TABLE III

X-RAY POWDER PHOTOGRAPHIC DATA

$[(C_2H_5)_4N]_3[Cr_2Cl_9]$		$[(C_2H_5)_4N]_3[Rh_2Cl_9]$	
d, Å	Rel intens[a]	*d*, Å	Rel intens[a]
11.3	4	11.3	4
9.53	2	. . .	. . .
8.638	8	8.514	8
8.014	1	7.978	1
5.641	3	5.641	3
4.925	6	4.904	6
4.509	1	4.475	1
4.244	1	4.268	1
4.022	4	3.995	4
3.743	2	3.719	2
3.404	1	3.372	1
3.263	1	. . .	. . .
3.215	1	3.209	1
3.027	1	3.041	1
2.835	3	2.816	3
2.650	1	2.660	1
2.408	1	2.411	1
2.286	2	2.280	2
2.205	1	2.213	1
2.110	1	2.117	1
1.991	10	1.987	10
1.733	7	1.728	7
1.239	3	1.238	3

[a] Relative intensities range 1–10, 10 being most intense.

absorption maxima which were observed in the region 150–400 cm^{-1} for the extracted species and for tetraethylammonium nonachlorodirhodate(III) are the same within the limit of error of the method. In addition, the observed spectra consist of the same number of bands of the same relative intensity and position as those of the complex tetraethylammonium nonachlorodichromate(III). In an early paper by Adams, *et al.*,[5] this chromium complex was prepared and the far-infrared spectrum was taken. These workers observed only two maxima. The higher frequency band was assigned as the "terminal" chromium–chlorine stretching mode and the lower as the "bridged" chromium–chlorine stretching mode. These assignments were made on the basis of the X-ray analysis performed by Wessel and Ijdo[7] which indicated that the complex ion consists of two distorted octahedra sharing a face. Recently, Walton, *et al.*,[8] reported new far-infrared data which substantiate the results reported here. These workers observed three distinct bands, an intense doublet and a band of medium intensity of lower frequency. An ion of the type $M_2Cl_9^{n-}$ of D_{3h} symmetry is expected to have two "terminal" stretching modes and two "bridged" stretching modes. However, only three bands are observed for both the rhodium and the chromium complex. In the case of chromium, the absent band, a "bridged" stretching band, is thought either to be obscured by the terminal stretching bands or to occur at a frequency lower than 200 cm^{-1}.[8] For the rhodium complex, it seems unlikely that this absent band is below 150 cm^{-1} since the "bending" mode for $RhCl_6^{3-}$ is found at 205 cm^{-1}. The only reasonable alternative is that it is obscured by one of the "terminal" stretching modes. It should also be noted that no bands are observed in the "bridged" stretching region (~270 cm^{-1}) for either $RhCl_6^{3-}$ or $RhCl_5(H_2O)^{2-}$, the other probable products. In Figure 1 the spectra of the chromium and rhodium complexes as well as that of the extract are shown for comparison. Note the remarkable similarity between the three spectra. The greater splitting of the doublet for the solid nonachlorodirhodate(III) ion as compared to the extracted species may be attributed to lowering of the symmetry of the complex ion in the crystal lattice due to its site symmetry, while in the solution no such restrictions are placed on the ion pair formed.

As further evidence of the structure of this complex ion, X-ray diffraction powder photographs of the two compounds, tetraethylammonium nonachlorodirhodate(III) and tetraethylammonium nonachlorodichromate(III), were taken. A comparison of the powder patterns indicated that the two compounds were isomorphous (see Table III).

This information is completely consistent with the basic structure assigned by Wessel and Ijdo[7] for $Cr_2Cl_9^{3-}$; that is, two pyramidally distorted octahedra sharing a face.

Acknowledgments.—The X-ray equipment used to obtain crystal powder photographs was purchased under NIH Grant No. GM-08348. The authors wish to thank Tulane University for the use of their Beckman IR-11 purchased partially by funds from National Science Foundation under Grant No. 28709. The original extraction work was begun under AEC Contract No. AT(40-1)-2576.

---

(7) G. J. Wessel and D. J. W. Ijdo, *Acta Cryst.*, **10**, 466 (1957).

(8) See footnote *d*, Table II.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
HOWARD UNIVERSITY, WASHINGTON, D. C. 20001

Formation Constants of Substituted Pyridine Complexes of Cadmium(II) and Mercury(II) α,β,γ,δ-Tetraphenylporphin. The Hammett ρ as a Measure of Cation Polarizing Ability

BY CARL H. KIRKSEY[1a] AND PETER HAMBRIGHT[1b]

Received July 17, 1969

We have previously shown[2] that zinc(II) α,β,γ,δ-tetraphenylporphin (ZnTPP) forms only 1:1 complexes in solution with a variety of substituted pyridine ligands and that their proton magnetic resonance spectra exhibit exchange-averaged patterns and chemical shifts similar to those of the MgTPP adducts. The stability constants for the ZnTPP reactions show both log *K*–pK_a and Hammett-type correlations.

We now report stability constants for the formation

---

(1) (a) Abstracted from the Ph.D. Thesis of C. H. K., Howard University, 1969. (b) To whom inquiries concerning this work should be addressed.

(2) C. H. Kirksey, P. Hambright, and C. B. Storm, *Inorg. Chem.*, **8**, 2141 (1969).

of the corresponding HgTPP and CdTPP adducts. The Hammett ρ values derived suggest the use of this parameter as an index of the effective polarizing power or tendency toward metal–ligand covalency, for a given metal ion.

These studies are similar to others involving the addition of nitrogenous bases to preformed inner complexes, for example to copper(II) acetylacetonates,[3,4] zinc(II)dialkyldithiocarbamates,[5] other divalent metalloporphyrins,[6] and iron(II) dimethylglyoxime.[7]

Experimental Section

$\alpha,\beta,\gamma,\delta$-Tetraphenylporphin[8] and its Cd(II) and Hg(II) complexes were prepared by literature methods and had absorptivities as reported.[9] The stability constants were measured in benzene at 25.0 ± 0.1° by the spectrophotometric titration method of Miller and Dorough.[9] The applicability of their method to the ZnTPP system was shown in detail previously.[2] The formation of the monopyridinates of CdTPP were followed at 618 mμ, while those of HgTPP were at 625 mμ. The usual sets of isosbestic points found in such titrations in porphyrin systems were present. The spectra of the cadmium and mercury species both complexed and uncomplexed were the same as reported by other workers.[9] The titrations were done at *ca.* 1×10^{-5} *M* porphyrin and the ligand concentrations were varied from 10^{-3} to 3 *M*.

Results and Discussion

In a similar manner, as shown previously[2] with ZnTPP, the HgTPP and CdTPP form only 1:1 pyridine adducts, in agreement with other studies.[9] Table I gives the log K_f constants, for reactions of the type

$$\mathrm{M^{II}TPP + L = L\text{-}M^{II}TPP} \qquad K_f \qquad (1)$$

TABLE I
FORMATION CONSTANTS OF ZnTPP, HgTPP, AND CdTPP WITH SUBSTITUTED PYRIDINES AT 25°

	Log K_f[a]		
	ZnTPP[b,c]	CdTPP	HgTPP
4-Aminopyridine	4.65	4.73	2.92
4-Methyl	4.02	3.83	1.62
3-Methyl	3.81	...	1.41
4-Hydrogen	3.78	3.51	1.21
4-Cyano	2.90	2.27	0.22

[a] Deviation ±0.05 unit. [b] Data from ref 2. [c] Measured in benzene.

The data are in good agreement with those of Miller and Dorough.[9] Their values for CdTPP and HgTPP with pyridine at 25° are log K_f = 3.47 and 1.16, respectively.

It is seen that for the range of ligands studied, the stability order is Zn > Cd > Hg. For the metalloporphyrins, the adduct formation can be viewed as dative bonding between the Lewis base ligand and an empty hybridized orbital on the metal ion. Insofar as orbital overlap effects stability, the more diffuse character of the hybrid orbital on Hg(II) compared to Zn(II) would be an explanation of the observed lower stability of HgTPP adducts.

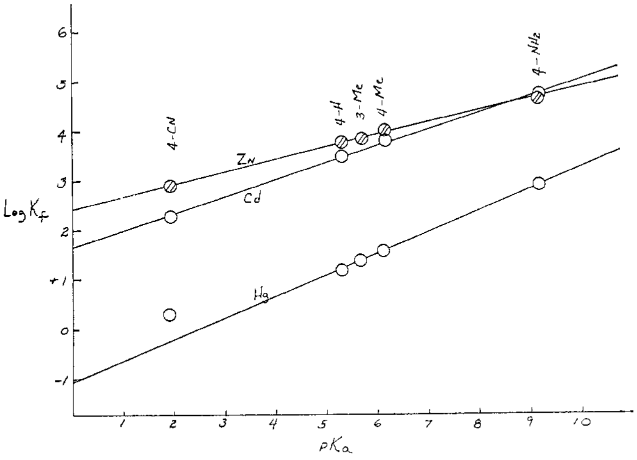

Figure 1.—Log K_f–pK_a plots for Zn(II), Cd(II), and Hg(II) TPP with substituted pyridines.

Figure 1 shows the linear relationship between log K_f (benzene) and the proton affinity of the base, pK_a (aqueous solution) which is of the form

$$\log K_f = a\mathrm{p}K_a + b \qquad (2)$$

For the zinc, cadmium, and mercury porphyrins, a = 0.25, 0.34, and 0.44, and b = 2.45, 1.65, and −1.10, respectively. This equation has been widely used as an empirical representation of stability constant data.[10,11] It has been suggested that "a" is related to the σ-polarizing power of a cation,[11–13] which we find to be Zn(II) < Cd(II) < Hg(II). In general the polarizing power of a cation, or its tendency to have either class b or class a character,[14,15] increases from Zn(II) to Hg(II). From Figure 1, an extrapolation shows that the HgTPP adducts will become more stable than their zinc or cadmium counterparts as ligand basicity increases. The higher ligand basicities place more electron density on the pyridine nitrogen making it more polarizable. This increased polarizability will be of greater consequence, the more polarizing the metal ion, *i.e.*, Hg(II) > Cd(II) > Zn(II), or in the order of increasing "a" values.

The increase in stability with ligand basicity presumably indicates that ligand to metal σ bonding is predominant. Inverse correlations such as found with silver(I)[15] or iron(II) porphyrins[16] and glyoximes[7] with substituted pyridines have been explained in terms of appreciable metal–ligand back-bonding. The

---

(3) D. P. Graddon and E. C. Watton, *J. Inorg. Nucl. Chem.*, **21**, 49 (1961).

(4) W. R. May and M. M. Jones, *ibid.*, **25**, 507 (1963).

(5) E. Coates, B. Rigg, B. Saville, and D. Skelton, *J. Chem. Soc.*, 5613 (1965).

(6) See ref 2 for a brief review.

(7) B. A. Jillot and R. J. P. Williams, *J. Chem. Soc.*, 462 (1958).

(8) A. D. Adler, F. R. Longo, F. D. Finarelli, J. Goldmacher, J. Assour, and L. Korsakoff, *J. Org. Chem.*, **32**, 475 (1968).

(9) J. R. Miller and G. D. Dorough, *J. Amer. Chem. Soc.*, **74**, 3977 (1952).

(10) M. M. Jones, "Elementary Coordination Chemistry," Prentice-Hall Inc., Englewood Cliffs, N. J., 1964, p 340.

(11) G. Schwarzenbach, G. Anderegg, W. Schnieder, and H. Senn, *Helv. Chim. Acta*, **38**, 1147 (1955).

(12) J. G. Jones, J. B. Poole, J. C. Tomkinson, and R. J. P. Williams, *J. Chem. Soc.*, 2001 (1958).

(13) S. Ahrland, J. Chatt, and N. R. Davies, *Quart. Rev.* (London), **12**, 265 (1958).

(14) D. P. Craig and R. S. Nyholm in "Chelating Agents and Metal Chelates," F. P. Dwyer and D. P. Mellor, Ed, Academic Press, Inc., New York, N. Y., 1964, Chapter 2.

(15) R. K. Murman and F. Basolo, *J. Amer. Chem. Soc.*, **77**, 3484 (1955).

(16) J. E. Falk, J. N. Phillips, and E. A. Magnusson, *Nature*, **212**, 1531 (1966).

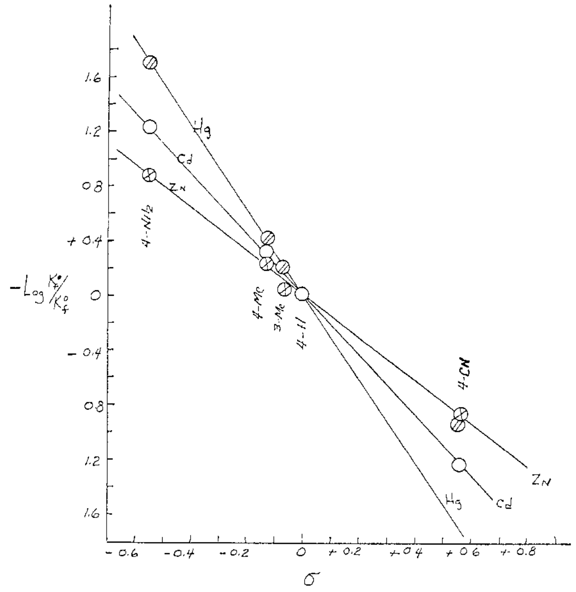

Figure 2.—Hammett plots for Zn(II), Cd(II), and Hg(II) TPP with substituted pyridines.

relatively higher stability of HgTPP with 4-cyanopyridine as compared to its normal behavior with Zn- and CdTPP could argue for some back-bonding of Hg(II) to pyridine. While the case for HgTPP donation simply rests on one observation, similar phenomena have been observed with Pt(II)-styrene complexes.[17]

Figure 2 shows that the equilibrium data fit a Hammett correlation of the form

$$-\log K_f\cdot/K_f^\circ = \rho\sigma \qquad (3)$$

where K_f° is for M$^{\text{II}}$TPP-pyridine, $K_f\cdot$ is for M$^{\text{II}}$-TPP-substituted pyridines, and σ is the Hammett substituent constant.[18] The ρ values observed were +1.5 for ZnTPP, +2.2 for CdTPP, and +3.1 for HgTPP. The positive ρ values indicate that the reaction is favored by electron-donating substituents, or ligand to metal σ-bonding influences. In general terms, the ρ values show the HgTPP reactions to be more sensitive to substituent effects than those of ZnTPP. This can be interpreted on the following basis.[19] The higher ρ value of HgTPP compared to ZnTPP indicates that in the complex the pyridine nitrogen on HgTPP has a higher formal positive charge than that on the nitrogen in the Zn(II) adduct. Thus a given electron-donating group on pyridine will have more effect (greater sensitivity) in stabilizing the higher positive change on the nitrogen adjacent to Hg(II) than in the corresponding Zn(II) species. The higher positive charge on the pyridine nitrogen in HgTPP results from the Hg(II) accepting relatively more of the electron pair from nitrogen than did Zn(II). In other words, the Hg(II) is a better σ polarizer than Zn(II), a conclusion reached earlier on the basis of the a values.

Hence the cation polarizing tendencies of metal ions in metalloporphyrins are in the order Zn(II) < Cd(II) < Hg(II). A quantitative order on the basis of ρ or a values is *ca.* 1:1.4:2. These tendencies, as expected, parallel the ionic size and electronegativity[20] of the divalent ions. The observed order is also in agreement with predictions of the order of class b character for these three cations.[14]

It has been shown that the magnitudes of these equilibrium constants found in solution parallel the temperatures at which pyridine type ligands are liberated from the pyridine-metalloporphyrins in the solid state.[21] For tetraphenylporphine complexes, the liberation temperatures increase with ligand basicity, and decrease with increasing metal ion size (Mg > Zn > Cd > Hg).

Attempts were made to measure the formation constants of the Cu(II), Pd(II), Ni(II), and VO(II) tetraphenylporphin-pyridine adducts to extend the order of metal ions. However, the absorption spectral changes between the complexed and uncomplexed metalloporphyrins were too small to allow the equilibria to be observed.

---

[17] J. R. Roy and M. Orchin, *J. Amer. Chem. Soc.*, **81**, 308 (1959).

[18] P. R. Wells, *Chem. Rev.*, **63**, 171 (1963).

[19] C. G. Swain and W. P. Langsdorf, *J. Amer. Chem. Soc.*, **73**, 2813 (1951).

[20] A. L. Allred, *J. Inorg. Nucl. Chem.*, **17**, 215 (1961).

[21] R. Lee and P. Hambright, *ibid.*, in press.

Contribution from the Chemistry Department,
East Carolina University,
Greenville, North Carolina 27834,
and the Chemistry and Life Sciences Laboratory,
Research Triangle Institute,
Research Triangle Park, North Carolina 27709

The Rearrangement of Some Bis(diphenylphosphino)amines upon Chloramination

By Donald F. Clemens,[1a] Myron L. Caspar,[1a]
David Rosenthal,[1b] and Robert Peluso[1a]

Received July 25, 1969

We now have evidence that the structure that we previously postulated[2] for the chloramination products of bis(diphenylphosphino)amines should be modified. In the course of extending this work[3] we have had occasion to reexamine the chloramination of bis(diphenylphosphino)methylamine. While chloramination takes place on the phosphorus atoms, as previously demonstrated,[4,5] we find that during the course of the reaction an apparent nitrogen to nitrogen methyl migration has occurred to yield compound III which is expected to be strongly resonance stabilized.

---

[1] (a) East Carolina University. (b) Research Triangle Institute.

[2] D. F. Clemens and H. H. Sisler, *Inorg. Chem.*, **4**, 1222 (1965).

[3] D. F. Clemens, W. Woodford, E. Dellinger, and Z. Tyndall, *ibid.*, **8**, 998 (1969).

[4] R. P. Nielsen, J. F. Vincent, and H. H. Sisler, *ibid.*, **2**, 760 (1963).

[5] W. A. Hart and H. H. Sisler, *ibid.*, **3**, 617 (1964).