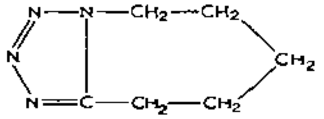
Tetrazole itself is a rather strong acid[1] with an aqueous K_a of 1.54×10^{-5}. It is seen, therefore, that its acidic strength equals that of acetic acid. The replaceable hydrogen is attached in position (1) and, in fact, all 5-substituted tetrazoles behave as weak acids[4]. The hydrogen atom attached to the carbon, on the other hand, does not exhibit any acidic properties. All tetrazoles are polar compounds with high dipole moments, those of pentamethylenetetrazole, (Metrazole, hereafter abbreviated as PMT), 8-t-butyl PMT, 8-sec-butyl PMT, and 1-cyclohexyl-5-methyltetrazole being 6.14, 6.20, 6.18 and 6.00 *D* respectively[5].

The 1,5-disubstituted tetrazoles where the substituent groups are either alkyl or aryl radicals, form a series of interesting compounds which should act as bases both in the Brönsted and in the Lewis sense. It should be noted, however, that the basic or the donor properties of these compounds have not been thoroughly explored. The only exception is the pentamethylenetetrazole, whose powerful stimulating activity on the central nervous system led to its use in chemotherapy This application of PMT focused the attention of several investigators on the chemistry and in particular, on the electron donor properties of this compound.

The 1-substituted as well as the 5-substituted tetrazoles also form a series of interesting coordination compounds which have been studied primarily by Brubaker[6] and Jonassen[7]. The properties of these complexes, however, differ quite markedly from those of the 1,5-disubstituted tetrazoles and will not be reviewed here.

B. PROTON AFFINITY OF THE 1,5-DISUBSTITUTED TETRAZOLES

The 1,5-disubstituted tetrazoles are characterized by their very low basic strength, although, here again the main work has been carried out only on pentamethylenetetrazole (III). In aqueous solutions PMT does not exhibit any basic properties In fact, even 10% solutions of this compound exhibit a neutral pH[8]. It should be noted, however, that there is a report in the literature on the preparation of a 1:1 solid addition compound with sulfuric acid[8] PMT·H_2SO_4. The latter compound is claimed to have been prepared by the addition of a 10% solution of sulfuric acid in ethyl ether to a saturated PMT solution in the same solvent.



(III)

Potentiometric titration of PMT dissolved in glacial acetic acid with perchloric acid solution in the same solvent yields a titration curve typical of very weak bases[9]. Similar titrations have been carried out in a more protogenic solvent, formic acid, with *p*-toluenesulfonic acid as the titrant[10]. In this case titration curves typical of strong bases were obtained with PMT as well as with some other 1,5-disubstituted tetrazoles such as 8-t-butylmetrazole, 7-methyl-8-isopropylmetrazole, 7-methylmetrazole, 8-isopentylmetrazole, 1-cyclohexyl-5-ethyltetrazole, 1-methyl-5-cyclohexyltetrazole. The data are shown in Table 1.

TABLE 1

TITRATIONS OF SOME 1,5-DISUBSTITUTED TETRAZOLES IN ANHYDROUS FORMIC ACID[9]

Compound	*Milliequiv taken*	*Milliequiv. found*
PMT	1 01	1 01
7-Methyl-8-isopropyl PMT	1 05	1 05
7-Methyl PMT	0.93	0 93
8-Isopentyl PMT	0 94	0.93
1-Cyclohexyl-5-ethyltetrazole	1 12	1.12
1-Methyl-5-cyclohexyltetrazole	1.04	1 06

Because of the very weak protophilic properties of the 1,5-disubstituted tetrazoles it is impossible to obtain the basicity constants of these compounds in aqueous solutions. Comparison of their basic strength can be made conveniently, however, in formic acid solutions by means of a concentration cell with quinhydrone electrodes[11]. The pK_b values for the reaction $Tz + HCOOH \rightleftarrows TzH^+ + HCOO^-$ are given in Table 2 The basicity constant of urea in the same solvent is included for comparison. The data show that even in formic acid solutions the protonation of the tetrazoles is incomplete. The leveling effect of the solvent, however, makes it difficult to recognize the differences in the basic strengths of the tetrazoles. Recently, the basicity constant of PMT was checked by electrical conductance measurements[12]. The pK_b value of 2.02 obtained by this technique compares very favorably with the potentiometric value of 2.03.

TABLE 2

THE pK_b VALUES FOR SOME 1,5-DISUBSTITUTED TETRAZOLES IN ANHYDROUS FORMIC ACID[11]

Compound	*pK_b*
PMT	2 03
8-t-Butyl PMT	2 08
8-Isobutyl PMT	2.07
7-Methyl-8-isopropyl PMT	2 27
7-Methyl PMT	2 07
8-Isopentyl PMT	2 18
1-Cyclohexyl-5-ethyltetrazole	1 98
1-Isobutyl-5-methyltetrazole	2 18
1-Cyclohexyl-5-methyltetrazole	1 89
1-Methyl-5-cyclohexyltetrazole	2 24
Urea	1 75

It is interesting to note that PMT can react with metal ions in acetic acid solution but not in formic acid (p. 471) where protonation by the solvent is too great to allow the formation of the complexes.

C. MOLECULAR COMPLEXES

With the exception of PMT and some of its derivatives there appear to be no studies on the molecular complexes of 1,5-disubstituted tetrazoles. Even in the case of PMT the studies have not been extensive. Dister reported the formation of a 1:1 addition compound[13] with bromoethane which he prepared by heating 1 g of PMT with 10 g of C_2H_5Br in a sealed tube for six hours at 100°. The compound was obtained in the form of colorless crystalline needles, with a melting point of 95°, quite stable but very hygroscopic and very soluble in water, ethanol and chloroform.

Electron donor properties in PMT are amply illustrated[14] by the ease with which it forms 1:1 addition compounds with the halogens and interhalogens. A crystalline addition compound PMT·ICl can be easily prepared by mixing the solutions of the two components in carbon tetrachloride and the amorphous precipitate can be recrystallized from chloroform[14]. The crystal structure of this compound has been recently reported[15]. The results clearly indicate that PMT acts as a monodentate ligand with the nitrogen in the 4-position acting as the donor. The N-I-Cl group is linear with the N-I distance being 2.34 Å and I-Cl distance 2.44 Å. The ICl is essentially coplanar with the tetrazole ring. The comparison of the N-I distance with that in the pyridine-ICl complex[16] of 2.26 Å shows that the transfer of charge from the nitrogen to the iodine atoms is not as complete in the PMT complex as in the pyridine-ICl complex. At the present time it is not possible to say why the bonding occurs through the 4-nitrogen or whether it is the donor site in all tetrazole complexes.

Attempts to prepare solid complexes of PMT with other halogens such as iodine or iodine bromide, were unsuccessful[14]. Even with substituted PMT such as 7-methyl, 8-sec-butyl and 8-t-Butyl PMT attempts to prepare solid compounds by using the same procedure as with PMT were, so far, unsuccessful[17] although, in this case, the strength of the complexes were equal or greater than that of the PMT-ICl complex.

Formation constants of the halogen complexes with PMT and substituted PMT's were determined spectrophotometrically in carbon tetrachloride solutions (Table 3). It is seen that PMT is a moderately strong electron donor. At least

TABLE 3

FORMATION CONSTANTS OF TETRAZOLE-HALOGEN COMPLEXES IN CARBON TETRACHLORIDE AT 25°

Complex	$K_f(\text{M}^{-1})$	*Ref*
PMT ICl	2.0×10^3	14
PMT IBr	1.5×10^2	14
PMT I_2	7.5	14
7-Methyl PMT·ICl	2.55×10^3	17
8-Isobutyl PMT·ICl	3.20×10^3	17
8-t-Butyl PMT·ICl	3.48×10^3	17

vis-a-vis halogens its donor strength is intermediate between such weak donors as acetonitrile (K_f for ICl complex 6.9) and strong donors such as pyridine (K_f for ICl complex 4.8×10^5). The addition of alkyl groups to the pentamethylene chain apparently has some inductive effect since the formation constants of the substituted PMT-ICl complexes are larger than that of the PMT complex.

The donor strength of PMT is also evident from the shift in the frequency of the I-Cl stretch in the complex which falls at 310 cm^{-1} as compared with 352 cm^{-1} in $CH_3CN{\cdot}ICl$ and 270 cm^{-1} in $C_5H_5N{\cdot}ICl$[18].

Recently a more thorough study was carried out on the complexes of iodine with cyclopolymethylenetetrazoles[19]. The formation constants were determined spectrophotometrically in 1,2-dichloroethane solutions in the 5–35° temperature range and thermodynamic constants for the complexation reaction were computed from the temperature variance of K_f. The data are shown in Table 4. It is seen that the formation constants increase with increasing length of the polymethylene chain except in the case of PMT which seems to be out of order. It is interesting to note that in this series of compounds other properties of PMT show some singularities. For example, its solubility in water and in other polar solvents is much higher than of its lower or higher homologues.

TABLE 4

THERMODYNAMIC CONSTANTS[19] FOR COMPLEX FORMATION BETWEEN CYCLOPOLYMETHYLENETETRAZOLES AND IODINE IN 1,2-DICHLOROETHANE SOLUTIONS AT 25°

Tetrazole	K_f (M^{-1})	$\Delta G°$ *cal. mole*$^{-1}$	$\Delta H°$ *kcal. mole*$^{-1}$	$\Delta S°$ *e.u.*
Trimethylenetetrazole	1.42 ± 0.09	−215	−3.4	−10.8
Tetramethylenetetrazole	2.34 ± 0.06	−504	−5.0	−15.2
Pentamethylenetetrazole (PMT)	2.18 ± 0.04	−461	−4.1	−12.3
Hexamethylenetetrazole	2.44 ± 0.05	−529	−4.7	−14.2
Heptamethylenetetrazole	2.64 ± 0.05	−575	−4.1	−11.9

Spectroscopic evidence has also been obtained for the interaction of PMT with iodine cyanide[20,21]. Both the I-C stretching motion and the I-C-N bending motion are quite sensitive to complexation reactions. The ν(CN) band in benzene

TABLE 5

FORMATION CONSTANTS[22] OF TETRACYANOETHYLENE COMPLEXES WITH 1,5-DISUBSTITUTED TETRAZOLES IN DICHLOROMETHANE AT 25°

Tetrazole	K_f (M^{-1})
PMT	1.31 ± 0.02
1-Cyclohexyl-5-ethyltetrazole	1.88 ± 0.07
1-Cyclohexyl-5-methyltetrazole	1.39 ± 0.10
1-Methyl-5-cyclohexyltetrazole	2.02 ± 0.14
1,5-Diphenyltetrazole	0.90 ± 0.15
1-Ethyl-5-phenyltetrazole	1.46 ± 0.07
1-Phenyl-5-ethyltetrazole	1.21 ± 0.03

solutions shifts from 476 cm^{-1} to 453 cm^{-1} upon addition of 1M PMT. The effect on the bending frequency is somewhat smaller ν(ICN) going from 320cm^{-1} in pure benzene to 333 cm^{-1} in 1M PMT. On the basis of the infrared measurements the formation constants of the PMT-ICN complex was calculated to be $15 \pm 3M^{-1}$.

In addition to the formation of σ-complexes described above, the tetrazoles have a rather limited tendency to coordinate to the π-acid, tetracyanoethylene[22] (TCNE) (Table 5). The interaction with other π-acids are smaller by an order of magnitude (Table 6) and in the case of trinitrobenzene and fluorenone, while spectrophotometric data unambiguously indicate some interaction, the values of the formation constants are so small that they cannot be taken too seriously. It is interesting to note that the formation constants of benzene-TCNE and PMT-TCNE complexes are comparable in magnitude while the formation constant of iodine monochloride complex with PMT is three orders of magnitude larger than that of the benzene-ICl complex.

TABLE 6

FORMATION CONSTANTS[22] OF PMT COMPLEXES WITH π-ACIDS IN DICHLOROMETHANE SOLUTIONS AT 25°

π-Acid	K_f (M^{-1})
Tetracyanoethylene	1 31
Tetracyanoquinodimethane	0 22
Chloranil	0.16
Trinitrobenzene	0 10
Trinitrofluorenone	0 06

D. METAL COMPLEXES

As in the preceeding case, the studies of actual complexes of 1,5-disubstituted tetrazoles have been limited almost exclusively to PMT. This compound was first prepared by Schmidt[23] in 1924. As a result of this work and subsequent experiments by many other investigators, PMT was recognized to be a strong central nervous system stimulant It was used in shock therapy for many years and is still used occasionally in cardiac cases. Pharmaceutical use of PMT stimulated the search for analytical spot-tests as well as for inorganic precipitating agents. Numerous complexes of PMT were prepared and reported, but for the most part, rather poorly identified, and their properties were not adequately characterized.

The first metal complex of PMT was prepared by Schmidt[23], who prepared a 1:1 addition compound $HgCl_2$·PMT in the form of a white crystalline compound with a melting point of 175°. Later, Zwikker[24] reported a series of additional compounds of PMT with $H_2Cr_2O_7$, $H_4Fe(CN)_6$, $H_3Fe(CN)_6$, $Cd(SCN)_2$,

$Cd(ClO_4)_2$, $Hg(CN)_2$ and $Zn(SCN)_2$ It appears that the complexes were formed in 1:1 ratio. In the case of cadmium salts, precipitations from aqueous solutions gave complex hydrates, $CdCl_2 \cdot PMT \cdot 3H_2O$ and $CdI_2 \cdot PMT \cdot H_2O$. The most insoluble precipitate was the copper(I) chloride complex which, according to Zwikker had the stoichiometry indicated by $PMT \cdot 2CuCl$.

In 1942 Rheinboldt and Stettiner[25] reported the preparation of several PMT complexes (Table 7) with salts of zinc(II), mercury(II), cadmium(II), copper(II), and silver(I) cations The method of preparation consisted predominantly in mixing concentrated aqueous solutions of the two components and concentrating the resulting mixture under reduced pressure. It is interesting to note that both 1:1 and 1:2 complexes were formed. In the case of the silver complex, the proposed 1:1 stoichiometry has not been confirmed by subsequent investigations (see below).

TABLE 7

COMPLEX COMPOUNDS OF PENTAMETHYLENETETRAZOLE WITH METAL SALTS[25]

Complex	*M p.*	*Complex*	*M.p*
$ZnCl_2 \cdot 2PMT$	112°	$HgCl_2$ PMT	177°
$ZnBr_2$ 2PMT	154–156°	$HgBr_2$ PMT	138°
$ZnI_2 \cdot 2PMT$	189–190°	$Hg(CN)_2$ PMT	192°
$CdCl_2$ 2PMT	346–350°	$Hg(NO_3)_2$ 2PMT	143.5°
$CdBr_2 \cdot PMT$	>300°	$CuCl_2$ PMT	260–265°
CdI_2 PMT	215°	$AgNO_3$ PMT	117°

A very exhaustive but rather qualitative study of PMT complexes was reported by Dister[8] in 1948. The prime aim of the author was to find a convenient analytical precipitating agent for PMT. Numerous metal salts were tried but rather cursorily studied. Table 8 indicates reagents which gave a precipitate with PMT but except for the copper(I) chloride the precipitates were not analyzed. Order of magnitude of solubility in water was determined. All of the precipitations, with the exception of mercury(II) iodide, were carried out in water. The latter complex, however, was obtained in alcohol, ether or acetone. Analysis of the

TABLE 8

PRECIPITATING REAGENTS FOR PENTAMETHYLENETETRAZOLE[8]

Molybdic acid
Ammonium molybdate
Cadmium iodide
Cadmium chloride
Cadmium perchlorate
Cadmium thiocyanate
Copper (I) chloride
Copper (II) perchlorate
Mercury (II) chloride
Mercury (II) iodide
Mercury (II) cyanide
Mercury (II) perchlorate
Potassium ferrocyanide
Potassium ferricyanide
Potassium triiodide (Lugol Solution)
Gold(III) chloride
Platinum(III) chloride
Sodium tungstate
Zinc thiocyanate
Phosphomolybdic acid
Silicotungstic acid

copper(I) complex led to the stoichiometry given by the formula $8PMT \cdot 7Cu_2Cl_2 + (PMT)_2Cu_2Cl_2$. A detailed quantitative study of the PMT precipitation by copper(I) chloride by Golton[26], however, showed that the composition of the precipitate was not constant. Statistical study of the experimental data indicated that the ratio of the weight of the precipitate to the weight of PMT taken was 2.308±0.097 or a variation of ±4.4%. The variation in the composition of the precipitates could not be correlated with any change in the reaction conditions.

Subsequent studies[5,27] on the $AgNO_3$–PMT system unambiguously showed that under the experimental conditions described by Rheinboldt and Stettiner the solid complex had the stoichiometry corresponding to a 1:2 complex $AgNO_3 \cdot 2PMT$. Dissociation constants of the above complex as well as of several other silver complexes of substituted pentamethylenetetrazoles were determined potentiometrically[5], (Table 9). Acetonitrile solutions had to be used since substituted PMT's were very insoluble in water. It is seen that the complexes are quite weak and that the inductive effect of the substituted groups is minimal

TABLE 9

EQUILIBRIUM CONSTANTS[5] FOR THE REACTION $AgTz_2^+ \rightleftharpoons Ag^+ + 2Tz$ IN ACETONITRILE SOLUTIONS AT 25°

Tz	*pK*
Pentamethylenetetrazole	2.14
8-*t*-Butyl PMT	2.14
8-*sec*-Butyl PMT	2.18
7-Methyl-10-isopropyl PMT	2.22
7-Methyl-9-isopropyl PMT	2.19
1-Cyclohexyl-5-methyl tetrazole	2.26

Half-wave potentials of cadmium(II), thallium(I) and cobalt(II) ions in aqueous solutions were not affected by the addition of 50–100 fold excess of PMT. It appears, therefore that the complexes are largely dissociated in aqueous solutions. Simular results were obtained by Brubaker in his study of copper complexes of tetrazoles[28]. The interaction between copper(II) ions and 1,5-dimethyltetrazole was very weak by comparison with complexing abilities of 5-substituted tetrazoles.

Potentiometric study of the silver complexes with cyclopolymethlenetetrazole has also been carried out recently in aqueous solutions[27]. The results (Table 10)

TABLE 10

THE AVERAGE pK_f VALUES[19] FOR THE REACTION $Ag^+ + 2Tz \rightleftharpoons AgTz_2$ IN AQUEOUS SOLUTION AT 25°

Tetrazole	*pK_f (in 0.1 M KNO_3)*	*pK_f (in 0.4 M KNO_3)*
Trimethylenetetrazole	−3.01 ± 0.01	−2.98 ± 0.05
Tetramethylenetetrazole	−3.07 ± 0.03	−3.03 ± 0.03
Pentamethylenetetrazole	−3.05 ± 0.04	−3.00 ± 0.05
Hexamethylenetetrazole	−3.05 ± 0.01	−2.98 ± 0.03
Heptamethylenetetrazole	−3.08 ± 0.04	−3.32 ± 0.03

again indicate rather weak interaction and essentially no influence of the length of the hydrocarbon chain on the stability of these complexes. The effect of the ionic strength on the complexation reaction is rather minor (except for heptamethylenetetrazole) as would be expected since the reaction does not involve separation of charges.

The above results clearly indicate that while PMT and its derivatives are capable of forming complexes with some transition metal ions, the complexing ability of its tetrazole ring is rather weak and in aqueous solutions, the donor properties of the solvent are sufficiently strong to hinder the formation of tetrazole complexes. In fact, addition of large amounts of PMT to the aqueous solutions of transition metal salts does not change the visible absorption spectrum of the latter[29]. Attempts to prepare PMT complexes with the transition metal perchlorates were unsuccessful (except for Ni(II), see below) even in non-donor solvents because of the water of hydration accompanying the transition metal ion. Such complexes, however, can be conveniently prepared if the water of hydration is removed chemically. Thus the complexes are readily formed in 2,2-dimethoxypropane from which anhydrous complexes can be precipitated out by PMT. The list of complexes obtained and some of their properties are given in Table 11.

TABLE 11

PENTAMETHYLENETETRAZOLE COMPLEXES WITH TRANSITION METAL PERCHLORATES[28,29]

Complex	*Color*	*M.p.*	*Magnetic Mom. (BM)*
$Mn(PMT)_6(ClO_4)_2$	white	195–212°	5.90
$Fe(PMT)_6(ClO_4)_2$	light brown	194° (dec)	5.20
$Co(PMT)_6(ClO_4)_2$	rose	195–201°	4.60
$Ni(PMT)_6(ClO_4)_2$	light blue	237° (dec)	2.92
$Zn(PMT)_6(ClO_4)_2$	white	145–150°	—
$Cu(PMT)_6(ClO_4)_2$	light blue	117.5°	1.74
$Cu(PMT)_4(ClO_4)_2$	blue	141–145°	2.21
$Cu(PMT)_2(ClO_4)$	white	226° (dec)	—

Preparation of the above complexes can also be carried out in acetic acid solutions[30]. The water of hydration is removed by the addition of calculated amount of acetic anhydride. Protonation of the PMT does not occur to the extent where it would interfere with the complexation reaction. On the other hand, PMT is largely protonated in formic acid solutions so that under similar conditions the reaction product is the corresponding metal formate rather than the complex[31].

$$PMT + HCOOH \rightleftharpoons PMTH^+ + HCOO^-$$
$$M^{2+} + 2HCOO^- \rightleftharpoons M(HCOO)_2$$

The hexakis complexes are soluble in water and in other polar solvents. In donor solvents, however, solution is accompanied by the dissociation of the complex. The only exception found so far is the Ni(II) complex which is not only stable in aqueous solutions but can actually be recrystallized from water to give large blue crystals of $Ni(PMT)_6(ClO_4)_2$. All other complexes have only been obtained in the forms of microcrystalline powders. The compounds are quite stable at room temperature and will melt smoothly if heated gradually. They do tend to explode on rapid melting. It should be noted that the transition metal salts of tetrazoles are quite unstable and can be easily detonated by shock.

The reflectance spectra of cobalt, nickel and iron complexes were characteristic of the respective metal ions in an octahedral field. Powder diffraction patterns for all species containing six ligands showed the compounds to be isomorphous It is interesting to note that hexacoordinated complexes of PMT, a rather bulky ligand, can be easily prepared while considerable difficulty has been experienced in the preparation of solid analogues with pyridine. Yet pyridine is a much stronger electron donor than PMT *vis-a-vis* transition metal salts and Lewis acids such as the halogens. Likewise, pyridine is a much stronger base than PMT.

Electron spin resonance spectra were obtained for the $Mn(PMT)_6(ClO_4)_2$, $Cu(PMT)_6(ClO_4)_2$ and $Cu(PMT)_4(ClO_4)_2$ complexes[32]. The data indicate that in the manganese complex the metal–ligand bond is 91% ionic and that the distortion from the octahedral symmetry is small. The corresponding hexacoordinated copper complex has a substantial tetragonal distortion. The metal–ligand bond was found to be 80% ionic.

Metal–ligand stretching frequencies were identified in the far infrared spectral region[33]. A plot of νM^{II}-N *vs.* the electronegativities of the metals gives an essentially straight line. The copper(II) complex shows a doublet which may indicate that the complex has two Cu-N bond distances. This conclusion would be in agreement with the proposed tetragonal structure of the complex.

Substitution of the perchlorate salts by the corresponding halides produces a profound change in the stoichiometry of the resulting complexes[34]. Since PMT is a rather weak ligand, the more polarizable halide ions, by contrast to the perchlorate ion, can successfully compete with PMT for the coordination positions around the metal ion.

The list of the halide complexes, together with some of their physical properties, are given in Table 12 It is seen that only one or at most two PMT molecules coordinate with a metal halide while six PMT molecules can coordinate with a metal perchlorate.

Physical properties of the halide complexes are quite different from those of the perchlorates. Halide complexes containing only one molecule of PMT are quite insoluble in water and in most polar and non-polar solvents. Magnetic moments, in general, agree rather well with the values predicted for the spin-free complexes although the magnetic moment of Cu(II) complex is somewhat low. In the case of the cobalt complexes, the magnetic moments seem to indicate that the bis-PMT complex is tetrahedral while the mono-PMT complex is octahedral.

TABLE 12

TRANSITION METAL HALIDE COMPLEXES WITH PENTAMETHYLENETETRAZOLE[34]

Complex	*M.p.*	*Color*	*$\mu_{(eff)}$ B.M.*	*Spin-free complexes*	
				No. of unpaired electrons	*$\mu_{(eff)}$ (exptl.) B.M.*
$Cr(PMT)_2Cl_2$	160° (dec)	Lt. blue-green	4.55	4	4.40–4.90
$Mn(PMT)Cl_2$	>300°	pale pink	5.44	5	5.65–6.10
$Fe(PMT)Cl_2$	140° (dec)	yellow	5.32	4	5.1–5.5
$Co(PMT)Cl_2$	>300°	pink	5.12	3	4.30–4.80 (tetra) 4.80–5.20 (octa)
$Ni(PMT)Cl_2$	>300°	Lt. green	3.28	2	2.80–3.50
$Cu(PMT)Cl_2$	250° (dec)	Lt. green	1.55	1	1.70–2.20
$Zn(PMT)_2Cl_2$	107–109°	white	—	–	—
$Mn(PMT)Br_2$	>300°	Lt. pink	5.63	5	5.65–6.10
$Co(PMT)_2Br_2$	159–161°	Deep blue	4.48	3	4.30–4.80 (tetra) 4.80–5.20 (octa)
$Ni(PMT)Br_2$	>300°	yellow-green	3.29	2	2.80–3.50
$Cu(PMT)Br_2$	190° (dec)	brown	1.55	1	1.70–2.20
$Zn(PMT)_2Br_2$	154–156°	white	—	–	—

This conclusion is reinforced by the reflectance spectra of the complexes where the mono-PMT complexes have spectra characteristic of an octahedral field.

It seems safe to assume that the latter complexes are polymeric in nature but it is somewhat difficult to visualize an octahedral environment for the metal ions even if we assume bridging halide ions. There is little evidence, if any, for a metal–metal bond in these structures and yet, in all previous studies of the complexes of 1,5-disubstituted tetrazoles the latter behaved as monodentate ligands. Nevertheless, in the case of the halides, it seems that the polymeric form of the complexes forces PMT into the bridging position. It should be noted that the crystal structure of a similar complex of copper chloride with 1,2,4-triazole, $Cu(Trz)Cl_2$, unambigously indicates that the copper ion is octahedrally coordinated and that the triazole ring acts as a bridging ligand[35].

It is seen from the above review that 1,5-disubstituted tetrazoles form rather interesting series of coordination compounds, which, however, have not been explored in any detail and even the structures of the known complexes remain unknown. Just as in the case of pyridines, it is possible to prepare compounds with two or more tetrazole rings linked together to give, hopefully, chelating tetrazoles. While some work on bitetrazole complexes is now in progress[36], much remains to be done before the chemistry of the tetrazole complexes will be elucidated.

REFERENCES

1 E. OLIVERI-MANDALA, *Gazz. Chim. Ital.*, 44 (1914) 175.
2 D. W. MOORE AND A. G. WHITTAKER, *J. Amer. Chem. Soc.*, 82 (1960) 5007.
3 J. B. LOUNSBURY, *J. Phys. Chem.*, 67 (1963) 721.

4 (a) T S Mihina and R.M Herbst, *J Org Chem*, 15 (1950) 1082; (b) R M Herbst and K R Wilson, *ibid* 22 (1957) 1142.

5 A I Popov and R D. Holm, *J Phys Chem*, 66 (1962) 158

6 G. L. Gilbert and C. H. Brubaker, *Inorg. Chem*, 2 (1963) 1216, b) L. L Garber and C H Brubaker, *J. Amer. Chem Soc*, 88 (1966) 4266; c) L L Garber, L B Sims and C H. Brubaker, *ibid*, 90 (1968) 2518 and references listed therein.

7 (a) A D. Harris, R H Herber, H B Jonassen and G K. Weitheim, *J. Amer Chem Soc*, 85 (1963) 2927, (b) A D. Harris, M B. Jonassen and R. D. Archer, *Inorg. Chem*, 4 (1965) 147; (c) H. B. Jonassen, T Paukert and R. A Henrv, *Appl Spectros*, 21 (1967) 89 and references cited therein

8 A. Dister, *J. Pharm Belge*, 3 (1948) 190

9 A I. Popov and R D. Holm, *J Amer Chem Soc*, 81 (1959) 3250.

10 A I Popov and J. C. Marshall, *J. Inorg. Nucl. Chem*, 19 (1961) 340.

11 A I. Popov and J. C. Marshall, *ibid*, 24 (1962) 1667.

12 T. C Wehman and A I Popov, *J. Phys Chem*, 72 (1968) 4031

13 A. Dister, *J. Pharm. Belge*, 3 (1948) 247.

14 A I Popov, C. C Bisi and M Craft, *J Amer Chem Soc*, 80 (1958) 6513

15 N C Baenzinger, A D Nelson, A. Tulinskv, J. H. Bloor and A. I. Popov, *ibid*, 89 (1967) 6463.

16 O Hassel and C Roemming, *Acta Chem Scand*, 10 (1956) 696

17 J. W. Vaughn, T C Wehman and A I. Popov, *J. Inorg Nucl. Chem*, 26 (1964) 2027

18 W B. Person, R. E Humphrey, W. A. Deskin and A I Popov, *J Amer Chem Soc*, 80 (1958) 2049.

19 F. M. D'Itri and A I. Popov, *ibid*, 90 (1968) 6476.

20 W. B Person, R. E Humphrey and A I Popov, *ibid*, 81 (1959) 273

21 A I. Popov, R. E Humphrey and W. B. Person, *ibid* 82 (1960) 1850

22 T. C. Wehman and A I. Popov, *J. Phys. Chem*, 70 (1966) 3688

23 K. F Schmidt, *Klin Wochschr*, 4 (1925) 1678

24 J. J L. Zwikker, *Pharm. Weekblad*, 71 (1934) 1170

25 M Rheinboldt and H. Stettiner, *Bol Fac filosof. cien lettrus, Univ. San Paulo, Quimica*, 14 (1942) 27, *Chem Abstr*, 40 (1946) 1502

26 W C Golton, M S Thesis, University of Iowa, 1959

27 F. M. D'Itri and A. I Popov, *J Inorg Nucl. Chem*, 31 (1969) 1069

28 C. H. Brubaker, *J. Amer. Chem. Soc*, 82 (1960) 82

29 F. M. D'Itri and A. I. Popov, *Inorg. Chem*, 5 (1966) 1670

30 F. M D'Itri and A I. Popov, *ibid*, 6 (1967) 597.

31 T C Wehman and A I. Popov, *J Inorg. Nucl. Chem*, in press

32 H A. Kuska, F. M D'Itri and A I Popov, *Inorg Chem*, 5 (1966) 1272

33 F. M. D'Itri and A. I. Popov, *ibid*, 6 (1967) 1591.

34 D. M Bowers and A. I Popov, *ibid*, 7 (1968) 1594

35 J A. J. Jarvis, *Acta Cryst.*, 15 (1962) 964

36 D. M. Bowers and A. I Popov, unpublished results.