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Pentamethylenetetrazole Complexes of Copper(I) and Copper(II) Perchlorates[1]

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Received July 30, 1966

Anhydrous complexes of pentamethylenetetrazole (PMT) with Cu(I) and Cu(II) perchlorates were prepared by allowing the ligand to react with copper(II) perchlorate hexahydrate in acetic acid or 2,2-dimethoxypropane solutions. Three complexes, having the compositions $Cu(PMT)_2ClO_4$, $Cu(PMT)_4(ClO_4)_2$, and $Cu(PMT)_6(ClO_4)_2$, were isolated and characterized. Physicochemical measurements indicate that the hexacoordinated PMT complex is situated in a tetragonal environment.

Introduction

In our previous communications[2] we described complexes of pentamethylenetetrazole (hereafter abbreviated as PMT) with iron(II), manganese(II), cobalt(II), nickel(II), and zinc(II) perchlorates. This work is now expanded to include the PMT complexes of copper(I) and copper(II) perchlorates.

Various investigators have reported the preparation of hexaammine copper(II) complexes. Recently Elliott and Hathaway[3] prepared and examined a series of hexaammine copper(II) complexes of $[Cu(NH_3)_6][X_2]$, where X^- represents Cl^-, Br^-, I^-, BF_4^-, or ClO_4^-. Elliott, *et al.*,[4] have described a six-coordinate hexanitro complex $K_2M^{II}[Cu(NO_2)_6]$ where M^{II} represents Pb^{2+}, Ba^{2+}, or Cu^{2+} and in which the copper(II) ion is in a tetragonal environment.

Although from time to time the preparation of the hexakis(pyridine)copper(II) complex has been reported,[5] the assumption that these complexes contain six pyridine molecules coordinated to the central copper atom has not been adequately demonstrated. A report by Royer[6] seemed to indicate that complexes of the type $Cu(pic)_6(ClO_4)_2$ and $Cu(pic)_6(NO_3)_2$ (where pic represents 3- or 4-picoline) were isolated but these compounds have not been unambiguously characterized in the solid state.[7] Biagetti, *et al.*,[8] reporting on the copper(II) nitrate–pyridine system, could only find evidence for the existence of $Cu(py)_2(NO_3)_2$, $Cu(py)_4(NO_3)_2$, and $Cu(py)_4(NO_3)_2 \cdot 2py$ species in the solid state. These three complexes form a reversible system with interconversions by the addition or removal of pyridine. All of the pyridine molecules in the bis- and tetrakis(pyridine)copper(II) nitrate are coordinated to the copper ion. Infrared data, however, indicate that in the complex with six pyridine molecules only four of them are actually coordinated with the Cu(II) ion.

Various hexacoordinated copper chelate complexes have been reported. Inskeep,[9] for example, prepared six-coordinated chelate copper(II) nitrate complexes with 2,2′-bipyridine and 1,10-phenanthroline as ligands.

This work was undertaken to determine the formation, stability, and structure of the copper(I)- and copper(II)-PMT complexes.

Experimental Section

Materials.—Nitromethane (CP grade) was first passed through a cationic exchange resin,[10] refluxed over barium oxide for 24 hr, and distilled directly into storage bottles.

Technical grade 2,2-dimethoxypropane (hereafter abbreviated as DMP) was used without further purification. Hydrated copper(II) perchlorate (G. F. Smith Chemical Co.) was dried *in vacuo* at 75° for 48 hr. The PMT used in this investigation was obtained from the Knoll Pharmaceutical Corp. under the registered name "Metrazol" and purified by recrystallization from anhydrous ether. It was stored over P_2O_5.

Bis(pentamethylenetetrazole)copper(I) Perchlorate.—A solution containing 3.71 g (0.01 mole) of copper(II) perchlorate hexahydrate in 65 ml of DMP was prepared. The mixture was stirred long enough to disperse the copper(II) salt which has limited solubility in DMP. To the mixture was added 3.45 g (0.025 mole) of dry PMT. A blue oily substance formed immediately. The stirring was continued for approximately 3 hr during which the oily substance slowly solidified to a white solid interspersed in a brown decomposition mixture. The precipitate was washed several times with chilled acetone (which removed the brown impurity), filtered, and dried at 110°. The white solid was slightly soluble in acetone and nitromethane but insoluble in most other common solvents. It could not be purified by recrystallization. The compound was stable at room temperature and began to decompose at 226°. *Anal.* Calcd for $Cu(PMT)_2ClO_4$: Cu, 14.46; C, 32.80; H, 4.56; N, 25.51. Found: Cu, 14.53; C, 32.41; H, 5.05; N, 25.12.

Tetrakis(pentamethylenetetrazole)copper(II) Perchlorate.—A 3.71-g sample (0.01 mole) of copper(II) perchlorate hexahydrate was added to 50 ml of DMP. The mixture was stirred for about 5 min and then 5.52 g (0.04 mole) of dry PMT was added. After approximately 5 min a blue precipitate was formed. This precipitate was filtered, washed several times with chilled ether, and dried at 110°. The product was obtained in 96% yield and had a melting point of 141–145°. *Anal.* Calcd for $Cu(PMT)_4(ClO_4)_2$: Cu, 7.80; C, 35.39; H, 4.95; N, 27.52. Found: Cu, 7.60; C, 35.40; H, 5.14; N, 26.73.

This compound was also prepared by adding 3.72 g (0.01 mole) of vacuum-dried copper(II) perchlorate hexahydrate to 200 ml of anhydrous acetic acid. After the copper perchlorate was completely dissolved, a stoichiometric amount of acetic anhydride (5.67 ml or 0.06 mole) required to react with the hydrated water

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[1] Taken in part from the M.S. Thesis of F. M. D'Itri, Michigan State University, Feb 1966.

[2] (a) F. M. D'Itri and A. I. Popov, *Inorg. Chem.*, **5**, 1670 (1966); (b) H. A. Kuska, F. M. D'Itri, and A. I. Popov, *ibid.*, **5**, 1272 (1966).

[3] H. Elliott and B. J. Hathaway, *ibid.*, **5**, 885 (1966).

[4] H. Elliott, B. J. Hathaway, and R. C. Slade, *ibid.*, **5**, 669 (1966).

[5] R. Weinland, K. Effinger, and V. Beck, *Arch. Pharm.*, **265**, 352 (1927).

[6] D. J. Royer, *J. Inorg. Nucl. Chem.*, **11**, 151 (1959).

[7] D. J. Royer, personal communication.

[8] R. V. Biagetti, W. G. Bottjer, and H. M. Haendler, *Inorg. Chem.* **5**, 379 (1966).

[9] R. G. Inskeep, *J. Inorg. Nucl. Chem.*, **24**, 763 (1962).

[10] G. H. Clarke and S. Sandler, *Chemist Analyst*, **50**, 76 (1961).

of the copper(II) perchlorate was added, and $Cu(ClO_4)_2 \cdot x HOAc$ precipitated as light blue crystals in 4–6 hr. These crystals were filtered and redissolved in hot acetic acid. Dry PMT (11.04 g, 0.08 mole) was added to the hot solution which turned deep blue. Large, deep blue crystals precipitated in 4–6 hr. The product was obtained in a 43.2% yield. The crystals were purified by recrystallization from acetic acid and dried at 110°. *Anal.* Calcd for $Cu(PMT)_4(ClO_4)_2$: Cu, 7.80; C, 35.39; H, 4.95; N, 27.52; Cl, 8.71; ClO_4, 24.52. Found: Cu, 7.71; C, 35.37; H, 5.06; N, 27.39; Cl, 8.85; ClO_4, 24.16.

Hexakis(pentamethylenetetrazole)copper(II) Perchlorate.—This complex was prepared by the method described earlier.[2a] A light blue precipitate was obtained in 96% yield. The melting point of the complex was 117.5°. *Anal.* Calcd for $Cu(PMT)_6(ClO_4)_2$: Cu, 5.80; C, 39.65; H, 5.55; N, 30.83; ClO_4, 18.20. Found: Cu, 5.71; C, 39.62; H, 5.63; N, 31.10; ClO_4, 18.75.

Elemental Analyses.—Copper was determined by EDTA titration, and perchlorate was determined gravimetrically as the tetraphenylarsonium salt. Carbon, hydrogen, nitrogen, and chloride analyses were performed by the Spang Microanalytical Laboratory, Ann Arbor, Mich.

X-Ray Powder Patterns.—These were taken with a 114.6-mm camera (Type 52056) using nickel-filtered Cu Kα radiation. The solid samples were first ground to the consistency of fine powder and packed into 0.3-mm thin-walled glass capillary tubes. These data have been submitted to the A.S.T.M. X-Ray Powder Diffraction File.

Spectral Measurements. Infrared Spectra.—Spectra in the 5000–680-cm^{-1} region were obtained with a Beckman IR5A infrared spectrophotometer, using Nujol mulls.

Visible and Near-Infrared Spectra.—Spectra in the 380–1200-mμ region were obtained with a Cary Model 14 recording spectrophotometer.

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 visible and the reflectance spectra are summarized in Table I.

TABLE I

ELECTRONIC ABSORPTION SPECTRA (IN mμ) OF THE COPPER(II) COMPLEXES OF PENTAMETHYLENETETRAZOLE IN NITROMETHANE AND IN THE SOLID STATE

Complex	State	λ_{max} (ϵ_{molar} for solution)
$Cu(PMT)_4(ClO_4)_2$	Soln	670 (81)
$Cu(PMT)_4(ClO_4)_2$	Solid	625
$Cu(PMT)_6(ClO_4)_2$	Soln	680 (103)
$Cu(PMT)_6(ClO_4)_2$	Solid	740

Magnetic Susceptibilities.—Magnetic moments, μ_{eff}, of the complexes were determined at 23.5° by the Gouy method. The values are listed in Table II and have been corrected for the diamagnetic susceptibilities of PMT, perchlorate anion, and copper(II) cation.

TABLE II

MAGNETIC MOMENTS OF COPPER(II) PERCHLORATE–PMT COMPLEXES

Complex	Color	$10^4\chi_M$ (corr)	μ_{eff}, BM
$Cu(PMT)_4(ClO_4)_2$	Blue	20.324	2.21
$Cu(PMT)_6(ClO_4)_2$	Light blue	12.424	1.74
$Cu(PMT)_2ClO_4$	White	. . .	Diamagnetic

Thermogravimetric Analysis.—This analysis was performed at the Dow Chemical Co., Midland, Mich. The analysis of $Cu(PMT)_6(ClO_4)_2$ was carried out in a nitrogen atmosphere with a heating rate of approximately 2°/min.

Results

The following three copper(II) perchlorate systems were investigated spectrophotometrically in nitromethane.

Copper(II) Perchlorate Hexahydrate.—As increasing amounts of PMT are added to a 0.01 *M* copper(II) perchlorate hexahydrate solution in nitromethane, a hypsochromic shift with an accompanying hyperchromic effect was noted. The solvated copper ion absorption band shifted progressively from 770 mμ (molar absorptivity 15) down to 670 mμ at a 4:1 PMT to Cu^{2+} ratio (apparent molar absorptivity 82.5). As the PMT to copper ratio was increased further, the peak started to shift in the opposite direction. The maximum displacement was obtained at a PMT: Cu^{2+} ratio of 40:1 at which point the absorbance maximum was at 705 mμ with an apparent molar absorptivity of 113 (Figure 1). As additional PMT was added, the maximum did not shift but the absorbance increased. Although the limiting absorbance was not reached, it appeared that the absorbance tended toward a limiting value.

Hexakis(pentamethylenetetrazole)copper(II) Perchlorate.—The apparent molar absorptivity of 0.01 *M* hexakis(pentamethylenetetrazole)copper(II) perchlorate in nitromethane was 103 at 680 mμ (Table I). When additional PMT was added, a bathochromic shift to 705 mμ with an accompanying hyperchromic effect was noted, similar to the behavior described above.

Tetrakis(pentamethylenetetrazole)copper(II) Perchlorate.—A 0.01 *M* solution of tetrakis(pentamethylenetetrazole)copper(II) perchlorate in nitromethane had an absorbance maximum at 670 mμ with an apparent molar absorptivity of 81. Upon addition of excess PMT the peak shifted to a limiting value of 705 mμ (apparent molar absorptivity 119) at a 20-mole excess of PMT.

The absorption spectra of the respective complexes (Figure 2) in nitromethane solutions closely resemble those obtained by reflectance measurements except for a moderate difference in the position of the absorption bands. It seems, therefore, that the absorbing species in the solid and in solutions must be very similar in nature. From the shifting of the absorbance maxima to higher wavelengths with the addition of excess PMT, it appears that six-coordinated Cu(II)–PMT complex must also exist in nitromethane solution. The method of continuous variation[11] was used in an attempt to determine the stoichiometry of the PMT–Cu(II) complex in solution. The total concentrations were 0.025 and 0.05 *M*. Maxima were obtained at a ligand mole fraction of approximately 0.8. The measurements were carried out at four different wavelengths, and the shifting of the maxima to lower values of mole fraction of the ligand was noted as the wavelength was decreased. The presence of more than one absorbing species in solution was thus indicated. Therefore, the spectrophotometric study of the complex in

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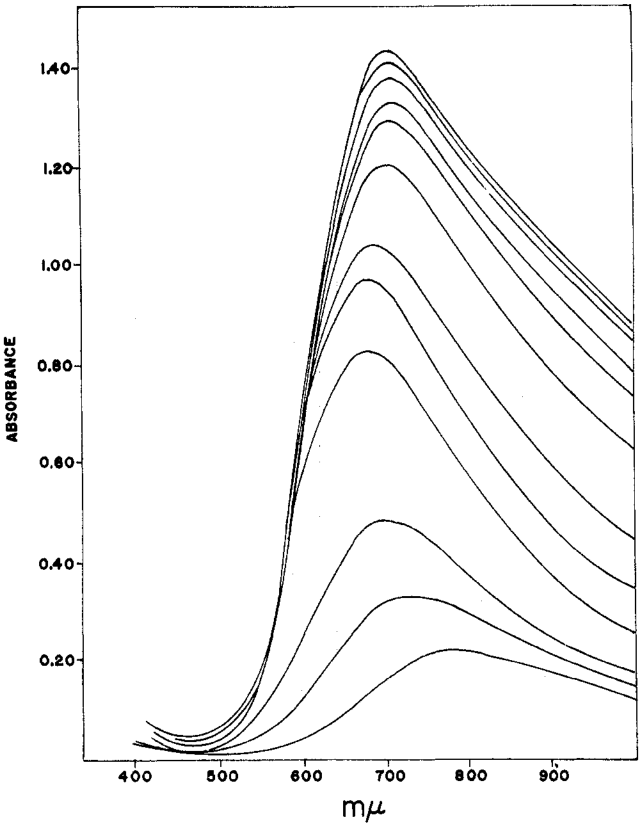

Figure 1.—The spectrophotometric study of the $Cu(ClO_4)_2 \cdot 6H_2O$–PMT system in nitromethane. Concentration of the complex is 1.0×10^{-2} *M*. The PMT:$Cu(ClO_4)_2 \cdot 6H_2O$ ratios are, respectively (starting with the lower curve), 0, 1, 2, 4, 5, 6, 10, 15, 20, 30, 40, and 50.

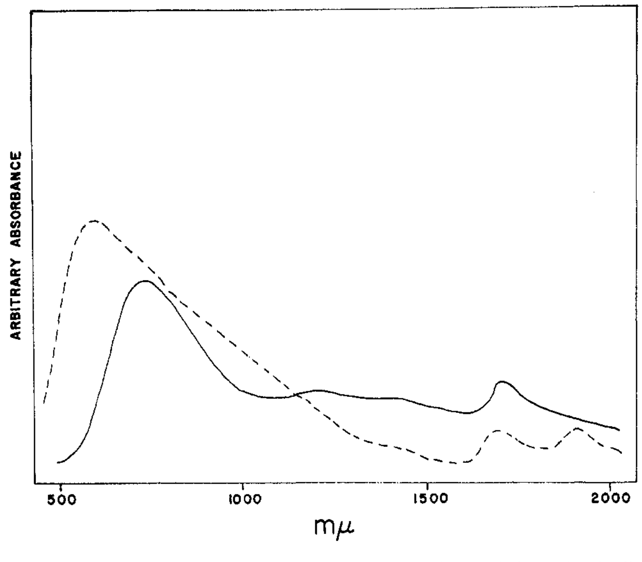

Figure 2.—The reflectance spectra of $Cu(PMT)_6(ClO_4)_2$ (solid line) and $Cu(PMT)_4(ClO_4)_2$ (broken line).

solution presented considerable difficulty since various products of the stepwise dissociation of the complex according to the general equations

$$Cu(PMT)_n{}^{2+} \rightleftharpoons Cu(PMT)_{n-1}{}^{2+} + PMT$$
$$Cu(PMT)_{n-1}{}^{2+} \rightleftharpoons Cu(PMT)_{n-2}{}^{2+} + PMT, \text{ etc.}$$

may be present in equilibrium in the solution depending on the concentration of the ligand.

Since we could not obtain a precise value of the limiting absorbance of the (presumably) $Cu(PMT)_6{}^{2+}$ complex, it was not possible to use conventional spectrophotometric techniques[12] for the determination of successive formation constants.

Since the tetragonal distortion splits the E_g and T_{2g} levels, three transitions from the $d_{x^2-y^2}$ to d_{xy}, d_{z^2}, and degenerate (d_{xz}, d_{yz}) orbitals, respectively, are possible. The mole ratio study of copper(II) perchlorate hexahydrate and tetrakis- and hexakis(pentamethylenetetrazole)copper(II) perchlorates (Figure 1), as well as reflectance spectra (Figure 2) of the tetrakis- and hexakis(pentamethylenetetrazole)copper(II) perchlorates, all show a single unsymmetrical absorption band in the 680–800 mμ (15,000–12,500 cm^{-1}) region. This absorption consists of two and possibly all three of the above-mentioned transitions.

The infrared spectra of $Cu(PMT)_2ClO_4$, $Cu(PMT)_4(ClO_4)_2$, and $Cu(PMT)_6(ClO_4)_2$ in the sodium chloride region were essentially those of the ligand. The spectra also appeared, in all practical respects, to be identical with the infrared spectrum of hexakis(pentamethylenetetrazole)manganese(II) perchlorate illustrated in our previous paper.[2a] Evaluation of the spectra indicates that the perchlorate ions are not coordinated[13–15] to the copper ion since there is no splitting of asymmetric stretching vibration ν_3 at 1100 cm^{-1} or activation of the theoretically infrared-inactive symmetric vibration ν_1 which usually appears as a very weak band at 932 cm^{-1}.

The thermogravimetric decomposition of $Cu(PMT)_6(ClO_4)_2$ began at approximately 165°. The rate of the reaction increased rapidly, and at 180° the rate of volatilization reached explosive limits. The momentum imparted to the sample holder carried it past the point of 100% weight loss. The reaction was exothermic, judging by the increase in temperature at the end of the decomposition of the sample.

X-Ray powder diffraction studies show that $Cu(PMT)_6(ClO_4)_2$ is isomorphous with the octahedral PMT complexes of Fe(II), Mn(II), Co(II), Ni(II), and Zn(II) perchlorates.[2a] Bis(pentamethylenetetrazole)copper(I) and tetrakis(pentamethylenetetrazole)copper(II) perchlorates are not mutually isomorphous or isomorphous with hexakis(pentamethylenetetrazole)copper(II) perchlorate.

The magnetic moments of tetrakis- and hexakis(pentamethylenetetrazole)copper(II) perchlorates were found to be 2.21 and 1.74 BM, respectively (Table II), while the observed values of the magnetic moment for most copper(II) compounds having ionic or rather weak covalent bonds are 1.70–2.20 BM.[16] The magnetic moments of tetrakis- and hexakis(pentamethylenetetrazole)copper(II) perchlorates compare well with these values.

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Discussion

Experimental evidence seems to indicate rather unambiguously that pentamethylenetetrazole is a somewhat unusual monodentate ligand in that it readily forms a hexacoordinated complex with Cu(II) ion. This is surprising in view of the inability of ligands such as pyridine to form similar complexes. Yet, in general, pyridine seems to be a much stronger ligand than PMT with regard to metal ions[17] and nonmetallic Lewis acids such as the halogens.[18] Likewise, pyridine has relatively pronounced basic properties which parallel its complexing ability toward metal ions. On the other hand, PMT does not seem to possess any proton-acceptance ability, at least in aqueous solutions, and behaves as a very weak base in such protogenic solvents as acetic acid.[17]

An alternate configuration for the hexakis(pentamethylenetetrazole)copper(II) perchlorate has been considered, namely, $[Cu(PMT)_4](ClO_4)_2 \cdot 2PMT$, but was rejected on the following basis. (1) The X-ray powder diffraction studies showed that $Cu(PMT)_6(ClO_4)_2$ is isomorphous with the octahedral PMT complexes of Fe(II), Mn(II), Co(II), Ni(II), and Zn(II).[2a] (2) Electron spin resonance studies of the $Cu(PMT)_6(ClO_4)_2$ complex indicate that it has a distorted octahedral symmetry.[2b] (3) Thermogravimetric decomposition of the complex did not indicate any transitory formation of $Cu(PMT)_4(ClO_4)_2$.

Spectral measurements on the PMT–Cu(II) system in nitromethane likewise seem to indicate that hexacoordination may exist in solution. It is interesting to note that in aqueous solution the replacement of water molecules by ammonia in the coordination sphere of Cu^{2+} ion causes a steady shift of absorption maximum from 800 mμ (ϵ 11) to 590 mμ (ϵ 50) until four ammonia molecules are coordinated.[19] The addition of a fifth ammonia molecule shifts the absorption band back to lower energy (660 mμ). No spectrophotometric evidence was found, however, for the addition of a sixth ammonia molecule even in liquid ammonia solution.[19] Ethylenediamine complexes behave similarly while pyridine does not seem to form complexes with a pyridine:copper ratio greater than 4:1.

The absence of spectral shifts in aqueous solutions upon addition of PMT to Cu(II) indicates that PMT cannot compete successfully with water for the coordination position around the Cu(II) ion, at least when water is present in a large excess. It should be noted that similar behavior was observed with other first-row transition metal ions with the exception of Ni(II) where the PMT complex could readily be isolated from the aqueous solution.[2a]

The mechanism of formation of bis(pentamethylenetetrazole)copper(I) perchlorate remains obscure. The oxidation state of copper in the complex has been unambiguously established by esr, magnetic susceptibility, and polarographic studies (in acetonitrile solutions), as well as by the elemental analysis. Since the complex is prepared starting with copper(II) perchlorate, a redox reaction obviously takes place, but the nature of the reductant has not been established as yet.

Acknowledgment.—The authors gratefully acknowledge the support of this work by Grant MH-07825 from the Institute of Mental Health, Public Health Service. They also wish to express their appreciation to Professor L. Sacconi, University of Florence, for the reflectance spectra and some of the X-ray powder data, to Professor R. S. Nicholson of this department for help with the polarographic study of the Cu(I) complex, and to the Dow Chemical Co. for 2,2-dimethoxypropane and for the thermogravimetric analysis of the Cu(II) complex.

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