ORGANIC AND BIOLOGICAL CHEMISTRY

[CONTRIBUTION OF THE DEPARTMENT OF CHEMISTRY, CLARK UNIVERSITY]

Metal Chelates of Tetraphenylporphine and of Some *p*-Substituted Derivatives[1,2]

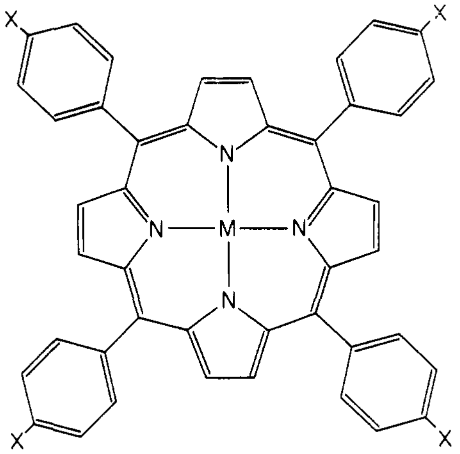
BY DANIEL W. THOMAS AND ARTHUR E. MARTELL

RECEIVED AUGUST 18, 1958

The preparation, purification and properties of the Cu(II), Co(II), Ni(II), Pd(II) and Pt(II) chelates of $\alpha,\beta,\gamma,\delta$-tetraphenylporphine, $\alpha,\beta,\gamma,\delta$-tetra-(*p*-methoxyphenyl)-porphine and $\alpha,\beta,\gamma,\delta$-tetra-(*p*-chlorophenyl)-porphine are described. Relative strengths of the metal–ligand bonds, deduced on the basis of shifts in the frequencies of absorption bands in the infrared spectral region, follow the series Pt(II) > Pd(II) > Ni(II) > Co(II), Cu(II), and phenyl > *p*-chlorophenyl > *p*-methoxyphenyl. Assignments of infrared absorption bands to various atomic groupings are made, and the influence of structural variations on the assigned frequencies are discussed.

In the course of an investigation of the nature of the coördinate linkage in metal porphines, the synthesis of tetraphenylporphine and a number of its *p*-substituted derivatives[3] and the absorption spectra of these compounds[4] have been reported. In the present work, a series of metals, chosen on the basis of their tendencies to form square planar complexes, have been chelated with three of these ligands, tetraphenylporphine and its *p*-methoxy and *p*-chloro derivatives, and infrared spectrophotometric studies of each chelate compound are reported. The influence of the *p*-phenyl substituents on the electron-donor properties of the central nitrogen atoms and on the stabilities of the metal–nitrogen bonds is also described.

The synthesis[5–7,11] and the visible and ultraviolet spectra of metal tetraphenylporphines[6,8–11] and of pyridinated[9,12] tetraphenylporphines have appeared previously, but of the *p*-substituted tetraphenylporphines only the vanadyl chelates[11] of the *p*-methyl, methoxy and chloro derivatives have been reported. Neither the synthesis nor the spectra of the palladium(II) or platinum(II) chelates of any tetraphenylporphines has appeared in the literature. The infrared spectra of some vanadyl tetraphenylporphines and some of its derivatives[11] and a discussion of a frequency assignment for metal chelates of tetra-(*p*-chlorophenyl)-porphine[13] are the only infrared data available. The visible absorption curves of all the metal porphyrin compounds presented here have been reported earlier.[14] The ligands and metal chelates employed in the present investigation are indicated by formula I.



I

Discussion

Synthesis.—In the synthesis of the metal chelates from the tetraphenylporphines, which contained a small amount of chlorin impurity, one would expect products consisting of some of the metal chlorin derivative as well as the normal tetraphenylporphine chelate. Although such was generally the case, it was noted in some of the reactions, particularly those of the *p*-methoxy derivatives, listed in Table IV, that no metal chlorin was produced, even after 5–7 hours of heating. Since these reactions were conducted with free access of air in glacial acetic acid or in acetic acid–dioxane mixtures, it appears that the chlorin was probably dehydrogenated to the corresponding porphine during the formation of the metal chelate.

The rather low yields of the cobalt chelates could be attributed to oxidation of the cobalt(II) salt to the cobalt(III) state, as was apparent from the brownish colored reaction mixtures obtained. The low (27%) yield of the *p*-chlorotetraphenylporphinopalladium(II) chelate may be attributed to two factors: the low solubility of the ligand in the various reaction solvents used, and the repeated chromatographic purifications which were necessary.

All of the platinum(II) compounds were obtained in low yields of 10% or less, the best yield being obtained for tetraphenylporphine in a

---

[1] Abstracted from the dissertation submitted by D. W. Thomas in partial fulfillment of the requirements for the degree of Doctor of Philosophy, Clark University, 1957.

[2] This work was supported by a grant from the U. S. Public Health Service, National Institutes of Health (no. 3819$^{\text{C}}$).

[3] D. W. Thomas and A. E. Martell, THIS JOURNAL, **78**, 1335 (1956).

[4] D. W. Thomas and A. E. Martell, *ibid.*, **78**, 1338 (1956).

[5] P. Rothemund and A. R. Menotti, *ibid.*, **70**, 1808 (1948).

[6] G. D. Dorough, J. R. Miller and F. M. Huennekens, *ibid.*, **73**, 4315 (1951).

[7] J. T. Horeczy, B. N. Hill, A. E. Walters, H. G. Schutz and W. H. Bonner, *Anal. Chem.*, **27**, 1899 (1955).

[8] V. M. Albers and H. V. Knorr, *J. Phys. Chem.*, **9**, 497 (1941).

[9] V. M. Albers, H. V. Knorr and D. L. Fry, *ibid.*, **10**, 700 (1942).

[10] J. W. Barnes and G. D. Dorough, THIS JOURNAL, **72**, 4045 (1950).

[11] K. Ueno and A. E. Martell, *J. Phys. Chem.*, **60**, 934 (1956).

[12] J. R. Miller and G. D. Dorough, THIS JOURNAL, **74**, 3977 (1952).

[13] J. R. Goldstein, W. H. McNabb and J. F. Hazel, *ibid.*, **78**, 3543 (1956).

[14] D. W. Thomas and A. E. Martell, *Archiv. Biochem. and Biophys.*, **76**, 286 (1958).

glacial acetic acid–benzene mixture. Benzene was found to be useful in increasing the yield by retaining the ligand in solution. The main reason for the low yields is the reduction of the platinum salt (K_2PtCl_4) to platinum metal. The presence of catalytically-active platinum in the reaction product made it necessary to avoid the use of methanol as a washing solvent, and to avoid drying the solid, which would result in spontaneous combustion. The same precautions were also observed in the preparation of the palladium chelates.

An additional porphyrin chelate was obtained from the reaction mixture of tetra-(*p*-methoxyphenyl)-porphinoplatinum(II). Unlike the other platinum chelates which absorb strongly in benzene near 510 and 405 mμ,[14] this material had absorption bands at 530 and 420 mμ. The absorption curve and the maxima observed strongly resemble those of the nickel chelate. The possibility that this compound might be a dichloroplatinum(IV) chloride chelate of the paramethoxytetraphenylporphine, or a 5-coördinated chloroplatinum(II) porphyrin,[15] were investigated, but the carbon, hydrogen and metal analyses obtained excluded these compositions. The analyses indicated a non-chlorinated Pt(II) compound, but the data obtained were inconclusive. A similar compound was obtained from a reaction in dioxane between tetraphenylporphine, potassium chloroplatinite and sodium acetate. A minute amount of material with absorption maxima at 528 and 416 mμ in benzene was isolated. The maxima and the shape of the curve also resemble those of the corresponding nickel chelate.

The platinum(II) chelates of all the tetraphenylporphines were characterized by changes in absorption spectra in chlorinated solvents, and in trichloroethylene and chloroform in particular. The strong maxima near 510 and 405 mμ were gradually replaced with bands near 540 and 422 mμ, and similar shifts of the weaker vibrational bands also occurred at room temperature. The change occurring over a period of days was significant, and within a month it was found to be practically complete. Since the platinum(II) chelates were chromatographed in chlorinated solvents, it was necessary to check the ratio of the optical densities of the peaks near 540 and 510 mμ of various fractions obtained from the chromatographic process as well as after recrystallization of the product. The lowest ratio obtained from each platinum chelate was considered to be indicative of its maximum purity. The spectra of tetraphenylporphineplatinum(II) appeared to be quite sensitive to chlorinated solvents. Consequently, final purification steps and crystallization of this compound was carried out with benzene.

This side reaction seems to be entirely dependent on the nature of the solvent. A trichloroethylene solution of the by-product was replaced with benzene and the benzene solution was boiled for one-half hour. However, no apparent change in the absorption spectrum was observed. Consequently, if a solvation reaction is involved it appears to be irreversible. The quantities obtained were too small for direct elementary analysis.

Infrared Spectra.—The main absorption bands of the metal chelates of tetraphenylporphine and its *p*-methoxy and chloro derivatives, which appear near 1600 cm.$^{-1}$ and at lower frequencies, as well as the assignments to various modes of vibration, are listed in Table I. Examples of the spectra obtained for a typical ligand and its metal chelate are given in Fig. 1. The weak N–H stretching vibrations above 3300 cm.$^{-1}$ for all the ligands disappear in the chelates, since the acidic hydrogens are replaced by the metal ion. Replacement of these imino hydrogen atoms results in shifts of many absorption bands of the ligand to both higher and lower frequencies. The shift to higher frequencies is most evident for three sharp absorption bands for the tetraphenylporphine ligands near 960, 980 and 1000 cm.$^{-1}$, which were previously assigned to C–H rocking vibrations of the pyrrole ring.[4] In all the chelates these bands are associated with the many sharp bands or shoulders near a very strong absorption band in the vicinity of 1000 cm.$^{-1}$. Many of the C–H vibrations are listed in Table I. The strong absorption band near 1000 cm.$^{-1}$ appears to be a vibration characteristic of all the tetraphenylporphine chelates, the frequency of the band varying with the nature of the metal ion. This intense band may be a rocking vibration of the porphine ring or the pyrrole units. which is sensitive to the nature of the metal ion and which is directly related to the strength of the metal–nitrogen bonds in the tetraphenylporphine chelates. Similar relationships of rocking vibrations and the strengths of metal–ligand bonds have been reported for simpler chelate and complex compounds.[16,17] The correlation of this vibration near 1000 cm.$^{-1}$ with that of the metal ligand bonding is further supported by shifts previously reported[14] of the absorption maxima in the visible region of the spectra for each metal tetraphenylporphine chelate in a manner which parallels the variations of infrared frequencies given in Table II.

It is clear from the above values that the frequencies for all the tetraphenylporphines increase in the order Cu(II), Co(II), Ni(II)<Pd(II)<Pt(II). In view of the nature of the metal ions involved, it is probable that the bond strengths increase in the order Cu(II), Co(II), Ni(II)<Pd(II)<Pt(II). Although the copper chelates might be expected to have stronger metal–nitrogen bonds than either the nickel or cobalt chelates, according to the usual order of stabilities of metal chelates, there are some exceptions. Quagliano and co-workers,[18] for example, have shown that in the salicylaldimine complexes the nitrogen–nickel(II) bond is stronger than nitrogen–copper(II) bond. A similar conclusion was reached from some isotopic exchange experiments with some complexes of salicylaldehyde ethylenediamine and acetylacetone ethylenediimine[19] and from studies on

---

[15] C. M. Harris, R. S. Nyholm and N. S. Stephenson, *Nature*, **77**, 4520 (1956).

[16] J. Fujita, K. Nakamoto and M. Kobayashi, THIS JOURNAL, **78**, 3296 (1956).

[17] J. P. Faust and J. V. Quagliano, *ibid.*, **76**, 5349 (1954).

[18] G. F. Stavos, C. Curran and J. V. Quagliano, *ibid.*, **77**, 6159 (1955).

[19] D. C. Atkins, Jr., and C. S. Gardner, *ibid.*, **74**, 3529 (1952).

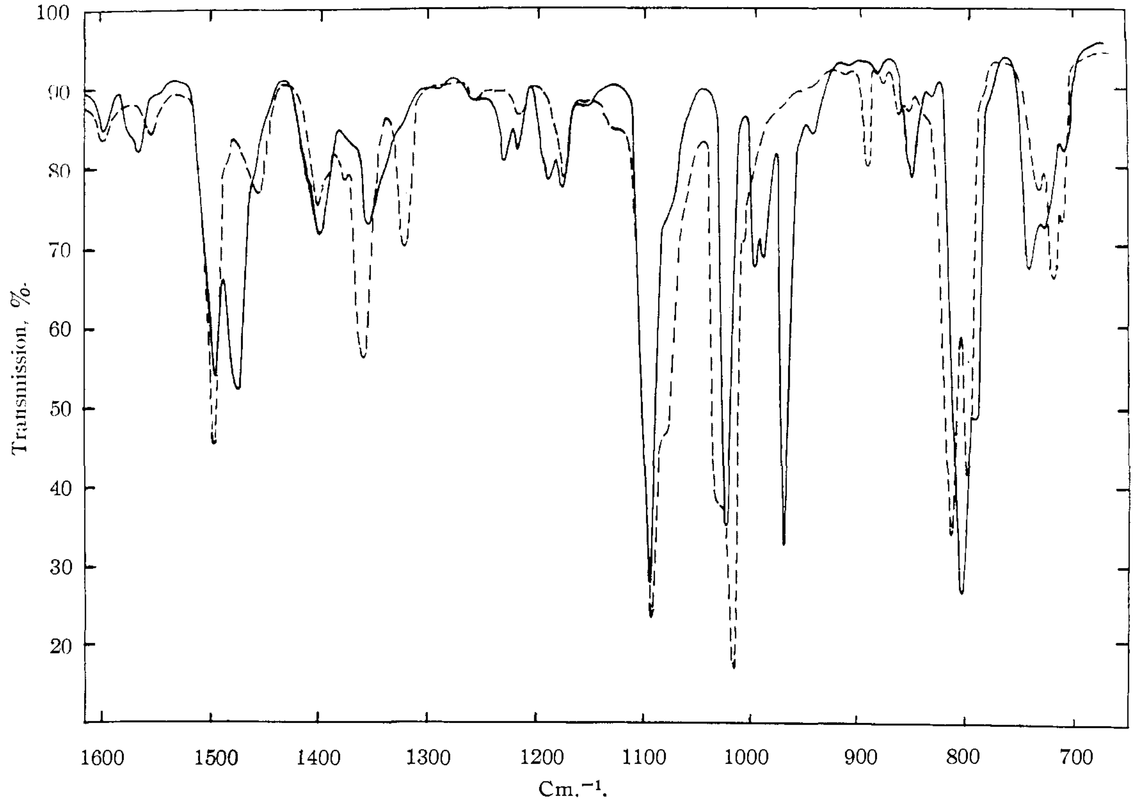


Fig. 1.—Absorption spectra of tetra-(*p*-chlorophenyl)-porphine, ———, and its Pt(II) chelate, ------, between 1600 and 700 cm.$^{-1}$ (Kbr pellet technique employed).

etioporphyrins.[20] If one neglects the small mass effect for Cu, Ni and Co, the frequency values indicate the relative stabilities to be Ni(II)>Co(II), Cu(II).

For any one metal of the above series, with the exception of the palladium(II) and platinum(II) chelates of the methoxy ligand, the frequencies near 1000 cm.$^{-1}$ decrease in the order TPP>*p*-ClTPP>*p*-OCH_3TPP. If the absorption band at 1009 cm.$^{-1}$ of the palladium chelate and the less intense band at 1010 cm.$^{-1}$ for the platinum compound are tabulated for the *p*-methoxy derivative, this same frequency order TPP>*p*-ClTPP>*p*-OCH_3TPP, would also be indicated for these metal chelates. The decreased frequencies for the *p*-substituted chelates may be due in part to the mass effect, but it appears that another effect is also in operation. It is seen that these frequencies follow the electron-attracting properties of the *p*-substituted groups. Since the phenyl and porphine rings are not co-planar, it is reasonable to conclude that the interactions of these substituents with the metal–ligand bonds is mainly an inductive rather than a resonance effect. These frequencies further indicate that the *p*-methoxy group apparently exerts a greater inductive effect than does the *p*-chloro substituent.

No definite assignments could be made for metal–ligand vibrations in the KBr region of the spectrum. Although weak vibrations, which were absent in the ligands, appeared at 444–469 cm.$^{-1}$ for the tetraphenylporphine chelates and at 437–469 cm.$^{-1}$ for the *p*-methoxy derivatives, no similar weak vibrations were observed for the tetra-(*p*-chlorophenyl)-porphine chelates.

Weak but fairly sharp bands at 1556, 1556 and 1560 cm.$^{-1}$ for tetraphenylporphine and its *p*-chloro and *p*-methoxy derivatives, respectively, were observed to shift to lower frequencies upon chelation. For the *p*-substituted compounds the order of magnitude of the shift to lower frequencies is Cu(II) > Pd(II) > Pt(II) > Co(II) > Ni(II), but for the tetraphenylporphine chelates the shift to lower frequencies was in the order Cu(II) > Pd(II) > Co(II) > Pt(II) > Ni(II). This absorption band is probably the –C=C– stretching vibration of pyrrole[4] which undergoes a change of bond order on chelation.

Since the porphine and phthalocyanine nuclei are somewhat distorted in the ligand[21,22] but completely symmetrical in the chelates,[23,24] a change in the carbon–nitrogen bond order of the central atoms might be expected to occur. In the ligands more than one carbon–nitrogen vibration might be expected as a result of the unsymmetrical nature of the porphyrin system, but an increase in symmetry of the chelates should result in the disappearance of one of these vibrations. Accordingly, in all the tetraphenylporphine ligands absorption

[20] W. S. Caughey and A. H. Corwin, THIS JOURNAL, **77**, 1509 (1955).

[21] G. D. Dorough and K. T. Shen, *ibid.*, **72**, 3939 (1950).

[22] J. M. Robertson, *J. Chem. Soc.*, 1195 (1936).

[23] A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice-Hall, Inc., New York, N. Y., 1952, p. 278.

[24] J. M. Robertson and I. Woodward, *J. Chem. Soc.*, 219 (1937).

TABLE I

INFRARED FREQUENCIES AND ASSIGNMENTS

Ligand	Cu	Ni	Co	Pd	Pt	Assignment
Tetraphenylporphine						
1597m[a]	1597m	1600m	1598m	1598m	1600m	—C=C— (phenyl)
1575w	1575w	1576w	1575w	1576w	1576w	Conj.
1556w	1537w	1550w	1541w	1539w	1544w	(—C=C— (pyrrole)
1545wsh	1520w	1535w	1522wsh			
1492w	1490w	1492w	1492w	1492w	1495w	—C=C— (phenyl)
1474m						—C=N—
		1464w	1465wsh		1465wsh	
		1456wsh				
1462wsh	1450wsh	1452wsh	1454wsh	1452wsh	1455	
1443m	1443m	1443m	1443m	1443m	1443m	C—H bend (pyrrole)
1443wsh	1432wsh	1440wsh	1425wsh	1427wsh	1427wsh	
1402w						
		1378wsh			1385w	
1362wsh	1375w	1365w	1373w	1370w	1375wsh	
1350m	1346s	1351s	1350s	1354s	1360s	=C—N— stretch
1325wsh						
1310wsh						
	1306w	1312w	1309w	1311m	1316m	
1286vw	1277vw	1277vw	1277vw	1277vw	1277vw	
1250w	1240w	1240w	1235w	1245w	1250w	
1222w						
1213w	1205m	1207w	1206m	1210w	1211w	
1188w						
1177m	1177m	1177m	1177m	1177m	1177m	
1155w	1155w	1155w	1155w	1155w	1155w	Monosubst.
		1077m				
1072m	1072m	1072m	1072m	1075m	1077m	
1052w	1050wsh	1050w	1050vw	1050vw	1050vw	
1030w						
1003m	1017msh	1023m	1020m	1018ssh	1030msh	C—H rock (pyrrole)
	1004s	1007s	1005s	1014s	1019s	
980m						
966s	996s	1000ssh	997s	1005s	1009msh	
	966ws	964w	966wsh	966w	966w	
		940w				
916vw	916vw	912vw	920vw	916vw	916vw	
876w	876vw	876vw				
845w	845w	845wsh	842wsh	845w	842wsh	
	835w	835w	835m	836w	837w	
825vwsh	825vwsh	825vwsh	825vwsh	825vwsh	825vwsh	
813msh						
799s	798s	794s	796s	796s	796s	Pyrrole ring
786msh			785msh	785wsh		
757msh		752msh				
752msh	752s	743s	751s	752s	754s	Monosubst. phenyl
745m						
727s	726m	723msh	725m	725m	725m	
723msh	715s	709s	715s	712s	713s	
699s	699s	695s	699s	699s	700s	Monosubst. phenyl
656w	660w	666w	665w	665w	666w	
637vw	650w	652w	653w	653vw	653vw	
617vw	618w	619w	619w	618vw	617vw	
560vw	558vw	557vw	563vw	559vw	557vw	
518vw	524w	530w	528w	528w	530w	
	444w	467w	467w	467w	469w	
Tetra-(*p*-methoxyphenyl)-porphine						
1609m	1608m	1608m	1608m	1608m	1608m	—C=C— (phenyl)
1575m	1574m	1574m	1574m	1575m	1575m	Conj. phenyl
1560w	1537m	1550w	1545w	1538w	1544w	—C=C— (pyrrole)
1530wsh	1530msh					
1510s	1504s	1506s	1506s	1505s	1506s	—C=C— (phenyl)
1475msh						—C=N—

TABLE I (*continued*)

Ligand	Cu	Ni	Co	**Pd**	Pt	Assignment
1467m	1464m	1464m	1463m	1464m	1463m	—CH$_3$ def.
1457msh	1456msh	1456msh	1452msh	1455m	1455m	
1442m	1440m	1441m	1442m	1442m	1442m	—C—H bend (pyrrole)
1410w	1410w	1410w	1410w	1410w	1410w	
1405w						
	1385vw				1385w	
	1370vw	1374w	1372vw	1370wsh	1372wsh	
1350m	1345s	1352s	1351s	1353s	1358s	=C—N stretch
	1311vwsh	1310wsh	1310wsh	1310m	1315m	
1303msh	1302m	1301m	1302m	1304m	1302m	
1289m	1285m	1287m	1287m	1288m	1288m	
1247s	1247s	1247s	1247s	1247s	1246s	—C—O stretch
1225msh	1225msh	1225msh	1225msh	1225msh	1225msh	
1214msh	1206m	1206w	1206w	1210w	1212w	
1175s	1174s	1175s	1175s	1175s	1175s	—OCH$_3$
1155m						
1106m	1105m	1105m	1105m	1106m	1106m	*p*-Subst. phenyl
1070w	1070m	1073m	1073m	1075m	1076m	
1034m	1036m	1038m	1037m	1044m	1045m	
1024msh	1022m	1026m	1025m	1027m	1030msh	C—H rock (pyrrole)
1014msh						
	998s	1002s	1001s	1016s	1020s	C—H rock (pyrrole)
993m						
984m						
967m				1009s	1010s	
	955vw	955vw	950vw	960vw	960vw	
940w						
877w	880vw	880vw	880vw	884w	884w	
842m	847m	848m	848m	850m	850m	
810ssh	810ssh	810ssh	810ssh	810s	813s	*p*-Subst. phenyl
803s	799s	799s	799s	798s	797s	Pyrrole ring
787msh	786m	786m	786m	794m	794m	
736m						
725msh	723msh	723msh	725msh	724msh	723msh	
710m	714m	712m	710m	713m	713m	
667vw	665vw	667vw	667vw	667vw	667vw	
		665vw		665vw	665vw	
645wsh						
635w	636w	636w	636w	636w	636w	
596m	603m	606m	606m	607m	610m	C—O—C (?)
558wsh	558wsh	558wsh	558wsh	558wsh	558wsh	
535w	537w	537w	536w	537w	539w	
	437w	445w	443w	439w	469w	
Tetra-(*p*-chlorophenyl)-porphine						
1595w	1595w	1595w	1595w	1595w	1595w	—C=C— (phenyl)
1582vwsh	1582vw	1582vw	1582vw	1582vw	1582vw	
1565wsh	1560vw	1570vw	1565vw	1565vw	1570vw	Conj. phenyl
1556w	1537w	1549w	1544w	1539w	1542w	—C=C— (pyrrole)
1548wsh						
1490m	1487m	1488m	1489m	1489m	1489m	—C=C— (phenyl)
1473m						—C=N—
1460wsh	1445w	1465w	1455w	1447w	1455w	
1443wsh						
1405wsh						
1396m	1396m	1396m	1396m	1396m	1396m	—C—H bend (pyrrole)
1370vw		1374vw	1374vw	1372vw	1374vw	
1348m	1344m	1352m	1350m	1354m	1359m	=C—N stretch
1338wsh	1335wsh	1340wsh	1335wsh	1340wsh	1340wsh	
	1305w	1312w	1310w	1312w	1316m	
1285vw						
1254w	1237w	1242w	1242w	1250w	1250w	
1223w						
1213w	1208w	1208w	1208w	1212w	1214w	
1187w						

TABLE I (*continued*)

Ligand	Cu	Ni	Co	Pd	Pt	Assignment
1177w	1177w	1177w	1177w	1177w	1177w	
1153vw						
1104wsh	1103wsh	1105wsh	1104wsh	1105wsh	1104wsh	*p*-Subst. phenyl
	1115vw	1120vw	1116vw	1120w	1125w	
1092s	1092s	1093s	1092s	1093s	1092s	
1075msh	1075msh	1076msh	1077msh	1080msh	1080msh	
1018s	1014m	1013s	1015s	1022msh	1021ssh	
	1000s	1004s	1002s	1013s	1014s	C—H rock (pyrrole)
994m						
983m						
967s	992msh	1000msh	994msh	1000msh	1004msh	
	965vw	965vw	960vw	960vw	965vw	
945w	945vw	945vw	945vw	945vw	945vw	
875w	880w	882w	882w	884w	884w	
852wsh	850w	850w	850w	851w	852w	
842m	845wsh	845wsh	845wsh	845wsh	845wsh	
823vw	825vw	825wsh	825wsh	827wsh	829wsh	
807ssh	805s	807s	805s	807s	807s	*p*-Subst. phenyl
800s	797s	797s	797s	796s	795s	Pyrrole ring
787msh						
732m	732w	727w	725msh	727m	726m	
721m	718m	715m	717m	715m	715m	
703m	708m	708m	707m	707m	707m	
665vw	668vw	665vw	668vw	668vw	655vw	
640w						
625vw	630vw	630vw	630vw	630vw	630vw	
556vw	562vw	556vw	558vw	557vw	557vw	
493m	501m	506m	506m	507m	508m	C—Cl stretch

[a] strong; m, medium; w, weak. vw, very weak; sh, shoulder.

TABLE II

VARIATION OF INFRARED FREQUENCIES WITH METAL ION

Metal	TPP	*p*-OCH$_3$TPP	*p*-ClTPP
Cu(II)	1004	998	1000
Co(II)	1005	1001	1002
Ni(II)	1007	1002	1004
Pd(II)	1014	1016	1013
Pt(II)	1019	1020	1014

near 1470 cm.$^{-1}$, previously assigned to a —C═N— stretching vibration,[11] disappears in the chelates. An absorption band, which appears at 1350 cm.$^{-1}$ for all the ligands,[4] increases in intensity and is shifted to higher frequencies upon chelation, the extent of the shift decreasing in the order Cu(II) < Co(II) < Ni(II) < Pd(II) < Pt(II). Only the copper chelates have somewhat lower frequencies than the ligands. This absorption band is associated with a C—N═ vibration and the frequencies indicate greater double bond character of this bond in the metal chelates. Such behavior would be expected if the porphine ring were to become more symmetrical.

Two additional sets of absorption bands appear in the tetraphenylporphine ligands but disappear in the chelates. Weak absorption bands were observed near 1400 cm.$^{-1}$ for all the ligands, and a doublet appeared at 1250 to 1225 and 1210 to 1190 cm.$^{-1}$ for tetraphenylporphine and its *p*-chloro derivative. For the methoxy compounds this doublet was masked by a strong absorption band in the same region. For all the ligands the 1400 cm.$^{-1}$ vibration and the higher frequency band of the doublet with the exception of the methoxy derivatives disappear when the metal chelate is formed. One of these bands may be due to the ═N—H in-plane bending vibration of the ligands although it is difficult to make such an assignment with any degree of certainty.[25] A weak absorption band, which appears for all the chelates at 1305–1316 cm.$^{-1}$, but is absent in the ligands, has not been assigned.

An absorption band at 1442 cm.$^{-1}$ is assigned to the C–H bending vibration of pyrrole for the ligand and chelates of tetraphenylporphine and its *p*-methoxy derivative, since its frequency is relatively constant for all these compounds.[4] A similar vibration was observed for the *p*-chloro derivative, but upon chelation it is shifted to higher frequencies in the order Cu < Pd < Pt, Co < Ni. An absorption band at 1396 cm.$^{-1}$ for all the *p*-chloro compounds is not shifted on chelate formation, and it is therefore assigned to the C–H bending vibration. However, it is difficult to understand why this mode of vibration is 46 cm.$^{-1}$ lower for the *p*-chloro derivatives than for the other ligands and chelates.

Little change was observed in the numerous —C═C— stretching vibrations of the phenyl rings. The absorption band near 1600 cm.$^{-1}$ is more intense in the chelates, as was observed previously,[11] but the frequency shift for the series, *p*-OCH$_3$>TPP>*p*-Cl, is the same as for the free ligands. The conjugated phenyl ring vibrations appear near 1570 cm.$^{-1}$. Another in-plane phenyl vibration occurs at 1500 cm.$^{-1}$. For the substituted tetraphenylporphines, chelate formation results in a shift to slightly lower frequencies (–OCH$_3$

---

(25) J. F. Falk and J. P. Willis, *Aust. J. Scient. Research*, **4**, 589 (1951).

>-Cl). For the tetraphenylporphine chelates, however, the position of this band does not change significantly.

A number of phenyl and *p*-disubstituted phenyl vibrations have been assigned in the 1155 and 1105 cm.$^{-1}$ regions in agreement with the observations of Bellamy.[26]

Strong absorption bands near 800 cm.$^{-1}$ were previously assigned to out-of-plane deformations of the disubstituted phenyl rings. However, from a further examination of the chelates for these ligands, it appears that the *p*-disubstituted phenyl vibration is associated with the strong band at 805–810 cm.$^{-1}$. For the ligands of the *p*-methoxy and *p*-chloro derivatives in KBr, this band appears as a shoulder on the 800 cm.$^{-1}$ band. However, it is very distinct for all the *p*-disubstituted metal chelate compounds, and it is absent in the unsubstituted tetraphenylporphine chelates.

The two out-of-plane deformations of the monosubstituted phenyl rings are reassigned to the vibrations near 750 and at 699 cm.$^{-1}$ for tetraphenylporphine and its chelates. The strong absorption band at 699 cm.$^{-1}$ is common to all tetraphenylporphine chelates and ligand, but no such vibration is evident in the other series of *p*-substituted compounds.

The strong band common to all ligands and chelates near 800 cm.$^{-1}$ appears to be a vibration of the pyrrole rings. In pyrrole a very strong vibration occurs near 730 cm.$^{-1}$. Fuson, Fowler and Dangl[27] have assigned a band in this region in pyrrole to a C–H vibration.

A strong absorption band, associated with the C–O stretching vibration of the methoxy group,[4,26a] occurs at 1247 cm.$^{-1}$. The strong vibration at 1175 cm.$^{-1}$ has also been assigned to this group. Further, a third band of medium intensity at 596–510 cm.$^{-1}$ is attributed to a C–O–C vibration, since no similar absorption was found in this region for any of the other ligands or chelates. This band may be a bending vibration.

The absorption bands near 1460 cm.$^{-1}$ are assigned to the C–H bending vibration of the methyl groups.

Recently Goldstein and co-workers[13,28] have assigned an absorption band in the 500 cm.$^{-1}$ region of tetra-(*p*-chlorophenyl)-porphine and some of its chelates to the C–Cl stretching vibration, and it was observed that the ligand absorption was shifted to higher frequencies for all the chelates. The same shift is also observed for all the chelates reported in this research. The order of frequency, ligand < Cu < Co < Ni < Pd < Pt, suggests that there is more double bond character in this C–Cl bond for the chelates than for the ligand. This same order was also observed near 600 cm.$^{-1}$ for the vibration of the methoxy group.

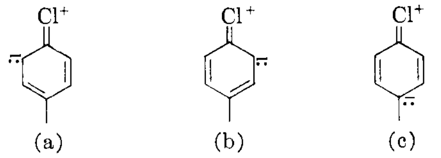
The frequencies for the C–Cl stretching vibration and for the C–O–C vibration are compared in Table III.

TABLE III

FREQUENCY SHIFTS OF *p*-SUBSTITUENTS (CM.$^{-1}$)

	C-Cl	Δ	C-O-C	Δ
Ligand	493	. .	596	. .
Cu(II)	501	8	603	7
Co(II)	506	13	606	10
Ni(II)	506	13	606	10
Pd(II)	507	14	607	11
Pt(II)	508	15	610	14

The increased frequencies indicate that the metals do exert some effect on the bonding to these *p*-substituents. However, the frequencies of the absorption bands associated with the metal-ligand vibrations suggest that the *p*-methoxy and *p*-chloro phenyl rings have an electron withdrawal effect, and therefore an inductive influence, upon the central coördinate linkages. It may well be, therefore, that the resonance interactions of these groups are mainly confined to the phenyl rings themselves, since the benzene rings are not coplanar with the porphine ring.[4,6,29] The C–Cl and C–O–C frequency changes may be interpreted on the basis of resonance interactions of the type



(a) (b) (c)

It is possible that the substitution of metals in the central porphine ring increases the extent to which such interaction can occur. Interactions of type (c) may have an appreciable effect on the π-charge of the adjacent carbon atoms of the pyrrole rings. The associated slight symmetry changes in charge and bond type of the porphine ring may thus also be sensitive to the size and electronegativity of the central metal ion. The net observed effect of the *p*-substituents, however, appears to be one of weak electron withdrawal from the central metal ion.

It is also interesting to note that the C—N= stretching vibrations, the C—Cl stretching vibrations and the C-O-C bending vibrations are also shifted to higher frequencies in the order Cu(II) < Co(II) < Ni(II) < Pd(II) < Pt(II). The same order was observed for the vibrations near 1000 cm.$^{-1}$, which seem to be associated with the metal-ligand bonds.

Experimental

Preparation of Metal Chelates.—All chelates of tetraphenylporphine and its *p*-methoxy and *p*-chloro derivatives were prepared under reflux in an all-glass apparatus. Each of the ligands used in these preparations contained a small amount of chlorin (dihydrotetraphenylporphine) by-product[8] which was not removed until after combination with the metal ion. The chlorin ligand was characterized by absorption in the 650 mμ region and the various amounts of

---

[26] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," London, Methuen, John Wiley and Sons, Inc., New York, N. Y., 1952, p. 69; (a) pp. 99, 102.

[27] N. Fuson, R. G. Fowler, H. M. Randall and J. R. Dangl, "Infrared Determinations of Organic Structures," D. Van Nostrand Co., Inc., New York, N. Y., 1952, p. 61.

[28] On the basis of the comparisons resulting from the present work, the assignment, originally made by Goldstein, *et al.*,[8] of the band near 500 cm.$^{-1}$ to the C-Cl stretching vibration is now accepted for these compounds. However, the band near 950 cm.$^{-1}$ cannot be an overtone of this stretching mode, as they suggested, since its frequency does not vary with the metal ion, whereas there is appreciable variation of the 500 cm.$^{-1}$ band as the metal ion is changed.

[29] W. D. Kumler, THIS JOURNAL, **64**, 2994 (1942).

metal chlorins produced in some reactions were determined from the characteristic absorption band near 610 mμ.[30]

Various reaction solvents and reflux periods were employed, but in all the preparations a 0.400-g. sample of the appropriate ligand was used, with the exception of preparation of the platinum(II) chelate of the *p*-chloro derivative. In this case a 0.200-g. sample of ligand was employed. For the preparation of all the copper(II), cobalt(II) and nickel(II) chelates a 2:1 excess of the copper(II) acetate monohydrate, nickel(II) acetate tetrahydrate or the cobalt(II) acetate tetrahydrate was allowed to react, either in a minimum amount of glacial acetic acid in mixed solvent systems, as was the case for the Ni(II) and Co(II) tetraphenylporphines and the Cu(II), Ni(II) and Co(II) chelates of the *p*-chloro derivative, or in the solid form such as was the case for the preparation of these three chelates of the *p*-methoxy derivative in glacial acetic acid and for preparation of the Cu(II) tetraphenylporphine in dioxane. The solid reaction product obtained from the dioxane or chloroform-free reaction solvents or from the acid solutions diluted with water was washed with water and methanol prior to chromatographic purifications on talc columns (U.S.P. talc, J. T. Baker Co.) as chloroform or trichloroethylene (City Chemical Co., N.Y.) solutions. On talc all the Cu(II), Co(II) and Ni(II) chelates appeared as orange-red bands which were only weakly adsorbed and which were easily eluted with additional developing solvent. The ligands adsorbed as a green band. Table IV lists the reaction conditions, method of purification, presence of by-products, yields, and other pertinent information for all the copper(II), nickel(II) and cobalt(II) chelates as well as for all the palladium(II) and platinum(II) chelates which are also described in more detail below.

Tetraphenylporphinopalladium(II) (X = H, M = Pd(II)).—The ligand was refluxed in glacial acetic acid with 0.3 g. of dry palladium(II) chloride (City Chemical Co.) for 10 minutes, and to the light brown-green solution obtained, 1 g. of sodium acetate was added. The color rapidly changed to maroon-brown and the reaction mixture was refluxed for 2 hours with an additional gram of sodium acetate. Spectral analysis indicated that the reaction mixture contained some unreacted TPP, some chlorin ligand, as suggested by absorption at 650 mμ,[30] and some metal chlorin with an absorption maximum near 610 mμ. Further refluxing with additional palladium salt did not result in any appreciable change. The acid solution was therefore diluted with water, filtered and the precipitated residue was washed with water, air-dried, dissolved in trichloroethylene, and chromatographed on a talc column, the upper region of which was filled with talc dried at 115° for 2 hours. Talc used in this manner was found to be especially convenient for separating metal–chlorin impurities which appear as a gray-red band. The unreacted ligand remained adsorbed as a green band on the upper section of the talc. The orange-red eluate was concentrated and distilled methanol was added. A 0.24-g. yield or 57% of the theoretical amount of light red-violet crystals was collected.

Tetraphenylporphinoplatinum(II) (X = H, M = Pt(II)).—The tetraphenylporphine sample was dissolved in 75 ml. of hot benzene and 175 ml. of hot glacial acetic acid was added. To the green-maroon colored solution thus obtained, a 20-ml. water solution of 0.6 g. of potassium chloroplatinite (City Chemical Co.) and 5 g. of sodium acetate was added and the reaction mixture was refluxed at 90–100° for 20 hours. A green-brown color developed in the solution near the beginning of the reaction period. After the cooled solution was filtered on a Büchner funnel, the solid material obtained was washed with water and was air-dried. It was then dissolved in chloroform and was chromatographed on a talc column. The initial orange eluate contained the purified chelate; additional orange-red fractions contained some ligand impurities. These fractions were taken up separately in benzene, were rechromatographed in benzene on talc, and the purity of the resulting eluate was examined spectrophotometrically. All the benzene fractions of the same purity were combined. An additional fraction of platinum chelate was obtained by extracting the original benzene–acetic filtrate with benzene in water, drying over anhydrous sodium sulfate, and finally chromatographing the benzene solution on a talc column. Since the purity of the orange eluate was comparable to

TABLE IV: SYNTHESIS OF METAL PORPHINES

Ligand[a]	Metal ion(II)	Reaction solvent	Reflux time,(hr.)	By-products Metal chlo.	Chlo. lig.	Chrom. solv.	Times chrom.	Crystn. solv.	Color	Yield, %	Ref.	Char. abspt.[d] λ_{max}	$\epsilon \times 10^{-3}$	Nitrogen, % Calcd.	Found
TPP[b]	Cu	Dioxane	2.5	Trace	Trace	TCE[c]	1	$CHCl_3$-CH_3OH	Violet	86	5, 6, 7, 11	540	20.4	8.28	8.35
	Ni	Dioxane–glHAc	3	Apprec.	Trace	TCE	3	$CHCl_3$-CH_3OH	Purple-red	52	5, 6, 7	529	17.1	8.34	8.40
	Co	Dioxane–glHAc	7	None	None	TCE	1	$CHCl_3$–CH_3OH	Violet-brown	59	5, 6, 7, 11	529	16.6	8.34	8.50
	Pd	glHAc	2	Apprec.	Trace	TCE	1	TCE–CH_3OH	Red-violet	57	......	524	29.3	7.79	7.88
	Pt	Benzene	20	Apprec.	Trace	$CHCl_3$–benzene	1								
							2	Benzene–CH_3OH	Red-brown	10	......	510	24.2	6.94	6.83
p-OCH_3TPP	Cu	glHAc	6	None	None	$CHCl_3$	1	$CHCl_3$-CH_3OH	Red-violet	70	......	542	22.2	7.04	7.19
	Ni	glHAc	6	None	Trace	$CHCl_3$	1	$CHCl_3$–CH_3OH	Red-violet	63	......	531	19.7	7.08	7.15
	Co	glHAc	5	None	None	$CHCl_3$	1	$CHCl_3$–CH_3OH	Red-violet	33	......	532	17.4	7.08	7.20
	Pd	glHAc (MeOH)	2	Apprec.	Trace	$CHCl_3$	2	$CHCl_3$-CH_3OH	Light red	58	......	527	30.1	6.68	6.75
	Pt	glHAc	20	Apprec.	Trace	TCE–$CHCl_3$	3	$CHCl_3$-CH_3OH	Orange-red	6	......	513	29.4	6.04	6.16
p-ClTPP	Cu	$CHCl_3$–glHAc	2	Apprec.	Trace	$CHCl_3$–TCE	2								
							2	TCE-CH_3OH	Violet	71	......	540	22.9	6.89	7.05
	Ni	$CHCl_3$–glHAc	2	Apprec.	Apprec.	$CHCl_3$–TCE	1								
							1	TCE–CH_3OH	Red-violet	74	......	529	18.0	6.92	6.90
	Co	$CHCl_3$–glHAc	3.5	Apprec.	Trace	TCE	1	TCE–CH_3OH	Red-brown	47	......	530	17.4	6.92	7.14
	Pd	$CHCl_3$–CH_3OH	1.5	Apprec.	Apprec.	TCE	3	TCE–CH_3OH	Pink-orange	28	......	525	30.4	6.54	6.66
		glHAc	2	Apprec.	Trace										
[d]	Pt	glHAc	24	Apprec.	Trace	TCE	1	TCE–CH_3OH	Orange-brown	4	......	511	27.0	5.92	..

[a] 0.400 g. of ligand employed unless otherwise noted. [b] TPP = tetraphenylporphine. [c] TCE = trichloroethylene. [d] 0.200 g. of ligand employed.

---

(30) G. D. Dorough and F. M. Huennekens, THIS JOURNAL, **74**, 3974 (1952).

those of the other fractions, the solutions were combined and were concentrated to 20 ml. The addition of 150 ml. of distilled methanol resulted in the immediate crystallization of the product. After the mixture had stood overnight, the reddish-brown crystals mixed with a waxy-white, low-melting solid were filtered off. The impurity, which was soluble in chloroform, benzene, methanol and water, was removed by washing the mixture repeatedly with hot water and methanol. The yield of crystalline residue of pure platinum(II) tetraphenylporphine was 52 mg. or 10% of the theoretical amount.

Tetra-(*p*-methoxyphenyl)-porphinopalladium(II) (X = OCH_3, M = Pd(II)).—This palladium(II) chelate was prepared with the same procedure as the one described above for tetraphenylporphinopalladium(II). All the metal chlorin, chlorin ligand, unreacted porphine and other impurities were removed by chromatographing a chloroform solution of this chelate on a talc column. Chloroform was also used as the developing solvent. The lustrous light red crystals weighed 0.263 g., which represents 58% of the theoretical yield.

Tetra-(*p*-methoxyphenyl)-porphinoplatinum(II) (X = OCH_3, M = Pt(II)).—A solution of the ligand in 200 ml. of glacial acetic acid was heated to 100° and 1.45 g. of potassium chloroplatinite dissolved in 4 ml. of water was added. A yellow-green color developed and a fine green precipitate appeared. Five grams of sodium acetate was then added and the reaction mixture was stirred. A slight brown-green color developed, but after the reaction mixture was heated at 100° for 20 hours, the color changed to yellow-green. The cooled solution was filtered on a Büchner funnel and the filtrate was saved. The purple-black solid was washed with water, dried at room temperature, dissolved in trichloroethylene, and was chromatographed on a talc column, the upper section of which contained oven-dried talc. A mixture of chloroform and trichloroethylene, and finally chloroform alone was used as the developing solvent. The first 500 ml. of eluate contained pure platinum chelate with absorption maxima at 540, 513, 475 and 407 mμ in benzene. Succeeding fractions, however, contained impurities with increased absorption at 540 mμ. Adsorbed in ascending order of the column were a section of gray-brown material, some unreacted ligand, and some brown-black deposits of platinum. The impure chloroform fractions were rechromatographed on talc. All the orange-colored solutions obtained were combined, concentrated and crystallized by dilution with distilled methanol. Only 31 mg. or 6% of the theoretical yield of pure orange-red crystals was obtained. *Anal.* Calcd. for $C_{48}H_{36}O_4N_4Pt$: C, 62.12; H, 3.88; Pt, 21.05. Found: C, 62.10; H, 3.90; Pt, 20.60.

Concentration of the acetic acid filtrate from this main reaction with 0.1 g. of additional potassium chloroplatinite at 10–20 mm. pressure and 53° yielded an amorphous green material which solidified from this solution as it was concentrated. The blue-black solid which formed when this material was dissolved in hot water was purified in a chloroform solution on a talc column. A 54-mg. sample of silvery-red-violet crystals was obtained after crystallization of the concentrated eluate with methanol.

Tetra-(*p*-chlorophenyl)-porphinopalladium(II)) (X = Cl, M = Pd(II)).—A chloroform solution of the ligand and a mixture of 0.25 g. of palladium(II) chloride in 75 ml. of hot methanol and 3 g. of sodium acetate was refluxed for 2 hours. Further refluxing in this solvent media resulted in the formation of more metal chlorin, but did not appreciably improve the yield of palladium porphyrin. After isolation of the solid in the usual manner, it was again heated for 2 hours with 250 ml. of glacial acetic acid, additional palladium chloride, and sodium acetate. The color change from green to red-brown in this acid medium indicated that additional chelate had formed. Three chromatograms in trichloroethylene were necessary in order to obtain the palladium porphyrin eluate in a pure form. The yield of lustrous, pink-orange crystals weighing 0.125 g. which represents 28% of the theoretical amount.

Tetra-(*p*-chlorophenyl)-porphinoplatinum(II) (X = Cl, M = Pt(II)).—To 0.200 g. of tetra-(*p*-chlorophenyl)-porphine in 250 ml. of hot glacial acetic was added 0.3 g. of potassium chloroplatinite and 5 g. of sodium acetate in 10 ml. of water. The resulting green-brown mixture was refluxed for 24 hours. The solution was then concentrated to 100 ml., the solid was filtered off, and the filtrate was saved. The residue was washed with water and air-dried. The green filtrate was further treated at 100° with excess platinum chloroplatinite and sodium acetate for 15 hours. This brown-green solution was concentrated, diluted with water and the product was filtered off. The solid material was dissolved in trichloroethylene together with the solid in the first step, and this filtered solution was chromatographed on a talc column, the upper section of which was oven-dried. The orange eluate was free from any unreacted ligand, metal chlorin or other impurity. The eluate was concentrated and was diluted to six times its volume with methanol. The lustrous, orange-brown crystals obtained weighed 10 mg., which represents 4% of the theoretical value.

The absorption spectra were employed to characterize the tetra-(*p*-chlorophenyl)-porphine platinum(II) chelate. The characterization and purity of all other chelates were determined from elemental analysis, and the quality of the visible and ultraviolet absorption spectra[14]; extinction coefficients listed in Table IV are given as criteria of purity.

Infrared Spectra.—Infrared absorption measurements were carried out with a Perkin-Elmer model 21 double beam 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. All spectra were determined on the solid form with potassium bromide as a diluent.

WORCESTER, MASS.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Binding of Organic Ions by Proteins. Effects of Changes in Solvent and their Implications as to the Nature of the Complexes

BY IRVING M. KLOTZ AND SAMUEL W. LUBORSKY[1]

RECEIVED DECEMBER 27, 1958

The binding of dyes by serum albumin has been found to increase in solutions to which glycine or β-alanine has been added. However, this effect is not due simply to the substantial increase in dielectric constant but reflects some specific interaction of the added amino acid. These observations, as well as many other aspects of the formation of protein complexes, can be interpreted in terms of a model which largely attributes the stability of such complexes to the cooperative formation of an ice-like hydration lattice between the complexing species.

Introduction

The stability of protein complexes reflects largely the character of the macromolecule and small ligand, but it is also affected by the nature of the environment. The energetics of binding, however, are not generally explicitly expressed in terms of these factors. Rather the free energy of binding is usually apportioned between two terms,

---

(1) Predoctoral Fellow of the National Institutes of Health, United States Public Health Service, 1954–1956.