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Pentamethylenetetrazole Complexes of Iron(II), Manganese(II), Cobalt(II), Nickel(II), and Zinc(II) Perchlorates[1]

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Anhydrous complexes of pentamethylenetetrazole (PMT) were prepared with iron(II), manganese(II), cobalt(II), nickel(II), and zinc(II) perchlorates by treating the ligand with the respective hexaaquo transition metal perchlorates in 2,2-dimethoxypropane solutions. The composition of the complexes is given by $M^{II}(PMT)_6(ClO_4)_2$. Powder X-ray diffraction studies as well as the magnetic and spectral properties of these complexes indicate that they are isomorphous and have an octahedral configuration.

Introduction

Complexing abilities of 1- and 5-substituted tetrazoles *vis-à-vis* metal ions have been studied by several investigators[3,4] who have isolated and characterized several transition metal complexes of the above ligands. Likewise solid complexes of a 1,5-substituted tetrazole, pentamethylenetetrazole (hereafter abbreviated as PMT) with silver nitrate and with iodine monochloride have been isolated.[5-7] It is interesting to note that although PMT was shown to be a moderately strong electron donor, it has an exceptionally weak affinity for protons.[5,8] Thus the donor properties of PMT differ from those of most of the heterocyclic amines (such as pyridines) where a definite correlation exists between the pK_b of the base and its donor strength. This work was undertaken to determine the formation, stability, and structure of PMT complexes with first-row transition metal ions.

Experimental Section

Materials.—Nitromethane (CP grade) was first passed through a cationic-exchange resin,[9] refluxed over barium oxide for 24 hr, and then fractionally distilled through a 1-m column directly into storage bottles. Technical grade 2,2-dimethoxypropane, obtained from the Dow Chemical Co., and hydrated transition metal perchlorates (G. F. Smith Chemical Co.) were used without further purification. The PMT used in this investigation was a product of the Knoll Pharmaceutical Corp. (under the registered name "Metrazol"). It was purified by recrystallization from anhydrous ether and stored over P_2O_5. The melting point of the crystals was 61°. The literature value is 61°.[6]

Preparation of the Transition Metal Complexes of PMT.—Hydrated transition metal perchlorates (0.01 mole) were added to 50 ml of 2,2-dimethoxypropane. The mixture was stirred for 5–10 min to disperse the metal salts which all have limited solubility in 2,2-dimethoxypropane. A slight excess of PMT (0.08 mole) was then added to the solution, and the respective transition metal complexes of PMT precipitated in about 5 min. The products were filtered, washed several times with chilled ethyl ether, and then dried at room temperature. Analytical and physical data are given in Table I.

Attempts to prepare these complexes in aqueous solutions were unsuccessful with the exception of the nickel complex. $Ni(PMT)_6(ClO_4)_2$ was prepared by adding a 20 molar excess of PMT to an aqueous solution of nickel(II) perchlorate. The complex slowly crystallized out of solution over a period of 5–10 days. The light blue product (decomposition point 235°) was identical in all respects with that obtained by the 2,2-dimethoxypropane method. In all other cases the complexes could not be isolated from the aqueous mixture and, in fact, addition of a large excess of PMT to an aqueous solution of a transition metal perchlorate did not produce any change in the absorption spectrum of the metal ion.

Attempts to prepare the respective iron(III) compound were unsuccessful and resulted in a material that, in all probability, contains a mixture of the iron(II) and iron(III) complexes.

All the complexes are nonhygroscopic microcrystalline powders which are quite stable below 150°. When heated gradually they reach their respective melting or decomposition points smoothly. However, if they are heated strongly, they may explode. The complexes are all soluble in water (the nickel(II) complex is only slightly soluble) and many polar nonaqueous solvents, but they are insoluble in most nonpolar solvents. Karl Fischer titrations and elemental analyses indicate that these complexes are essentially anhydrous.

Numerous attempts were made to purify the complexes by recrystallizations from a variety of polar solvents. In all cases solids appeared only when the solvent was essentially completely removed. The residues were either dense, oily liquids or microcrystalline powders.

Analyses.—The complexes were analyzed for the transition metal by the conventional complexometric titration with ethylenediaminetetraacetic acid. Perchlorate analyses were done gravimetrically by precipitating the anion as the tetraphenylarsonium salt. Carbon, hydrogen, and nitrogen analyses were performed by the Spang Microanalytical Laboratory, Ann Arbor, Mich.

X-Ray Powder Patterns.—The measurements were obtained with a North American Phillips Co. 114.6-mm camera (Type 52056) using nickel-filtered Cu $K\alpha$ radiation. The solid samples were first ground to the consistency of fine powder and then packed into 0.3-mm thin-walled glass capillary tubes. These data have been submitted to the "ASTM X-Ray Powder Diffraction File."

Magnetic Susceptibilities.—Magnetic moments, μ_{eff}, of the complexes were determined at 23.5° by the Gouy method. These values along with the corrected molar susceptibilities of the respective complexes are listed in Table II and have been corrected for the diamagnetic susceptibilities of PMT and the central metal ion.[10]

Spectral Measurements. Infrared Spectra.—Spectra in

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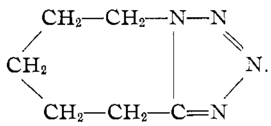
TABLE I

ANALYTICAL AND PHYSICAL DATA OF SOME TRANSITION METAL COMPLEXES OF PENTAMETHYLENETETRAZOLE

Complex[a]	Color	% yield	Mp, °C	% M Calcd	% M Found	% C Calcd	% C Found	% H Calcd	% H Found	% N Calcd	% N Found	% ClO_4 Calcd	% ClO_4 Found
$Mn(PMT)_6(ClO_4)_2$	White	94.5	195–212	5.08	5.30	39.97	39.11	5.59	5.54	31.07	31.05	18.34	19.74
$Fe(PMT)_6(ClO_4)_2$	Light brown	86	194 dec	...	...	39.93	39.11	5.54	5.60	31.05	30.30	18.33	19.84
$Co(PMT)_6(ClO_4)_2$	Rose	94.5	195–205	5.43	5.61	39.82	38.74	5.57	5.41	30.96	29.59	18.28	19.24
$Ni(PMT)_6(ClO_4)_2$	Light blue	95	237 dec	5.40	5.46	39.79	39.42	5.57	5.70	30.94	30.75	18.28	18.52
$Ni(PMT)_6(ClO_4)_2$[b]	Light blue	91	235 dec	5.40	5.43	39.79	39.67	5.57	5.56	30.94	31.09	18.28	18.36
$Zn(PMT)_6(ClO_4)_2$	White	97	148–150	5.98	5.98	39.58	38.83	5.49	5.39	30.77	30.64	18.16	18.98

[a] PMT = $C_6H_{10}N_4$, 

[b] This complex was precipitated from water.

TABLE II

MAGNETIC MOMENTS OF SOME TRANSITION METAL COMPLEXES OF PENTAMETHYLENETETRAZOLE

Complex	$10^4\chi_M$(cor)	μ_{eff}, BM
PMT	2.22	...
$Mn(PMT)_6(ClO_4)_2$	143.51	5.90
$Fe(PMT)_6(ClO_4)_2$	111.51	5.20
$Co(PMT)_6(ClO_4)_2$	98.72	4.60
$Ni(PMT)_6(ClO_4)_2$	35.22	2.92

the 5000–680-cm^{-1} region were obtained with a Beckman IR-5A infrared spectrophotometer with the samples dispersed in Nujol. The infrared spectrum of PMT and a representative complex $Mn(PMT)_6(ClO_4)_2$ are shown in Figure 1. The infrared spectra of the complexes were interpreted relative to the spectrum of PMT and the literature values for the various perchlorate bands. No attempts were made in this study to assign the bands of PMT or any of the complexes prepared.

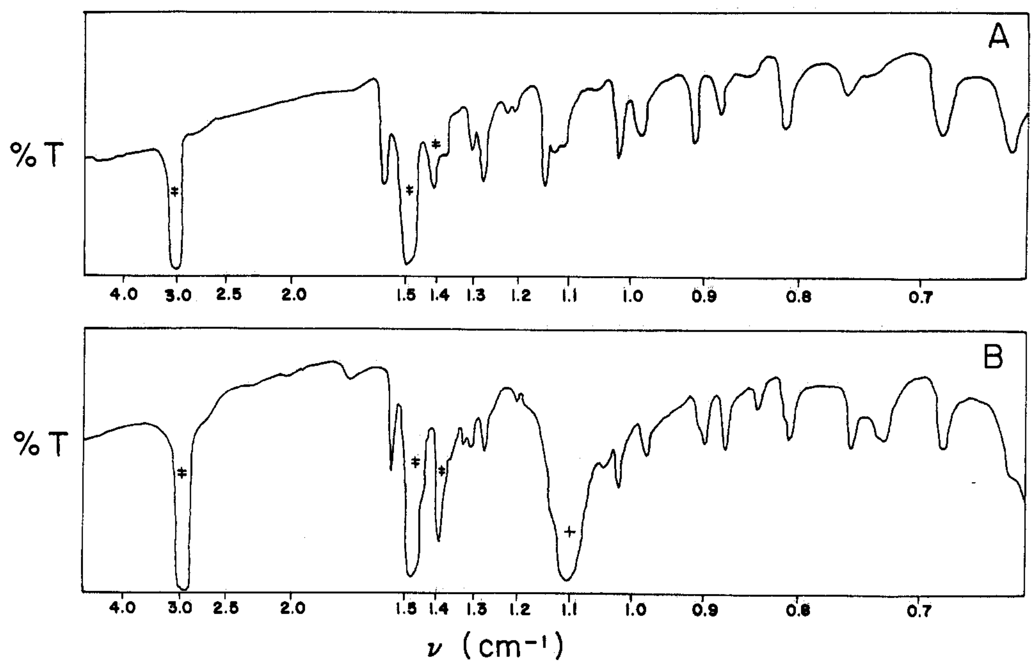


Figure 1.—Infrared absorption spectra of: A, PMT in Nujol mull; B, $Mn(PMT)_6(ClO_4)_2$ in Nujol mull; ‡, Nujol bands; +, perchlorate band.

Visible and Near-Infrared Spectra.—Spectra in the 380–1200-mμ region were obtained with a Cary Model 14 recording spectrophotometer. The electronic absorption spectra are summarized in Table III.

Reflectance Spectra—A Beckman DU spectrophotometer equipped with a reflectance attachment was used to record the reflectance spectra. These spectra were obtained by Professor Luigi Sacconi, Institute of Inorganic Chemistry, University of Florence, Florence, Italy. The data are summarized in Table III.

Results and Discussion

It is interesting to note that the six-coordinate species $M^{II}(PMT)_6(ClO_4)_2$ are readily formed with PMT as the ligand while only the four-coordinate species $M^{II}(py)_4{}^{2+}$ can be isolated in solid form. Weinland, Effinger, and Beck[11] reported the preparation and isolation of complexes of the type $M^{II}(py)_6(ClO_4)_2$. However, there is some doubt that these complexes were actually prepared. Drago and Rosenthal[12] spectrophotometrically determined the existence of hexakis(pyridine)nickel(II) ion in nitromethane solution in the presence of an excess of pyridine. Quagliano, Buffagni, and Vallarino[13] found that on addition

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TABLE III
ELECTRONIC ABSORPTION SPECTRA (IN CM^{-1}) OF SOME TRANSITION METAL COMPLEXES OF PENTAMETHYLENETETRAZOLE IN NITROMETHANE AND IN THE SOLID STATE

Complex	State	ν_{max}(ϵ_m for soln)
$Co(PMT)_6(ClO_4)_2$	Soln	20,600 (≈22), ≈8300 (≈5)
$Co(PMT)_6(ClO_4)_2$	Solid	20,400, 8500
$Ni(PMT)_6(ClO_4)_2$	Soln	17,400 (9.5), 10,500 (8.0)
$Ni(PMT)_6(ClO_4)_2$	Solid	26,300, 16,000, 9760
$Fe(PMT)_6(ClO_4)_2$	Solid	10,000

of an excess of 3,4- or 3,5-lutidine to a yellow dichloromethane solution of tetrakis(3,4-lutidine)nickel(II) perchlorate, the blue hexakis(3,4- or 3,5-lutidine)-nickel(II) perchlorate complex forms in solution. However, attempts to isolate the solid complex failed as it reverted back to the respective tetrakis(3,4- or 3,5-lutidine) complex.

Some general information about the configurations of all of these complexes can be obtained from their respective infrared spectra. The infrared region (5000–650 cm^{-1}) yields little information concerning the complexation of the PMT ligand to the metal. Some information is obtained, however, from the symmetric stretch ν_1 (≈932 cm^{-1}) and asymmetric stretch ν_3 (≈1090 cm^{-1}) of the perchlorate ion. Inspection of the spectra shows that, in all cases, the broad, degenerate ν_3 band is not split and the ν_1 symmetric stretching frequency, when it appears, is very weak. This suggests that the perchlorate group in these complexes is ionic, and it appears that the PMT ligands are arranged octahedrally around the central metal ion.[14]

Hexakis(pentamethylenetetrazole)nickel(II) Perchlorate.—The spectrum expected for octahedral complexes is obtained in nitromethane for $Ni(PMT)_6(ClO_4)_2$ (Figure 2) with the ν_1 and ν_2 absorption bands located at 10,500 cm^{-1} (955 mμ, apparent ϵ_{max} 8.0) and 17,400 cm^{-1} (575 mμ, apparent ϵ_{max} 9.5). The high-frequency absorption band, located at approximately 25,000 cm^{-1}, is shifted to higher energies on complexation and is not observed owing to the opacity of the solvent absorption at frequencies higher than 25,650 cm^{-1} (390 mμ).

This spectrum compares favorably with that of tris-(ethylenediamine)nickel(II) ion[15] indicating that PMT forms a fairly strong complex with the nickel ion. This may explain why $Ni(PMT)_6(ClO_4)_2$ can be precipitated from aqueous solution. The ratio ν_2/ν_1 for the complex is 1.66 which is the same as that observed for tris-(ethylenediamine)nickel(II) ion and compares well with the calculated value of 1.8 which is one of the distinguishing features of octahedrally coordinated complexes.[15]

The reflectance spectrum of the solid complex (Figure 3) is in good agreement with the above values and shows absorbances at 9760 (ν_1, 1025 mμ), 16,000 (ν_2, 625 mμ), and 26,300 cm^{-1} (ν_3, 380 mμ).

When a nickel(II) atom is surrounded by six identical groups such as the hexaammine- or hexaaquonickel(II) ions, the orbital contribution in excess of the "spin-

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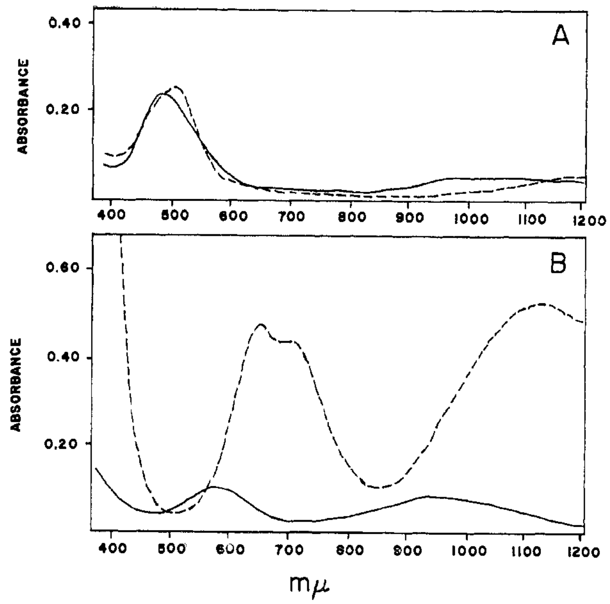

Figure 2.—The visible and near-infrared spectra: A, 1 × 10^{-2} *M* $Co(PMT)_6(ClO_4)_2$ (solid line, 1-cm cells) and 5 × 10^{-3} *M* $Co(ClO_4)_2 \cdot 6H_2O$ (broken line, 5-cm cells) in nitromethane; B, 1 × 10^{-2} *M* $Ni(PMT)_6(ClO_4)_2$ (solid line, 1-cm cells) and 6.72 × 10^{-3} *M* $Ni(ClO_4)_2 \cdot 6H_2O$ (broken line, 10-cm cells) in nitromethane. The spectrum obtained for $Ni(PMT)_6(ClO_4)_2$ precipitated from water is identical with that given by the solid line.

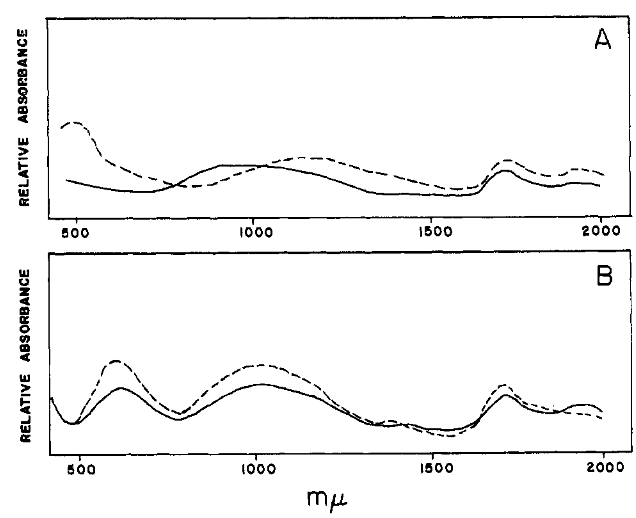

Figure 3.—The reflectance spectra of: A, $Fe(PMT)_6(ClO_4)_2$ (solid line) and $Co(PMT)_6(ClO_4)_2$ (broken line); B, $Ni(PMT)_6(ClO_4)_2$ precipitated from 2,2-dimethoxypropane (solid line) and water (broken line).

only" value of 2.83 BM is small; and magnetic moments of the order of 3.1–3.2 BM are observed.[16] Magnetic susceptibility measurements show that the $Ni(PMT)_6(ClO_4)_2$ complex has a magnetic moment of 2.92 BM corresponding to two unpaired electrons, as expected for the octahedral complex.

The high-spin octahedral spectrum of Co^{II} ion is characterized by three absorption bands of low molar absorptivity found at approximately 8350 (ν_1), 17,850 (ν_2), and 20,000 (ν_3) cm^{-1} (1196, 560, and 500 mμ,

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respectively).[17] The most intense band is ν_2 having a molar absorptivity of approximately 10 while ν_3 usually appears as a shoulder on the high-frequency side of the ν_2 band.

The expected spectrum for octahedral complexes is obtained in nitromethane for $Co(PMT)_6(ClO_4)_2$ (Figure 2) having a weak broad absorption band ν_1 at 8300 cm^{-1} (1205 mμ, ϵ_{max} 5) and a more intense unsymmetrical band at 20,600 cm^{-1} (485 mμ, ϵ_{max} 22) which is made up of ν_2 and ν_3. The shift of the absorption bands of cobalt(II) perchlorate hexahydrate upon addition of PMT (Figure 2) indicates that in this system PMT may be a slightly stronger ligand than water.

The reflectance spectrum of the solid complex (Figure 3) shows two absorption maxima, one at 8500 cm^{-1} (1178 mμ) and the other at 20,400 cm^{-1} (491 mμ). It is seen that the spectrum correlates closely to that in the nitromethane solution.

The magnetic moment of $Co(PMT)_6(ClO_4)_2$ was calculated to be 4.60 BM which agrees well with literature values of high-spin complexes ranging from 4.30 to 5.20 BM.[18]

Hexakis(pentamethylenetetrazole)zinc(II) Perchlorate.—Since there are no ligand field stabilization effects in zinc(II) compounds because of their completed d shells, the stereochemistry of these complexes is determined by the zinc(II) ion size as well as by the electrostatic and covalent bonding forces. While a coordination number of four, which utilizes a tetrahedral configuration, is more common for zinc(II) compounds, a coordination number of six and octahedral configuration have been observed with the hexaammine-,[19] hexaaquo-, and tris(ethylenediamine)-zinc(II) complexes.[20] Pauling[21] states that a square-coplanar configuration is theoretically not possible for metal ions that have filled shells, and, accordingly, only four tetrahedral or six octahedral bonds are to be expected.

Hexakis(pentamethylenetetrazole)manganese(II) Perchlorate.—The electronic and reflectance spectra of $Mn(PMT)_6(ClO_4)_2$ could not be obtained owing to its limited solubility and extremely low molar absorptivity.[22] The magnetic moment of the complex was 5.90 BM, indicating a spin-free system.

Hexakis(pentamethylenetetrazole)iron(II) Perchlorate.—The reflectance spectrum of $Fe(PMT)_6(ClO_4)_2$ (Figure 3) is that expected for an iron(II) ion in an octahedral field.[23] The magnetic moment of the complex was 5.20 BM which indicates a spin-free system.

The properties of the $Co(PMT)_6(ClO_4)_2$ and $Ni(PMT)_6(ClO_4)_2$ complexes indicate that they have an octahedral configuration. The configurations of the remainder of the $(PMT)_6$ transition metal perchlorates are postulated to be octahedral since the X-ray powder diffraction data showed that all of these six-coordinated complexes are isomorphous.

The electron spin resonance data[24] indicate that the complexes are in a distorted octahedral or tetragonal configuration, and the metal–ligand bond is about 91% ionic. These findings are in good agreement with Pauling's[25] proposed criterion for distinguishing between essentially ionic and essentially covalent bonding between the metal ion and its ligands.

A complete and satisfying explanation for the formation of the hexacoordinated transition metal–PMT complexes cannot be given at the present time. However, there are factors other than ligand field energies of the transition metal ion which must be considered. The actual geometry and coordination structure which define the ligand field in a given complex are largely determined by the bonding interaction between the metal ion and the ligand.[26] Certain configurations appear to be obtainable only with the assistance of certain anions such as the perchlorate ion.

Since the perchlorate ion is one of the least polarizable anions known, it has a very slight tendency to serve as a ligand in complexes which allow for more complete electrostatic polarization type of bonding of the PMT molecules to the respective central metal ion.

In contrast to the 1- and 5-substituted tetrazoles, the 1,5-substituted tetrazoles are incapable of forming simple salts with metal ions. In the case of PMT the complexation can occur through any one of the four nitrogen atoms or by the interaction of the π electrons associated with the tetrazole ring. Physicochemical properties of the complexes described in this paper agree with the former possibility. Steric considerations also indicate that the lone pair of electrons on the apex nitrogen (position 3) of the tetrazole ring form the bond with the respective metal ions. A detailed X-ray study of these complexes, which is now being carried out in this laboratory, should unambiguously resolve this problem.

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