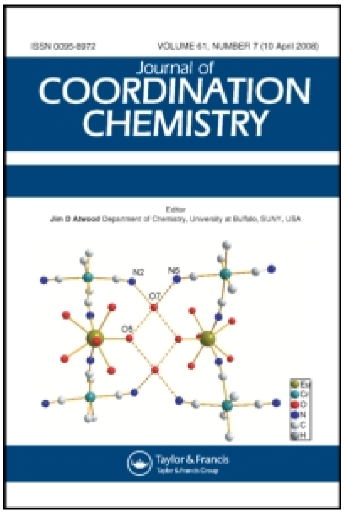

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SOME METAL COMPLEXES OF α, β, γ, δ-TETRA-(4-PYRIDYL) PORPHINE

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SOME METAL COMPLEXES OF $\alpha,\beta,\gamma,\delta$-TETRA-(4-PYRIDYL) PORPHINE

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The zinc (II), copper (II), nickel (II), cobalt (II), chloromanganese (III), and chloroiron (III) complexes of $\alpha,\beta,\gamma,\delta$-tetra(-4-pyridyl)-porphine (4-TPyP) were prepared. The magnetic susceptibilities from near 0° to 90°K and at room temperature were measured for solid Cu(4-TPyp), Ni(4-TPyP), Co-(4-TPyP), ClMn(4-TPyP) · H_2O and ClFe(4-TPyP). The Mössbauer spectra of ClFe(4-TPyP) were obtained at several temperatures. The infrared spectra and *d*-spacings were obtained for all of the solids. Electronic spectra of the complexes in pyridine and, where possible, in 0.1 N HCl solution were recorded. Evidence of intermolecular interaction was found for Co(4-TPyP), Ni(4-TPyP), and ClFe(4-TPyP).

INTRODUCTION

$\alpha,\beta,\gamma,\delta$-Tetra (-4 pyridyl)-porphine (4-TPyP) is an unusual porphyrin ligand. Porphyrins normally bind a single metal ion in a square planar arrangement. One or two molecules of nitrogen base, such as pyridine, are able to coordinate to the central metal ion along the axis perpendicular to the plane. H_2(4-TPyP) has attached, at its methine or *meso* positions, pyridyl groups capable of coordinating to metal ions. The 4-TPyP ligand would be expected to coordinate to a central metal ion, and also interact with the central ion of neighbouring complexes, by forming axial bonds with the *meso* pyridyl groups. This type of intermolecular interaction would be especially important in the solid state and should affect the solid state properties of the 4-TPyP metal complexes. Even though the metal-free porphyrin[1] H_2(4-TPyP), and some of its complexes[2] have been prepared, little information is available on the nature of these complexes. Therefore, the zinc (II), copper (II), nickel (II), cobalt (II), chloromanganese (III), and chloroiron (III) complexes were prepared and some of their properties measured. Of special interest, were those properties which might relate to intermolecular interactions.

EXPERIMENTAL

Synthesis

H_2(4-TPyP) was prepared by the procedure of Neri and Wilson.[3] All metalloporphyrins were prepared in 85% formic acid with the appropriate metal salt (Table I) under reflux. Refluxing was terminated when an aliquot of the reaction mixture showed no absorption band of the free base porphyrin. The solvent was removed under reduced pressure. The remaining acid was neutralized with 5% sodium bicarbonate solution. The solid was filtered, washed with distilled water and dried under suction. In the case of manganese (III) complex, the removal of the acid was done by a solution containing 5% sodium bicarbonate and 5% sodium chloride, followed by distilled water wash. For the iron (III) complex, after removing the acid under reduced pressure, the residue was suspended in a saturated sodium chloride solution, filtered, and washed with the saturated solution until the filtrate was colorless. Recrystallization was done either from acetic acid or pyridine (Table I). The samples were dried at 100° for eight hours over phosphorous pentoxide. All reagents were A.C.S. reagent grade quality. Analyses (Table I) were carried out by Galbraith Laboratories.

TABLE I

The preparation and analyses of the metal complexes α, β, γ, δ-(4-tetrapyridyl) porphines

Compound	Solids used in preparation[a]	Recrystallization solvent		Calculated %C	Calculated %H	Calculated %N	Found %C	Found %H	Found %N
Zn(4TPyP)	zinc acetate	pyridine	$C_{40}H_{24}N_8Zn$	70.43	3.55	16.43	70.78	3.80	16.56
Cu(4TPyP)	copper acetate	acetic acid	$C_{40}H_{24}N_8Cu$	70.62	3.56	16.48	70.56	3.48	16.10
Ni(4TPyP)	nickel acetate	acetic acid	$C_{40}H_{24}N_8Ni$	71.13	3.58	16.60	71.11	3.55	15.81
Co(4TPyP)	cobalt nitrate, sodium acetate	pyridine	$C_{40}H_{24}N_8Co$	71.11	3.58	16.59	71.18	3.48	16.62
ClMn(4TPyP)	manganous acetate	pyridine	$C_{40}H_{24}N_8MnCl$	67.94	3.42	15.85			
			$C_{40}H_{24}N_8MnCl.H_2O$	66.25	3.61	15.46	66.58	3.46	15.18
ClFe(4TPyP)	iron powder,	pyridine	$C_{40}H_{24}N_8FeCl$	67.86	3.42	15.83[b]	67.72	3.32	16.00[c]

[a] 85% formic acid used as solvent

[b] Calculate: Found for ClFe(4TPyP): %Cl, 5.01

[c] Found for ClFe(4TPyP): %Cl, 4.65

Instrumental Measurements

The magnetic susceptibilities were measured with a Foner-type sample magnetometer[4] manufactured by Princeton Applied Research Corp., and operated in the field of a 12-in. electromagnet. The magnetometer was calibrated with a nickel standard and with $HgCo(CNS)_4$. A variable-temperature, liquid helium dewar flask provided controlled temperature from 2.4 to 45°K for the low temperature measurements. The X-ray powder diffraction patterns were done as published earlier.[5] Infrared spectra were measured on a Perkin-Elmer Model 180 spectrophotometer in CsI matrix. Near u.v.-visible absorption spectra were measured on a Perkin-Elmer Model 202 and a Cary 14 spectrophotometers. Mössbauer spectra were obtained using the instrumentation previously described.[6] The ^{57}Co in a copper matrix source was about 10 mCi for Mössbauer measurements.

RESULTS AND DISCUSSION

The 4TPyP complexes are shown in Table I. The chloromanganese (III) complex appears to be a monohydrate as are many other halomanganese (III) complexes.[7] Attempts were made, without success, to prepare the metal complexes in glacial acetic acid, dimethylformamide, and pyridine. Since the complexes are insoluble in most solvents except pyridine and acetic acid, these two were used for recrystallization.

The lack of solubility of the M(4TPyP) complexes in common solvents is an indication of strong interactions among molecules in the solid state. Only those solvents which are able to displace a *meso* pyridyl group from a neighboring central metal atom are able to dissolve the complexes.

The properties of the complexes are discussed below. The properties of the chloroiron (III) complex are discussed in a separate section since the Mössbauer spectra of this complex were measured and some of the properties are related to these spectra.

Magnetic Data

The magnetic susceptibilities of the 4TPyP complexes were measured from 0° to 90°K at room temperature (Table II). At low temperatures the Cu(4TPyP) has a magnetic moment close to the spin only value of 1.73 B.M., but around 50°K the value begins to decrease slightly. At room temperature a normal moment is observed. The nickel (II) complex has a moment

TABLE II
Magnetic data for α, β, γ, δ-tetra (pyridyl) porphine complexes[a]

Cu(4TPyP)(θ = 0°K)													
Temp, °K	3.50	8.60	24.2	50.5	85	293							
10^6xg, cgsu	15.8	66.2	21.9	9.0	4.2	2.4							
μ_{eff}	1.74	1.77	1.72	1.62	1.48	2.2							
Ni(4TPyP)(θ = 1.2°K)													
Temp, °K	3.94	9.2	26.2	57.5	84	293							
10^6xg, cgsu	15.7	7.2	2.7	0.6	0.3	1.2							
μ_{eff}	0.67	0.66	0.70	0.61	0.63	1.7							
Co(4TPyP)(θ = 0.0°K)													
Temp, °K	3.69	9.25	24.5	51.2	90	293							
10^6xg, cgsu	155	62.5	19.9	9.1	4.2	2.2							
μ_{eff}	1.76	1.76	1.65	1.63	1.52	2.1							
ClMn(4TPyP)(θ = 0.0°K)													
Temp, °K	4.12	9.65	23	51	87	293							
10^6 xg, cgsu	632	320	135	61.4	33.4	12.6							
μ_{eff}	3.84	4.18	4.20	4.23	4.09	4.7							
ClFe(4TPyP)(θ = 3.8°K, 0–10°K)													
Temp, °K	3.25	3.51	3.78	4.11	4.13	4.25	4.31	4.81	5.50	6.21	7.24	8.42	9.71
10^6 xg, cgsu	57.3	55.0	53.0	50.2	50.2	49.6	49.2	46.1	43.1	40.0	35.9	33.0	30.4
μ_{eff}	1.52	1.52	1.52	1.52	1.51	1.51	1.51	1.51	1.52	1.52	1.51	1.52	1.54
ClFe(4TPyP)(θ = 11.2°K, 10°–293°K)													
Temp, °K	10.97	12.45	17.42	21.09	26.10	30.79	39.05	46.44	55.8	71.0	302.		
10^6 xg, cgsu	28.9	27.2	22.8	19.8	17.1	15.1	12.4	10.5	8.8	7.1	3.87		
μ_{eff}	1.92	1.93	1.95	1.93	1.93	1.93	1.92	1.90	1.88	1.89	2.81		

[a] Diamagnetic correction: 390 x 10^{-6} cgs units for 4TPyP ligand

slightly larger than zero at low temperatures with a value of 1.7 at room temperature. Co(4TPyP) shows low spin behavior at room temperature – one unpaired electron – and has a moment less than 1.72 B.M. at lower temperatures. The chloromanganese (III) complex μ_{eff} value ranges from around 4.2 at low temperature to 4.7 at room temperature. Of these complexes only the nickel (II) complex has a positive Weiss constant, θ; all the rest are zero.

The magnetic susceptibilities of a large number of metalloporphyrins have been measured over wide temperature ranges.[8] All had magnetic moments independent of temperature. Copper (II) porphyrins had magnetic moments of about 1.9; nickel (II), 0; cobalt (II), about 2.9; and chloromanganese (III), about 4.9. Forming an octahedral environment around the metal ion by adding two axial ligands would be expected to: produce little change in the magnetic moment of the copper complex; increase the moment of the nickel complex to 2.83; decrease the moment of the cobalt complex to 1.8; and produce little change with the manganese complex.[7]

For the 4-TPyP complexes, the magnetic data of the cobalt (II) complex gives an indication of intermolecular interaction. The S = ½ spin state, with little spin-orbit interaction, would be expected upon adding either one or two pyridyl groups to the metal ion.[9] The non-zero μ_{eff} value for the nickel (II) complex may be due to a percentage of the nickel (II) ions bound in a non-square planar environment. Temperature independent paramagnetism may also produce the small moment at the low temperatures.[10] Those compounds with values of μ_{eff} less than the expected spin-only values are considered below.

X-ray Data

The *d* spacing of the complexes were obtained (Table III) with the hope that intermolecular interaction might produce a relatively simple crystal or, at least, give some indication that the structures of the M^{II}(4TPyP) complexes might be of the same type. Neither of these goals was achieved.

TABLE III

d-Spacing for the α, β, γ, δ-(4-pyridyl) porphine complexes

Zn(4TpyP)	–	11.28[a] (s)[b], 9.08 (s), 8.09 (s), 7.44 (s), 6.69 (m), 6.20 (w), 5.31 (s), 4.69 (w), 4.65 (w), 4.53 (s, bd), 4.20 (s), 3.98 (s), 3.94 (m), 3.61 (w), 3.47 (m), 3.23 (w), 3.18 (w), 2.95 (s), 2.80 (w, bd), 2.70 (w), 2.55 (m), 2.41 (w)
Cu(4TPyP)	–	10.27 (s, bd), 9.40 (s, bd), 7.13 (s, bd), 5.90 (w, bd), 5.54 (w, bd), 5.21 (w, bd), 4.39 (s, bd), 4.16 (s, bd), 3.87 (w, bd), 3.87 (w, bd), 3.48 (w), 3.33 (s), 3.07 (w), 2.70 (w)
Ni(4TPyP)	–	10.45 (s, bd), 7.30 (s), 5.83 (m. bd), 4.47 (s), 4.28 (s), 3.95 (w, bd), 3.45 (s, bd), 3.15 (w), 2.88 (w), 2.74 (m), 2.51 (w), 2.43 (w), 2.26 (w, bd), 2.08 (w), 1.99 (w), 1.84 (w), 1.79 (w)
Co(4TPyP)	–	12.26 (w), 11.32 (s, bd), 9.35 (s, bd), 8.18 (w, bd), 7.59 (s), 7.37 (w), 6.06 (w), 5.57 (m, bd), 5.11 (m), 4.58 (m), 4.37 (w), 4.18 (s), 3.98 (m), 3.79 (m), 3.52 (m, bd), 3.34 (w), 3.10 (w), 2.97 (m), 2.55 (m), 2.29 (m), 2.24 (w)
ClMn(4TPyP)	–	10.68 (s), 9.53 (s), 8.13 (s), 5.00 (s), 4.63 (m), 3.80 (m), 3.25 (m)
ClFe(4TPyP)	–	13.31 (m), 11.42 (w), 918 (s), 8.69 (vs), 6.84 (s), 6.11 (m), 5.54 (m), 5.19 (w), 4.86 (vs), 4.57 (m), 4.12 (m), 3.93 (w), 3.80 (w), 3.60 (w), 3.40 (m), 3.19 (m), 3.08 (m), 2.75 (w), 2.57 (w), 2.43 (m), 2.13 (w), 1.99 (w)

[a] In A°; b-relative intensities: vs-very strong, w-weak, bd-broad

[b] s = strong; m = medium; w = weak; s, bd = strong, broad; m, bd = medium, broad; w, bd = weak, broad; vs = very strong.

Infrared Spectral Data

The infrared absorption spectra of the M(4TPyP) complexes were all similar. Each had strong bands at 1595 (pyridyl C=C stretch); 1545 (pyrrole C=C stretch); ca. 1350 (=C–N stretch); ca. 1000 (ligand deformation); and ca. 800 cm^{-1} (C–H out-of-plane bending of the pyridine rings). The precise position of the 1000 cm^{-1} band has been correlated to the stability of the metalloporphyrins by Thomas and Martell[11] and by Boucher and Katz.[12] The increasing infrared stability order for the M^{II}(4TPyP) complexes is: Ni(1010) > Co(1000) > Zn(997); while the order for the protoporphyrin IX dimethylester complexes is Co > Ni > Cu > Zn. The stability order of the M(4TPyP) complexes is probably affected by intermolecular interaction. Axial ligands would be expected to influence the metal porphyrin bond nature.[13]

In the far infrared region (500–200 cm^{-1}) the complexes show differences in their spectra. Unfortunately the absorption bands in this region are weak, broad, and numerous, making assignments difficult, if not impossible. Others[12] have found the far infrared region of metalloporphyrins difficult to treat.

Electronic Spectral Data

Insolubility of the 4TPyP complexes in organic solvents limited the electronic spectral measurements to 85% formic acid, 0.1 N HCl, and pyridine solutions (Table IV). The zinc complex decomposed rapidly in acid solution; therefore, its spectrum was only obtained in pyridine solution. The other complexes did not show any decomposition in 0.1 N HCl at 60° for 48 hours. Most of the spectra show the normal metalloporphyrin spectrum[14] – a single Soret band at ca. 430 nm and α and β bands in the 530–580 nm region. The acid solutions may contain a mixture of protonated complexes and this may produce the splitting of the Soret band.

The nickel complex shows two Soret bands of almost equal intensity in 0.1 N HCl, but only one band in formic acid and 1 N HCl[1]. The Co(4TPyP) pyridine spectrum also had a split Soret band which may be the result of a mixture of *mono-* and *bis*-pyridinated complexes being present. Low spin cobalt (II) porphyrins have been shown to involve the coordination by the cobalt (II) atom with either one or two moles of a nitrogen base.[9]

The ClMn(4TPyP) spectra, especially those of acid solutions, more closely resemble the common metalloporphyrin spectra than the spectra of other Mn(III) porphyrins. Manganese (III) porphyrin complexes have unusual electronic spectra displaying six to eight absorption bands in the 370 to 650 nm region.[7,15] The number of bands, wavelength and intensity strongly depend on the nature of the axial ligand(s).[16] In all of the solvents, the 4TPyP complex has an intense band around 470 nm (the position of Band V of Boucher's assignment) which is observed in the spectra of the halo (aquo) manganese (III) α,β,γ,δ-tetraphenylporphine (XMnTPP. H_2O) complexes as the most intense band.[17] The 4TPyP complex spectra in pyridine has bands which match closely those of the pyridine spectrum of ClMnTPP; however, bands

TABLE IV
Electronic spectral data

Compound	Solvent	Absorption bands (λ max), nm(ε x 10^{-3})				
Zn(4TPyP)	C_5H_5N		429(325),	523(2.3),	565(9.4),	603(3.6)
Cu(4TPyP)	C_5H_5N		421(301),	547(14.5),	591(3.0),	
	HCOOH		421(287),	545(11.4),	580(5.1),	
	0.1 NHCl (aq)		423(249),	548(17.9),	586(4.8),	
Ni(4TPyP)	C_5H_5N		433(129)		562(8.5),	604(6.3)
	HCOOH	417(149),		532(12.9),	561(6.7),	
	0.1 N HCl (aq)	416(136),	439(116),	534(9.6),	564(9.8),	
Co(4TPyP)	C_5H_5N	413(131),	424(119),	534(8.6),		605(2.4)
	HCOOH		434(160),	545(11.4),		
	0.1 N HCl(aq)		431(181),	545(12.2),		
ClMn(4TPyP)	C_5H_5N	443(58),	472(89),		547(9.4),	614(6.4)
	HCOOH		465(95),	563(5.1),	563(10.3),	
	0.1 N HCl(aq)		462(77),	506(4.6),	561(7.7),	
ClFe(4TPyP)	C_5H_5N	423(151),	529(24.1)	563(13.6),	603(4.5),	648(2.3)
	HCOOH	410(104),		518(9.7),		660(3.3)
	0.1 N HCL(aq)	402(115),		520(11.6),		656(3.8)

at 384, 408, and 430 nm found for ClMnTPP.H_2O are missing from the ClMn(4TPyP).H_2O spectrum. The more intense 470 band and the lack of high energy bands may be due to the *meso* pyridyl groups[1] effect on porphyrin π-levels, reducing the amount of metal-porphyrin π-bonding. The lack of a normal metalloporphyrin $\pi \rightarrow \pi^*$ spectrum with Mn(III) porphyrins has been related to the large amount of metal-porphyrin π-interaction.[15] Attaching a proton in acid solution to one or more of the pyridyl groups of the ClMn(4TPyP), increasing the electron-withdrawing power of the group, appears to produce a normal metalloporphyrin spectra, unique for Mn(III) porphyrins.

Iron (III) Complex

The magnetic susceptibility data for ClFe(4TPyP) (Table II) indicate a sharp change in the magnetic nature of the compound at 10°K, below 10° the magnetic moment is about 1.51 with a Weiss constant of 3.8°K, while above 10° the magnetic moment is 1.93 with a Weiss constant of 11.2°K. There is also an increase in the magnetic moment between 71 and 302°K.

Mössbauer spectra for ClFe(4TPyP) were measured at 77, 195, and 295°K for several samples. The age and past history of the sample appeared to influence the spectra, especially the splitting of the individual peaks. The spectra shown in Figure 1 is of a freshly prepared sample and are representative of the spectra obtained. Two broad peaks were observed at low temperatures. An increase in temperature produced a decrease in the intensity of the two peaks with the minimum shifting to lower velocity. The low velocity peak moved to even lower velocity and the high velocity peak split into two partially overlapping peaks with a temperature increase. In other samples at room temperature, the low velocity peak was split, and splitting was also observed at low temperatures.

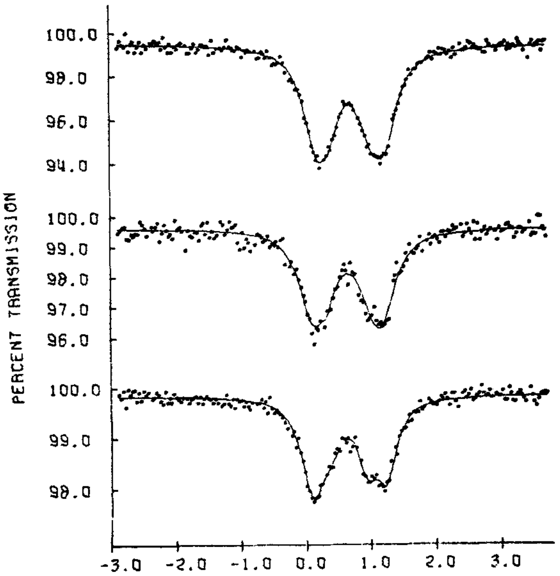

FIGURE 1 The Mössbauer spectra of Chloroiron (III) – α,β,γ,δ-tetra(4-pyridyl) porphine at (a) 77, (b) 195 and (c) 295°K. (Sodium nitroprusside reference.)

TABLE V
Mössbauer data on chloro iron (III) α, β, γ, δ-4-tetrapyridylporphine

T, °K	δ^a, mm/sec	Δ, mm/sec	Γ	% effect	*R*	χ^2
77	0.71	1.07	0.45	6.8	0.62	136
	0.71	0.64	0.45	5.1	1.81	
195	0.63	1.09	0.43	4.4	0.78	211
	0.67	0.71	0.47	2.9	1.11	
295	0.65	1.12	0.42	3.2	0.79	157
	0.64	0.55	0.37	1.6	2.0	

[a]See text for definition of symbols.

The spectra were analyzed using the MOSFIT computer program†, wherein it was possible to fit the spectra to two, three, and four absorption bands (KALFUN sub-routine). The parameters for this fit were the base line count and the intensity or percent effect, position, and width at half height for each line. A subroutine (Δ*Eq*) was also used in which only two peaks were assumed to be present and the parameters for the fit were base line count, isomer shift (δ), quadrupole splitting (Δ), width at half height (Γ), and total percent effect. Using a minimum value of χ^2, the sum of the squared deviation from the best fit divided by the variance at a single count, as criteria for a "good fit" the four line KALFUN fit was found to be best.[18]

The four bands in the ClFe(4TPyP) spectra were divided into a more intense outer set and a less intense inner set (Table V). The ratio of the percent effect of the outer to the inner set increased as the temperature increased. The two sets had approximately the same value at each temperature. The ratio of the intensity of the high velocity peak to that of the low velocity peak, *R*, was greater than one for the inner set, but less than one for the outer set.

Iron (III) porphyrins exist in two monomuclear forms.‡ One form is XFe (porphyrin), where the iron is in a square-pyramidal environment with a weak field monodentate ligand, X, bound axially to the iron. In this form the iron (III) is high spin ($S = 5/2$) and at 77°K a two line asymmetric Mössbauer spectrum is obtained.[19] The other form is [L_2Fe(porphyrin)] X, where strong field monodentate ligands, L, are bound axially to the iron. The X is not bound to the iron in this case and, for [L_2Fe(porphyrin)] X, the iron (III) is low spin ($S = ½$) and at 77°K a two line symmetric Mössbauer spectrum is observed.[20] No evidence of a mixed complex, XFe(porphyrin)L, where both X and L are bound to iron, has been found in solution[21] or the solid state.

Strong intermolecular interaction in ClFe(4TPyP) at low temperature produces low spin iron (III). ClFe(4TPyP) appears to have more than one low spin iron (III) site. The site having the largest value of Δ is favored at the higher temperature. The data might be explained by the presence of mixed chloro(pyridyl) complexes or iron (II)-pyridine bonds of varying length, creating sites where the two pyridine bonds about a single iron (III) might be equal or unequal in length. The crystal structure of low-spin Fe(III) complex, FeTPP (imidazole)$_2^+$ Cl$^-$, shows unequal bond lengths for the two imidazole N–Fe bonds.[23] The iron in this case is slightly displaced from the porphyrin place. A reviewer pointed out that these results may also arise from a systematic disorder of the crystal. This would result from the fact that there are more pyridine nitrogens than there are binding sites on iron to accommodate them. At this time it is difficult to formulate the exact nature of solid ClFe(4TPyP). A study of the sharp change in the magnetic nature at 10°K may lead to a better understanding of the structure of solid ClFe(4TPyP).

SUMMARY

Considerable interaction occurs between molecules in the solid of Co(4-TPyP), Ni(4-TPyP), and

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†We would like to thank Dr. J. G. Stevens of the University of North Carolina at Asheville for making this program available to us. Mr. C. P. Monaghan of Clemson University assisted us in adapting the program to our computer.

‡Iron (III) porphyrins also exist in a binuclear μ-oxo bridge form. Analysis indicates that this form does not need to be considered here.

ClFe(4-TPyP). The other solid complexes may also have some intermolecular interaction, but the properties considered in this study were not able to show conclusively that such interaction was present.

The complexes, Cu(4-TPyP), Co(4-TPyP), ClMn(4-TPyP) • H_2O, and ClFe(4TPyP), show evidence of metal–metal interaction through the ligand system, causing spin-pairing. At certain temperatures the values of μ_{eff} are less than the spin-only values. Since the pyridine-metal ion axial bond is a σ-type bond, metal–metal interactions were expected to be possible. π-interactions have been shown not to lead to metal–metal interaction.[22] However, there are other factors which might lead to the low values of μ_{eff}. These are abnormal magnetic behavior, such as quenching, and experimental effects, especially for small values of the magnetic susceptibilities. Unfortunately the equipment used for these measurements did not give high precision for the very low magnetic susceptibility values (±10%) and the temperature range from 90°K to below room temperature was not covered. A more thorough study of the solid state properties of these compounds is needed in order to determine if metal–metal interaction actually occurs through the ligand.

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