VANADYL CHELATES OF TETRAPHENYLPORPHINE AND ITS *PARA*-SUBSTITUTED DERIVATIVES[1]

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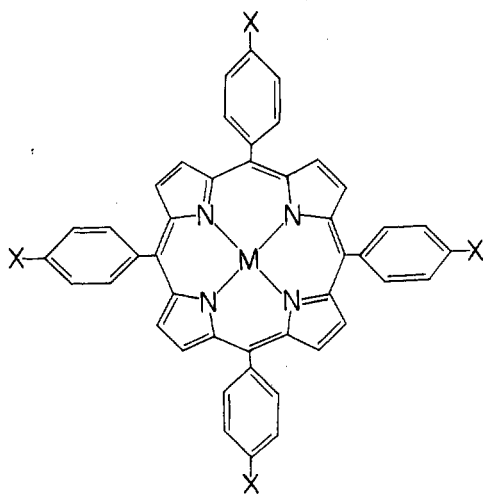
Received December 27, 1955

The preparation of the vanadyl chelates of tetraphenylporphine, and its *p*-methyl, *p*-methoxy and *p*-chloro derivatives are described, and a study of their ultraviolet, visible and infrared spectra are reported. The ultraviolet and visible spectra are found to resemble those of the Cu(II), Co(II), Ni(II) and Ag(II) chelates of tetraphenylporphine. Infrared frequencies are assigned to bond or group vibrations, and a comparison is made with the corresponding frequencies of chelates of various divalent metals with other ligands. Two bands at 1337 and 535–528 cm.$^{-1}$ are tentatively assigned to V–O stretching and bending vibrations, respectively, and two bands at 1000 and 465–435 cm.$^{-1}$ are tentatively assigned to metal–nitrogen in-plane and out-of-plane vibrations, respectively.

In the course of a general investigation of metal chelate compounds related to the natural and synthetic oxygen carriers, tetraphenylporphine and a number of its *para*-substituted derivatives[3] have previously been synthesized in these laboratories. It was thought of interest to prepare and study the corresponding vanadyl chelates of these compounds, because the presence of a single strongly-bound oxygen atom would provide a comparison with the weaker metal–oxygen bonds of the oxygen carriers. Although the ultraviolet spectra of a number of divalent metal chelates of tetraphenylporphine have been reported,[4] the preparation of the vanadyl chelates of the parent ligand and of its derivatives have not been described. However, a number of vanadyl chelates of β-diketones[5–7] and of the tetradentate ligand bissalicylaldehydeethylenediimine[8,9] have been reported. The ligands kindly made available for this research by Mr. D. W. Thomas are indicated by formula I.



I, *para*-Substituted tetraphenylporphines
X = —H, —CH_3, —OCH_3, and —Cl.

(1) This research was supported by the National Institutes of Health, U. S. Public Health Service, under grant #G3819(C2).

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Experimental

Vanadyl Tetraphenylporphines.—A finely-powdered mixture of 300 mg. of tetraphenylporphine and 300 mg. of vanadyl acetate was heated for 48 hours at 190–200° in 100 ml. of glacial acetic acid. The reaction mixture which was green at the beginning changed to brown near the end of the reaction. It was dispersed in water, extracted with benzene, and the benzene extract was evaporated to dryness. The crude product was dissolved in trichloroethylene, filtered and chromatographed on a talc column. Development with additional trichloroethylene resulted in the formation of a cherry-red band which passed through the column, while a green band remained behind. Evaporation of the effluent gave a dark violet solid, which was recrystallized from chloroform–methanol to yield 210 mg. (63%) of dark violet crystals. The green band which remained on the column was eluted with acetone and found by absorption measurements to be tetraphenylporphine.

The vanadyl chelates of the *para*-substituted tetraphenylporphines were synthesized in a similar manner, but differences in the solubilities of each compound in benzene and in trichloroethylene necessitated slight changes in the standard procedure described above. The order of solubility of the vanadyl chelates in the organic solvents employed is *p*-methyl-TPP > TPP > *p*-chloro-TPP > *p*-methoxy-TPP. The individual procedures and yields are listed in Table I.

TABLE I

PREPARATION OF VANADYL TETRAPHENYLPORPHINES

Ligand	Chromatographic solvent	Crystallization medium	Yield,[a] %
TPP[b]	Trichloroethylene	Methanol	63.4
p-Methyl-TPP	Trichloroethylene	Methanol–water	61.7
p-Methoxy-TPP	Trichlroethylene–chloroform	Methanol	65.8
p-Chloro-TPP	Trichloroethylene	Methanol	67.8

[a] Based on tetraphenylporphine. [b] TPP represents tetraphenylporphine.

The Cu(II) and Co(II) chelates of tetraphenylporphine were prepared by the method of Dorough, *et al.*,[4] and purified by the method described above.

Absorption Spectra.—Ultraviolet and visible spectra were measured with a Beckman DU spectrophotometer equipped with a photomultiplier attachment. Spectroscopic grade benzene was used as a solvent.

Infrared absorption spectra were measured with a Perkin–Elmer Model 21 double-beam recording spectrophotometer. Sodium chloride optics were used in the region from 4000 to 650 cm.$^{-1}$, and an interchangeable potassium bromide prism assembly was substituted in order to make measurements in the 650 to 400 cm.$^{-1}$ region. Since the potassium bromide pellet method did not give good resolution for tetraphenylporphines, Nujol and hexachlorobutadiene mulls were employed. The significant spectral bands found for the compounds studied are reported in Table II, together with the assignments which were possible in each case.

Discussion

Although other metal chelates of tetraphenylporphine are best prepared by heating the ligand and metal acetate in glacial acetic acid, various attempts to prepare the vanadyl chelate by this

TABLE II

INFRARED ABSORPTION SPECTRA OF VANADYL CHELATES OF TETRAPHENYLPORPHINES AND ITS *para*-SUBSTITUTED DERIVATIVES

TPP				*p*-CH_3		*p*-OCH_3		*p*-Cl		
Ligand	Cu(II)	Co(II)	VO(II)	Ligand	VO(II)	Ligand	VO(II)	Ligand	VO(II)	Assignments
1597m	1596s	1599s	1599s	1600m	1603s	1610m	1602vs	1595m	1595m	C:C & phenyl
1575m	1575w	1575w	1580[a] 1575 w	1582m	1582w	1575m	1571m	1582m	1580w	Conjugated phenyl
1560m	1563w	1559w		1560m		1563w	1560w	1565m	1562w	
1545w	1545w	1541w		1543w		1547w		1548w		
	1537w		1533w		1530w		1525m		1530m	
	1525w	1525w								
1512vw	1510w	1508w	1511w	1510w	1506m			1512w	1510w	
						1512vs	1510vs			
								1503w		
1497m	1487m	1490m	1490m	1487m	1485m	1497m	1494vs	1490m	1487vs	Phenyl
1477m				1470m		1475m		1473m		C:N?
			1461w		1460w		1465m		1462w	
								1463m		
								1455w		
				1452m	1453m					$-CH_3$ deformation
1444m	1441s	1442s	1443s	1438w	1443w	1442m	1440m	1443w	1442w	C–H deformation of pyrrole rings
							1410w			
1403m				1400w		1405w		1396m		
	1382w	1363w	1394w						1395m	
				1375m	1378s					$-CH_3$ deformation
1362m				1363m				1367m		
1350m				1347m		1350m		1347m		
	1345s	1348s	1345s							C–N stretching
			1337s		1338s		1337s		1337s	V–O stretching
1325w				1320w				1332m		
1310vw	1307w	1306m	1311w	1307vw	1301w	1303m	1300w	1285vw	1300w	
1286vw	1272w	1278w	1274w	1270w	1270w	1288m	1285s			
1250w		1250w		1245w	1252w			1255w		
						1247vs	1245vs			C–O stretching in methoxy group
		1235w							1235w	
1222w				1224m		1231m		1222m		
1213w				1226m		1214w		1213w		
	1202m	1204m	1204s		1206m		1203m		1206m	
				1198w						
1188m				1183w		1184m		1186w		
1176m	1173s	1175w	1175vs	1168w	1178m			1174m	1178m	
						1173vs	1175vs			$-OCH_3$?
1155m	1156m	1152m	1157w	1150m	1165m	1153m		1155w		Phenyl & *p*-subst. phenyl
				1105w	1104w	1105m	1105m	1100m	1110w	*p*-Subst. phenyl
1080m				1092m	1090m					
								1088s	1089vs	
1070m				1070w				1072m		
	1070s	1075s	1069vs		1066s		1070m			
		1065s								
1055w				1050w				1056w		
1030m				1036w		1034m				
					1033m		1029s			
		1018m		1018w		1010w		1013m		
	1000s	1002s	1001vs		1001vs		1015vs		1002vs	Metal-ligand vibration
999m				997m		989m		990m		
	987s	995s					995vs			
978m				977m		980m		980m		
963s				969s		964s		963m		
							956w		960w	
								941m	937w	C–Cl?
		927w	919w		920m		927m			
		920w		908m						
		898w								

TABLE II (*Continued*)

TPP				*p*-CH_3		*p*-OCH_3		*p*-Cl		
Ligand	Cu(II)	Co(II)	VO(II)	Ligand	VO(II)	Ligand	VO(II)	Ligand	VO(II)	Assignments
873m				883m	883m	875w	882w	872w	880m	
							861w			
								851m	845m	C–Cl stretching
847m		845m		838w		837m		837m		
	830m	830m	832m				847m			
825w				825w		818w		818w		
809m				812m				800s		
795vs	799s	792s	804vs	799vs	805vs	803s	806vs	790vs	803vs	Phenyl
	795s			793s	800vs					
783m				786vs		782s	786m	784s		
				772vs	774vs					
757s	747s	747s	748vs							Monosubst. phenyl
				750w	753w	759m	750w		745w	
744s		720s					738m			
727s		711s	724m	723vs	723s	734s	729s	725s	724s	
720s		705s								Monosubst. phenyl
702s	698s	699s	702s	706s	703m	704w		702m	707m	
694s				697m				699m		
654m	662m	668w	661m	655w	662m	666w	667w	665w	665w	
						644w				
637w				633w		635w	638w	635w	631w	
								629w		
						597s	603s			
559w						554m	561m	556w	570w	
						538m	542m			
			528m				532m		535w	V–O bending.
								505s	502vs	
								492m		
	444w	465w	455s		456w		440w		435w	Metal-ligand vibration
				444m	442m					
419vw			419vw	417w	418w	419w	419w	418w	418w	

[a] A broad band between the frequency regions indicated.

procedure, as outlined by Dorough, *et al.*,[4] were unsuccessful. After a study of the influence of the variation of starting material, temperature and reaction time, it was found that satisfactory yields are obtained by heating the free base and vanadyl acetate in glacial acetic acid in a sealed tube at about 200° for 48 hours. Chromatographic separation and spectrophotometric study of the reaction products revealed the presence of only a small amount of unchanged tetraphenylporphine in addition to the main reaction product.

The absorption spectrum of vanadyl tetraphenylporphine, illustrated in Fig. 1, is quite similar to those of the corresponding copper(II), nickel(II), cobalt(II) and silver(II) chelates described by Dorough, *et al.*[4] The visible and ultraviolet absorption spectra of the *p*-substituted tetraphenylporphine free bases have been noted to be quite similar to those of the parent compound,[3] with slight shifts in the positions of the bands as the result of substitution in the benzene rings. The change in the absorption spectra of the *para*-substituted porphines which occurs on coördination with the vanadyl ion, was found to be almost the same as occurs in tetraphenylporphine. The characteristics of the absorption bands of the metal chelates are listed in Table III.

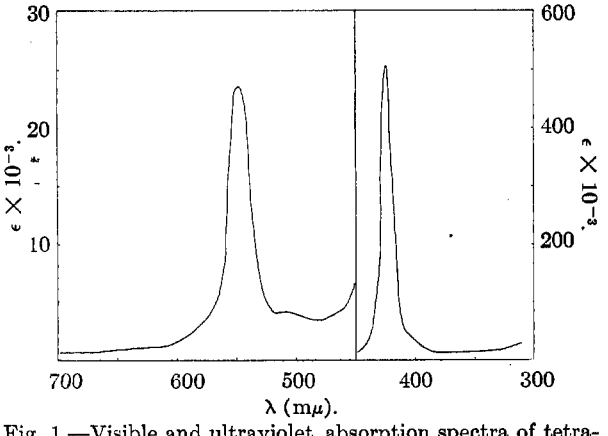


Fig. 1.—Visible and ultraviolet absorption spectra of tetraphenylporphine–VO(IV) in benzene.

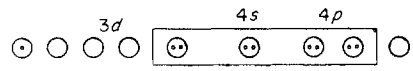
TABLE III

VISIBLE AND ULTRAVIOLET ABSORPTION BANDS OF VANADYL *para*-SUBSTITUTED TETRAPHENYLPORPHINES IN BENZENE

Ligand	Molarity × 10^1	λ_{1max}, mμ	ϵ_1 × 10^3	Molarity × 10^5	λ_{2max}, mμ	ϵ_2 × 10^3
TPP	1.40	548	23.6	0.28	424	509
p-Methyl-TPP	0.99	548	23.3	.198	425	530
p-Methoxy-TPP[a]	1.17	548	21.5	.117	429	441
p-Chloro-TPP	0.86	548	26.2	.172	425	564

[a] Additional weak absorptions were observed at 590 mμ (ε 4.6 × 10^3), 512 mμ (ε 3.6 × 10^3) and 481 mμ (ε 3.0 × 10^3).

The electronic configuration in the outer orbitals of vanadium in the vanadyl porphine complexes may be illustrated schematically as



The strong binding of the metal by the tetradentate ligand is probably covalent, as it is with the other transition metals. Thus, a set of dsp^2 orbitals of the metal, which correspond to a square-planar arrangement of covalent bonds, would be filled by four electron pairs donated by the ligand. If it is assumed that the V–O bond (Fig. 2) is ionic, a configuration with one unpaired electron would be expected. The only evidence for the covalent character of the metal–ligand bonds comes from the absorption spectra which fall in the same class as the spectra of the nickel(II) and cobalt(II) tetraphenylporphines, which have been shown by magnetic measurements to be covalent. In the observed visible spectra of tetraphenylporphine–VO(IV), illustrated in Fig. 1, any possible weak absorption bands arising from forbidden d-orbital transitions have been completely masked by the very intense K-type band at 548 mμ.

Infrared study of the *para*-substituted derivatives of the tetraphenylporphine free bases has been reported elsewhere,[3] and the following discussion will be limited to the interpretation of absorption spectra of the metal porphine chelates. However, the study of the spectra of the metal derivatives has resulted in the assignment of a vibration in the free bases. The weak absorption of tetraphenylporphine and its derivatives near 3350 cm.$^{-1}$ was found to be absent in all metal chelates. This absorption is therefore assigned to the hydrogen bonded N–H stretching vibration of the porphines, since, in the metal chelates, both hydrogens are replaced by the metal ion.

The main absorption bands of the metal chelates, which appear at around 1600 cm.$^{-1}$, and at lower frequencies, are listed in Table II.

Since both phenyl rings and C=C bonds are present, strong absorption bands would be expected in the double bond region. Thus, the first absorption at 1595–1610 cm.$^{-1}$, which is fairly constant in position, is due to both C=C and aromatic C=C stretching vibrations. Another absorption band at 1575–1582 cm.$^{-1}$, which is also stable in its position, is assigned to conjugated C=C vibrations in the phenyl rings. It is interesting to note that the first absorption, which has medium intensity in the free base, increases in intensity on metal chelation; however, the second band decreases in intensity.

It would be expected that absorption bands would be found which correspond to C=N stretch and N–H deformation for the ligand, and to C=N stretch for the metal chelate. However, the two or three absorptions occurring between 1560 and 1510 cm.$^{-1}$ cannot be assigned to these modes of vibrations with any degree of certainty. The bands of the free bases shift or split into several bands and also undergo a change of intensity when the hydrogens are replaced by a metal ion.

Another absorption of intermediate intensity at 1497–1485 cm.$^{-1}$, which undergoes little change of position on metal chelation, is assigned to the skeletal vibration of the phenyl rings. The next

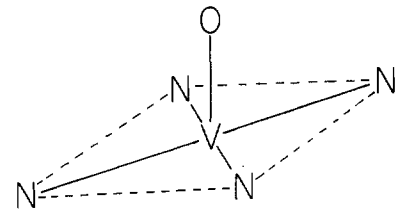


Fig. 2.—Steric configuration of VO in tetraphenylporphine-VO(IV).

band at 1444–1438 cm.$^{-1}$ which does not shift appreciably when the metal chelate is formed from the free base, is assigned to C–H deformation vibration of the porphine ring.

Carbon–hydrogen deformation vibrations of phenyl rings also should give rise to absorptions in the frequency range of 1225–650 cm.$^{-1}$. Thus an absorption band at around 1155 cm.$^{-1}$ is assigned to phenyl ring deformation, and an additional band at around 1105 cm.$^{-1}$ in the spectra of the *para*-substituted derivatives is assigned to a *para*-disubstituted phenyl ring deformation vibration. Another set of bands of very strong intensity at around 800–780 cm.$^{-1}$ are also assigned to a C–H deformation vibration of the phenyl rings.

In *para*-substituted derivatives, there are some additional absorptions which can be assigned to each substituent. Two bands at 1453–1452 cm.$^{-1}$ and 1378–1375 cm.$^{-1}$ of the *para*-methyl derivative are assigned to a $-CH_3$ deformation vibration; very strong absorptions at 1247–1245 cm.$^{-1}$ and at 1173–1175 cm.$^{-1}$ of the *para*-methoxy derivative are assigned to the $-OCH_3$ group; and an absorption at 851–845 cm.$^{-1}$ and probably another band at 941–937 cm.$^{-1}$ of the *para*-chloro derivative are assigned to C–Cl stretching vibrations.

There are additional groups of bands which are characteristic of the ligands or the metal chelates, and the latter group may be subdivided further into two groups, one of which contains absorption bands characteristic of the vanadyl chelates, while the other includes a number of bands which seem to be common to the other divalent metal chelates. An absorption band which appears at 1477–1470 cm.$^{-1}$, is observed only in the free bases, and not in the metal chelates. In the vanadyl chelates, a new band occurs in a slightly lower frequency region. The frequency of this band in the ligands is probably too low to be assigned to N–H deformation. The band is probably associated with the stretching vibration of conjugated C=N bonds, which probably undergo a change of bond order and mode of vibration when the ligand is coördinated with a metal ion.

The three absorptions observed at around 1400, 1360 and 1350 cm.$^{-1}$ are characteristic of the ligands. In the metal chelates of tetraphenylporphine, a new band of strong intensity is found at around 1345 cm.$^{-1}$, which is, however, absent in the metal chelates of the *para*-substituted ligands. These bands are tentatively assigned to C=N vibrations.

The absorption found at 1338–1337 cm.$^{-1}$ is characteristic of all vanadyl chelates, and cannot be found either in the ligands nor in the chelates of copper and cobalt. This absorption is rather

strong and is tentatively assigned to the V–O stretching vibration.

The steric configuration of five-coördinated vanadyl chelates have been discussed previously.[7] For the purposes of discussion in the present work, it is considered permissible to assume the structure to be that shown in Fig. 2. Such a structure is also supported by some preliminary measurements which indicate a significantly large dipole moment for vanadyl tetraphenylporphine.[10] This dipole moment must be due to the asymmetrical configuration of the V–O bond, which is normal to the plane of the porphine ring. The ligand is symmetrical and should not contribute to the dipole moment.

It is possible to estimate roughly the force constant of the V–O bond by the use of the simple equation[11] where ν is the absorption frequency in

$$\nu = 1307\sqrt{k/\mu}$$

wave numbers, k is the force constant for the stretching vibration and μ is the reduced mass which can be calculated from the masses of two bodies by $\mu = m_1m_2/(m_1 + m_2)$. The calculated value is 12.65×10^5 dyne/cm., which is about the same as the value of the C=O stretching force constant ($k_{C=O}$ (acetone) $= 12 \times 10^5$ dyne/cm.). The value obtained for the V–O bond is rather high in comparison with the value 7.54×10^5 dyne/cm., determined by Raman spectra,[12] for the force constant of the V–O stretching vibration in $VOCl_3$. However, the oxidation states, and the arrangement of electrons in the metal orbitals are different, and a difference in the bonding force of vanadium to oxygen would therefore also be expected.

The strong sharp band at 1015–1000 cm.$^{-1}$ is specific for all metal chelate compounds studied, while all ligands have a band of medium intensity at slightly lower frequency. The bands found for the metal chelates are unusually strong in comparison with the band of the ligand. Since this band is found not only in the vanadyl chelates but also in the copper and cobalt chelates, it cannot be due to an absorption related to the V–O vibration. The modes of vibration of the central metal ion in the metallo-porphines are both in-the-plane and out-of-the-plane of the porphine ring. Both modes of vibration result in changes of dipole moment and are, therefore, infrared active. Very few assignments of metal-ligand vibrations have been reported in the literatures. Several absorption bands below 700 cm.$^{-1}$ in the metal chelates of acetylacetone[13] and of bis-acetylacetone-ethylenediimine and related compounds[14] were assigned to metal–ligand vibrations. The extraordinary stability of the metalloporphines, however, indicates that the metal–ligand bonds are much stronger in metalloporphines than in the metal chelates of acetylacetone and bis-acetylacetone-ethylenediimine. This stabilization can be explained on the basis of the strong resonance effect of the porphine ring, which imparts more double bond nature to the metal–ligand bonds than would be true of the metal chelates formed from other ligands.

Since one can expect, therefore, that the metal–ligand absorptions would occur in a higher frequency region, the strong absorption gand at 1015–1000 cm.$^{-1}$ is assigned to the in-the-plane metal–ligand vibration, which should appear at higher frequency than the out-of-the-plane vibration.

In the lower frequency region another group of absorptions are found which are characteristic of all metal porphine chelates The frequency of these bands shifts considerably as one passes from one metal to another, and the intensity of the bands also varies from strong to weak. In the case of copper and cobalt chelates of tetraphenylporphine and of the vanadyl chelate of *p*-methyltetraphenylporphine, one band is missing; however, all of these bands are characterized by the fact that no corresponding bands can be found in the ligands. Similar bands in this region were observed in the metal chelates of bis-acetylacetone-ethylenediimine and its analogous compounds, and were also assigned to metal–ligand vibrations.[13] Thus the absorption bands in the 535–528 cm.$^{-1}$ region of all the vanadyl tetraphenylporphines with the exception of the *p*-methyl derivative, and an absorption which is observed in all metal porphine chelates in the region of 465–435 cm.$^{-1}$, are assigned to metal–ligand vibrations. Although it is not possible to assign each band to a specific mode of vibration, all of these bands correspond to a relatively feeble elastic force. One might tentatively assign the band at 535–528 cm.$^{-1}$ to the V–O bending vibration, and the band at 465–435 cm.$^{-1}$ to the out-of-plane deformation vibration of metal–nitrogen bonds.

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