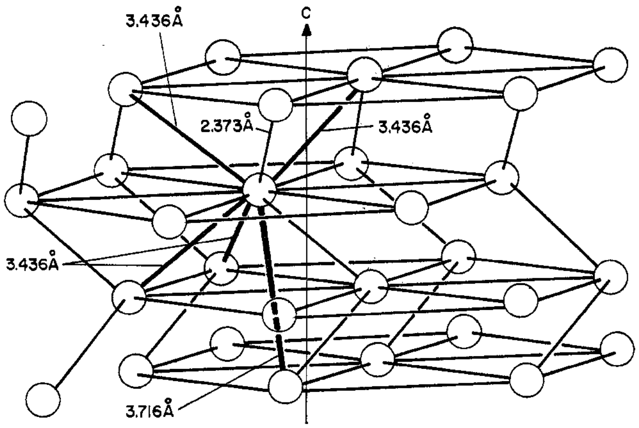

Figure 1.—Nearest neighbor distances in trigonal selenium.

Several important coordination distances are given in Figure 1. The nearest neighbor distance of atoms on adjacent chains (3.436 A) is considerably shorter than the 4.0 A one would expect if only van der Waals forces were operating between the chains.[10]

The reliability factor

$$R = \sum_{n}^{N} \frac{||F_o - |F_c||_n}{\sum_{n}^{N} |F_o|_n}$$

where N is the total number of observed reflections, for the combined data is quite good. However, with so few independent variables and data points (only *12* independent reflections were observed with Mo Kα radiation; see Table II), the standard deviations for each parameter (Table I) should be more indicative of the precision of this work.

Investigation of three-dimensional data is planned in order to learn more about the defect structure of the vibrational motion of the chains.

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The Infrared Spectra of Transition Metal Complexes of Pentamethylenetetrazole[1]

By Frank M. D'Itri and Alexander I. Popov

Received February 4, 1967

In our previous communications[2] we described the preparation and physical properties of three types of transition metal perchlorate complexes of pentamethylenetetrazole (hereafter abbreviated at PMT) having the compositions: $Cu(PMT)_2ClO_4$, $Cu(PMT)_4(ClO_4)_2$, and $M^{II}(PMT)_6(ClO_4)_2$, where M^{II} = manganese(II), iron(II), cobalt(II), nickel(II), copper(II), or zinc(II). Physicochemical measurements indicate that the hexacoordinated transition metal complexes are isomorphous and have octahedral configurations.

The present work was undertaken to determine the infrared spectra of these complexes in the 5000–180-cm^{-1} spectral region so as to obtain some information on the structure of these compounds and the nature of the metal–ligand bond.

Experimental Section

The materials, preparation, description, analytical data, and physicochemical properties of the transition metal complexes of PMT of the type $M^{II}(PMT)_6(ClO_4)_2$, $Cu(PMT)_4(ClO_4)_2$, and $Cu(PMT)_2ClO_4$ have been described in previous publications.[2]

Infrared Measurements.—Infrared spectra in the 5000–670-cm^{-1} spectral regions were obtained on a Beckman IR-5A spectrometer. The solid complexes were dispersed in Nujol. An attempt was made to measure the spectra of complexes in KBr pellets, but the compounds appeared to undergo a partial decomposition in the KBr press with the formation of metal–bromide complexes.

The measurements in the 670–180-cm^{-1} regions were carried out on a Perkin-Elmer 301 spectrometer. All of the spectra were obtained on Nujol mulls which were supported between plates of cesium bromide or polyethylene windows and using air or polyethylene of the same thickness as references. The entire system was continually flushed with dry nitrogen.

In order to obtain spectra of the complexes in the 700–100-cm^{-1} region, it was necessary to change gratings, mirrors, choppers, and restrahlen filters several times. It was, therefore, found convenient to obtain the spectra of all of the compounds under investigation in one region before modifying the instrument for the next region. For this reason, the relative intensities of bands for the same sample in different regions probably do not have much significance. The breaks in the spectra due to these changes are shown on the figures by interruptions in the traces.

The stabilities of the complexes in the Nujol mulls were checked by remeasuring some of the spectra after 24 hr. In all cases the spectra were reproducible.

Discussion and Results

(1) Infrared Spectra in the 5000–670-Cm^{-1} Region. Hexakis(pentamethylenetetrazole)–Transition Metal–Perchlorate Complexes.—The comparison of the spectrum of PMT with those of the hexakis(pentamethylenetetrazole)–transition metal–perchlorate complexes shows little change in the PMT spectrum upon complexation. There are, however, small (±3-cm^{-1}) absorption shifts which vary with the respective central metal ion. The uncomplexed perchlorate ion has a regular tetrahedral structure and belongs to the point group T_d.[3] If, in the process of complexation, the ClO_4^- ion becomes coordinated to the metal ion, the oxygen atom involved in the partial covalent bonding is no longer equivalent to the other three oxygen atoms, and the symmetry of the perchlorate group is lowered to C_{3v}. As a result, the broad, degenerate ν_3 band splits into two well-defined bands with maxima between 1200 and 1000 cm^{-1}. Likewise, the chlorine-coordinated oxygen (Cl—O*) stretching frequency ν_2

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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) H. A. Kuska, F. M. D'Itri, and A. I. Popov, *Inorg. Chem.*, **5**, 1272 (1966); (b) F. M. D'Itri and A. I. Popov, *ibid.*, **5**, 1670 (1966); (c) F. M. D'Itri and A. I. Popov, *ibid.*, **6**, 597 (1967).

(3) B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.*, 3091 (1961).

becomes infrared active and appears as a relatively intense band at about 950–925 cm^{-1}.[4–6]

It is seen that in our spectra, in all cases, the ν_3 band is not split and the ν_1 symmetric stretching frequency, if it appears, is very weak. This suggests that the perchlorate group in these complexes is ionic and that the PMT ligands are arranged around the central metal ion in such a way as to prevent coordination of the perchlorate group to the respective central metal ion.[3]

Tetrakis(pentamethylenetetrazole)copper(II) and Bis(pentamethylenetetrazole)copper(I) Perchlorate.—The spectra of tetrakis(pentamethylenetetrazole)-copper(II) (Figure 1B) and bis(pentamethylenetetrazole)copper(I) perchlorate (Figure 1A) are very similar to the spectra of the hexakis(pentamethylenetetrazole)–transition metal–perchlorate complexes and to the spectrum of uncomplexed PMT. Again, little information can be obtained from the slight shifts of the PMT bands on coordination. However, the perchlorate band is not split and the ν_1 perchlorate symmetrical stretching mode does not appear in the spectrum.

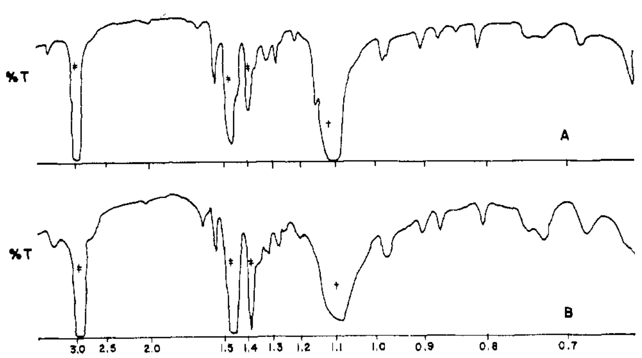

Figure 1.—Infrared absorption spectra (in cm^{-1} × 10^{-3}) of (A) $Cu(PMT)_2ClO_4$ and (B) $Cu(PMT)_4(ClO_4)_2$ in Nujol mull: ‡, Nujol bands; †, perchlorate band.

(2) **Infrared Spectra in the 680–180-Cm^{-1} Region. Pentamethylenetetrazole.**—The infrared spectrum of PMT shows eight absorption bands in the 680–180-cm^{-1} spectral region (Figure 2A). The two relatively strong bands occurring at 266 and 239 cm^{-1}, respectively, are probably due to the pentamethylene ring because they are absent in the spectra of 5-methyl-, 5-ethyl-, 5-*n*-propyl-, and 5-*n*-amyltetrazole.[7]

Hexakis(pentamethylenetetrazole)–Transition Metal Complexes.—When PMT is complexed with transition metal perchlorates, three new bands appear in the far-infrared spectrum of the complex (Figure 2B–G). The appearance of the perchlorate band is apparent as the broadening of the 628-cm^{-1} band. The other two new bands are located in the 302–276- and 236–198-cm^{-1} regions. Since they are not present in the spectrum of PMT and octahedral complexes exhibit only two infrared-active modes, *i.e.*, asymmetrical stretching and bending modes,[8] they evidently result from the coordination of PMT with the metal ions.

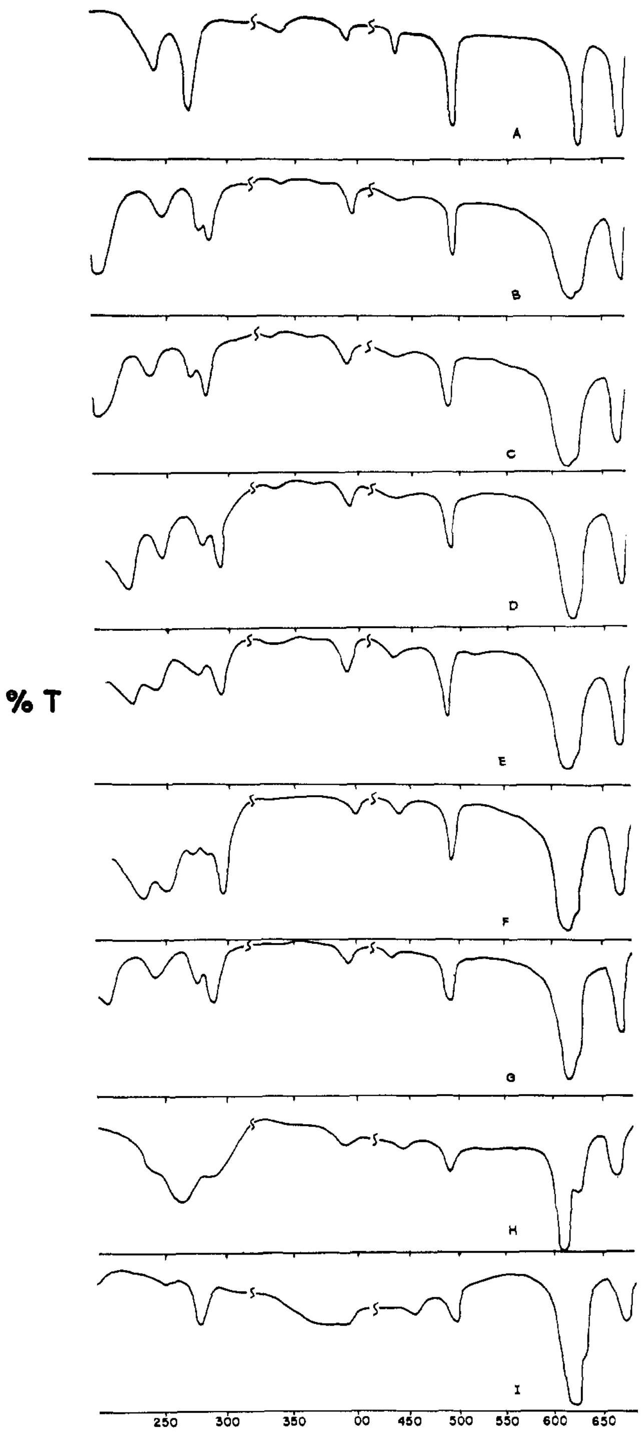

Figure 2.—Infrared absorption spectra (in cm^{-1}) of (A) PMT, (B) $Mn(PMT)_6(ClO_4)_2$, (C) $Fe(PMT)_6(ClO_4)_2$, (D) $Co(PMT)_6(ClO_4)_2$, (E) $Ni(PMT)_6(ClO_4)_2$, (F) $Cu(PMT)_6(ClO_4)_2$, (G) $Zn(PMT)_6(ClO_4)_2$, (H) $Cu(PMT)_4(ClO_4)_2$, (I) $Cu(PMT)_2ClO_4$ in Nujol mull.

The frequency of the metal–nitrogen asymmetrical stretch has been found to vary from approximately 250 to 450 cm^{-1}. Bands tentatively assigned to the metal–nitrogen asymmetrical stretch have also been found in the 267–249-cm^{-1} region for 2,2′-bipyridyl-

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[4] W. E. Bull and L. E. Moore, *J. Inorg. Nucl. Chem.*, **27**, 1341 (1965).

[5] A. E. Wickenden and R. A. Krause, *Inorg. Chem.*, **4**, 404 (1965).

[6] S. F. Pavkovic and D. W. Meek, *ibid.*, **4**, 1091 (1965).

[7] F. M. D'Itri, M.S. Thesis, Michigan State University, East Lansing, Mich., 1966.

[8] K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, p 118.

amine complexes of cobalt(II), copper(II), zinc(II), and palladium(II).[9] Goldstein, *et al.*,[10] assigned the asymmetric stretch to the 254 ± 13 cm^{-1} band of complexes of copper(II) halides and heterocyclic bases. Several investigations[10-13] have found that the spectra of many octahedrally coordinated transition metal–pyridine complexes with various anions show a band in the 195–280-cm^{-1} region which they considered as originating from a metal–nitrogen vibration. Allan, *et al.*,[14] investigating some transition metal halide complexes with substituted pyridines found that all spectra show broad bands, often at low intensity, near 240 cm^{-1}, which they assigned to the metal–nitrogen stretch. Brown,[15] *et al.*, reported the metal–nitrogen modes of high-spin transition metal pyridine perchlorato complexes in the region of 283–222 cm^{-1}.

Pentamethylenetetrazole is a neutral electron-donor ligand, and since all the complexes are of the high-spin type[1c,2b] it seems reasonable to assume that the transition metal–nitrogen bond must be of the σ type since the existence of strong π bonding would be expected to give rise to low-spin complexes.

In view of the above information, the lower frequency band of the doublet found in the 302–285-cm^{-1} region has been very tentatively assigned as the metal–ligand asymmetric stretch while the lowest frequency band in the 238–198-cm^{-1} region is tentatively assigned to the ligand–metal–ligand deformation mode.[10] It is interesting to note that the variation of these frequencies from metal to metal is appreciably smaller than for other metal-to-nitrogen bonds cited above.

Inspection of the spectra shows a shifting of all of the bands in the 320–180-cm^{-1} region, except for the 300-cm^{-1} band of the copper(II) complex and all of the bands of the zinc(II) complex, to higher energies (Figure 2). The frequencies increase with a decrease in ionic radius (increasing in polarizing ability) of the metal. This same type of systematic band shift has been noted in pyridine complexes of divalent transition metal halides.[16] The coordination shift of the 266- and 239-cm^{-1} bands of PMT follows the general tendency for the fundamental modes of the complexed base to be at a slightly higher frequency than those of the free base. This could arise from a general "tightening-up" of the pentamethylene ring of the ligand on coordination.[11] The data were treated (Figure 3) in the same manner as reported by Frank and Rogers.[13] The metal–ligand stretching frequencies closely approximate a linear relationship with the metal electronegativity while the ligand–metal–ligand deformation mode follows a smooth curve (with the exception of the Co^{2+} and Fe^{2+} complexes). Therefore, there appears to exist a direct relationship in which the relative stability of the complexes is given by

$$\mathrm{Cu(PMT)_6(ClO_4)_2 > Ni(PMT)_6(ClO_4)_2 > Co(PMT)_6(ClO_4)_2 \approx Fe(PMT)_6(ClO_4)_2 > Zn(PMT)_6(ClO_4)_2 > Mn(PMT)_6(ClO_4)_2}$$

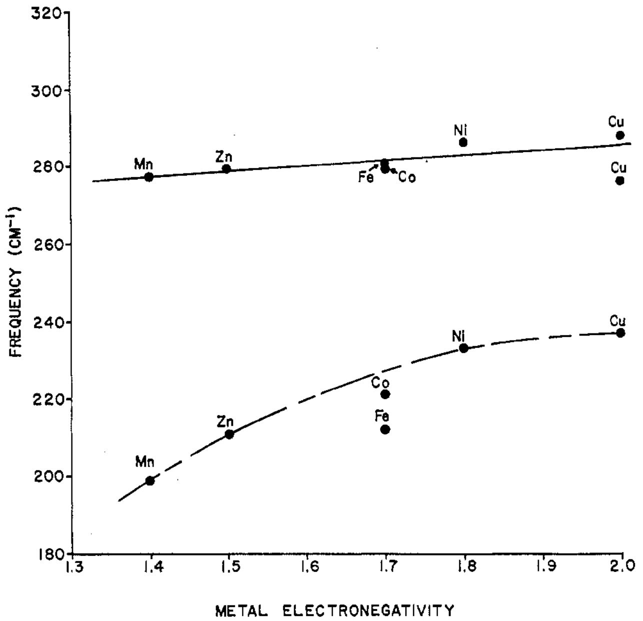

Figure 3.—Metal–ligand stretching (solid line) and deformation (broken line) frequencies as a function of metal electronegativity for $\mathrm{M^{II}(PMT)_6(ClO_4)_2}$ complexes.

The copper(II) complex shows an additional weak band at 276 cm^{-1}. This may be another metal–ligand stretching vibration with a greater bond distance which could indicate that the complex has two different Cu–N bond distances. This conclusion would be in accord with the proposed tetragonal structure of the complex.[2a] All of the hexakis transition metal complexes give rise to essentially the same type of spectrum which implies that their bonding must be very similar.

Tetrakis(pentamethylenetetrazole)copper(II) Perchlorate.—The infrared spectrum (Figure 2H) of this complex in the 680–350-cm^{-1} region is similar to the hexakis(pentamethylenetetrazole)copper(II) perchlorate complex. In the 350–180-cm^{-1} region, however, the absorption bands are much broader. The slight shoulder at 294 cm^{-1} could be the metal–ligand asymmetric stretch. The absorptions at 288 and 266 cm^{-1} could correlate with the 266- and 239-cm^{-1} bands of PMT, respectively, while the 246-cm^{-1} shoulder probably arises from the deformation of the metal–ligand bond.

Bis(pentamethylenetetrazole)copper(I) Perchlorate.—The infrared spectrum (Figure 2I) of this complex shows the characteristic bands of PMT in the region of 680–400 cm^{-1}. In the 400–180-cm^{-1} region there is little resemblance to the spectra of other coordinated complexes or to that of PMT. The band at approximately 380 cm^{-1} has not been assigned. In the 300–180-cm^{-1} region, there is a band at 281 cm^{-1} and what appear to be bands at 255 and 198 cm^{-1}. The 281- and 255-cm^{-1} bands could be the displaced 266- and 239-cm^{-1}

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[10] M. Goldstein, E. F. Mooney, A. Anderson, and H. A. Gebbie, *Spectrochim. Acta*, **21**, 105 (1965).

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[12] R. J. H. Clark and C. S. Williams, *Inorg. Chem.*, **4**, 350 (1965).

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[16] N. S. Gill, R. H. Nuttall, D. E. Scaife, and D. W. A. Sharp, *J. Inorg. Nucl. Chem.*, **18**, 79 (1961).

bands of PMT. An alternative possibility for the 281-cm^{-1} band is the metal–ligand asymmetric stretch. The 198-cm^{-1} band probably corresponds to the metal–ligand deformation mode.

Acknowledgment.—The authors gratefully acknowledge the support of this work by Research Grant MH-07825 from the Institute of Mental Health, U. S. Public Health Service.

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The Configuration of Bis(N-dimethylamino)tetrachlorotriphosphonitrile

BY C. T. FORD, F. E. DICKSON, AND I. I. BEZMAN

Received February 9, 1967

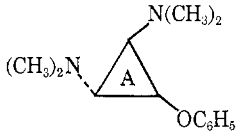
Three forms of the compound $P_3N_3Cl_4[N(CH_3)_2]_2$ have been reported, melting at 103,[1] 82,[2] and 62°.[2] The first of these, I, is formed predominantly and we reported previously[3] that it was a nongeminal *cis* isomer. This conclusion was drawn from the reaction sequence

$$\text{I} \xrightarrow[\text{AlCl}_3]{C_6H_6} \underset{\text{II}}{P_3N_3(Cl)_2(C_6H_5)_2[N(CH_3)_2]_2} \xrightarrow{(CH_3)_2NH(g)} \underset{\text{III}}{P_3N_3(C_6H_5)_2[N(CH_3)_2]_4}$$

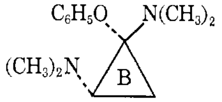
and the knowledge, from proton magnetic resonance measurements, that, in III, two $[N(CH_3)_2]$ groups are attached to the same phosphorus and the other two to separate phosphorus atoms and are *cis* to each other. In II, the spectra showed that the $[N(CH_3)_2]$ groups are each on a phosphorus atom to which a phenyl group is also attached. It was also based on the assumption that no isomerization takes place during the reactions. Since our report, two papers[2,4] have appeared in which evidence was given that I is the *trans* isomer. Further, there have appeared reports of isomerization of aminophosphonitriles in the presence of $AlCl_3$[5] or of amine hydrochlorides.[6] We, therefore, reinvestigated the structure of I and found other evidence that it is, indeed, the *trans* rather than the *cis* isomer.

This was obtained by proton nmr measurements for $P_3N_3Cl_3[N(CH_3)_2]_2(OC_6H_5)$, IV, mp 55°, which was prepared in 95% yield by the action of KOC_6H_5 on I (1:1 mole ratio) in refluxing benzene.

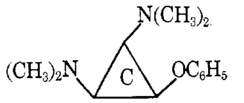
There are six possible configurations for IV as shown below. The apices of the triangles represent the phosphorus atoms in the ring. Given below each structure are the anticipated pmr spectral characteristics. The apparent[3] coupling constant, J'_{PH}, values are in cps.



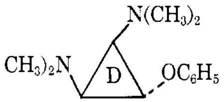
2 doublets
J'_{PH} = 17.5 for each



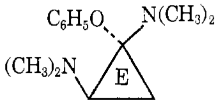
2 doublets
J'_{PH} = 17.5, 12.5



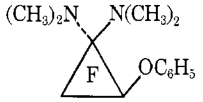
1 doublet
J'_{PH} = 17.5



1 doublet
J'_{PH} = 17.5



2 doublets
J'_{PH} = 17.5, 12.5



2 doublets
J'_{PH} = 11.6 for each

Proton nmr spectra were obtained for compound IV on a Varian A-60 nmr spectrometer system operating at 60 Mc/sec with tetramethylsilane employed as an internal reference. Samples were prepared as 20% solutions (w/v) in $CDCl_3$. The spectrum showed two distinct doublets, each having a J'_{PH} = 17.5 cps. This is uniquely characteristic of structure A.

It now appears that Friedel-Crafts phenylation of I to give II is accompanied by isomerization of the $N(CH_3)_2$ groups to the *cis* configuration, the effective agent being $AlCl_3$. Although isomerization probably was not complete, the yield of II, 38%, indicates that the *cis* isomer was more amenable to isolation under the conditions used.

Acknowledgment.—This work was carried out for the Armstrong Cork Co., Lancaster, Pa., to whom we are indebted for long-term financial support.

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The 20°K Spectrum of Sodium Thiochromite

BY S. L. HOLT AND A. WOLD

Received February 13, 1967

There has been much interest in recent years in the spectra of transition metal compounds in which the ligand field is essentially octahedral but possesses a small trigonal distortion.[1–3] Attempts have been made to determine the source of band intensity and the

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