

- discreet bipyrimidine-bridged species to our knowledge is a [Pt^{II}(bpyrm)Pt^{II}] complex: U. T. Mueller-Westerhoff, *Adv. Chem. Ser.*, No. 150, 41 (1976).
- (43) See, for example, ref. 20.
- (44) A. Zanella and P. C. Porter, *Inorg. Chem.*, **14**, 42 (1975).
- (45) C. Cretz and H. Taube, *J. Am. Chem. Soc.*, **91**, 3988 (1959); **98**, 1086 (1973).
- (46) D. N. Hendrickson, private communication
- (47) R. Bensasson, C. Salet, and V. Balzani, *J. Am. Chem. Soc.*, **98**, 3722 (1976).
- (48) The emission spectra, being uncorrected for instrument response, are probably actually centered at slightly longer wavelengths than are apparent for the given spectra since the response is expected to decrease with increasing wavelength in this region.
- (49) J. N. Demas and G. A. Crosby, *J. Am. Chem. Soc.*, **93**, 2841 (1971).
- (50) C. D. Hager and G. A. Crosby, *J. Am. Chem. Soc.*, **97**, 7031 (1975).

Contribution from the Chemistry Department,
University of Southern California, Los Angeles, California 90007

Manganese(II) and Chromium(II) Porphyrin Complexes: Synthesis and Characterization

CHRISTOPHER A. REED,*¹ JAY K. KOUBA, CAROL J. GRIMES, and STEPHEN K. CHEUNG

Received January 17, 1978

The chromous acetylacetonone reduction method has been applied to the synthesis of the highly reactive, coordinatively unsaturated, metalloporphyrins M(TPP) (TPP = tetraphenylporphyrin) and M(OEP) (OEP = octaethylporphyrin) for M = Mn(II) and Cr(II); all are high-spin complexes. Five-coordinate high-spin derivatives Mn(TPP)L and Mn(OEP)L are formed with axial ligands L = pyridines or imidazoles. No six-coordinate low-spin derivatives are formed with Mn(II). However, six-coordinate Cr(TPP)L₂ derivatives are readily formed and are low spin having two unpaired electrons. Synthesis and characterization difficulties are discussed in detail.

Our long term interest in the study of new dioxygen adducts of transition-metal complexes has necessitated the development of convenient synthetic routes to their low-valent precursors. In many cases the existence of low-valent metalloporphyrins has been indicated by electrochemical investigations and solution spectral observations² but the isolation and definitive structural characterization of such complexes have often proved difficult. In particular, the exact nature and number of axial ligands in many transition-metal porphyrin complexes has been ill-defined especially when the oxidation states involved are ones other than those of common occurrence with aerobic stability. The more recent application of alternate synthetic methods, aided well by the user-convenient inert atmosphere glovebox, has allowed the isolation of pure crystalline materials many of which have been the subject of single-crystal x-ray investigations to ultimately establish their structural identity. For example, all possible axial ligation states of iron(II) tetraphenylporphyrin complexes have been characterized,³⁻⁵ as have those for cobalt(II).⁶⁻⁸ The structural interest in these complexes has largely centered around the interplay of magnetic states and metal-ligand bond lengths (particularly out-of-plane displacements of the metal from the porphyrin) as a function of dⁿ configuration and axial ligation states.⁹ A consistent pattern of structural features, satisfyingly rationalized by simple ligand field considerations, is now emerging and its importance to the understanding of hemo-protein stereochemistry has been widely discussed.^{10,11}

One particularly attractive synthetic route to low-valent metalloporphyrins is the reduction of halogeno higher oxidation state derivatives with the acetylacetonone complex of chromium(II) since not only is Cr(acac)₂ a powerful one-electron reductant but it usually sequesters the halogeno ligand thereby creating a vacant coordination site (eq 1). A number of M^{III}Cl(por) + Cr(acac)₂ → M^{II}(por) + CrCl(acac)₂ (1)
por = porphyrin

hitherto unknown "bare" metalloporphyrins (without axial ligands) have been generated in this way providing convenient substrates for the addition of axial ligands of choice. In one case the assumed bridging ligand atom-transfer nature of the redox process implied by eq 1 has been established by tracer

methods.¹³ The other notable feature of Cr(acac)₂ is its solubility in organic solvents such as toluene allowing one to avoid the use of donor solvents which might otherwise end up as ligands. One interesting feature emanating from the structures of the toluene solvates Cr(TPP)·2(toluene)¹⁴ and Mn(TPP)·2(toluene)¹⁵ is the weak but significant π-complex interaction of toluene with the metalloporphyrin ring.

We have published preliminary notes on the formation of dioxygen adducts derived from manganese(II)¹⁶ and chromium(II)¹⁷ porphyrins and these studies will be the subject of future publications when their definitive structural characterization is complete. Herein we report the detailed syntheses and properties of a variety of manganese(II) and chromium(II) porphyrin complexes emphasizing how characterization difficulties have been overcome. In particular, the propensity of tetraphenylporphyrin complexes to form solvates, thereby complicating elemental analyses, led us to develop ligand and solvate analyses based on gas chromatographic techniques. In most cases good quantitative analyses were obtained. Certainly qualitative GLC solvate analyses are trivial suggesting that, at least, such solvate analysis should be obligatory for researchers who include solvates for proper fit of elemental analyses when other verification techniques such as mass or NMR spectroscopy are inaccessible. Full papers on the x-ray crystal structures of three of the compounds whose syntheses are reported herein have already been published: Mn(TPP)·2(toluene),¹⁵ Mn(TPP)(1-MeIm)·0.8THF,³⁰ and Cr(TPP)·2(toluene).¹⁴

That manganese(II) can be usefully employed as a substitute for iron in studying hemoglobin allosteric effects¹⁸ has furthered our interest in establishing the fundamental coordination chemistry of manganese(II) porphyrins. Several other hemoproteins have been investigated with manganese replacing iron.³⁷ We note in passing that manganese porphyrins have been investigated¹⁹ as possible models for the manganese-dependent evolution of oxygen in photosynthesis and also, the existence of manganese porphyrins in human²⁰ and rat²¹ erythrocytes has been reported. Their function is unknown although the similarities of their structural chemistry to iron uncovered by our studies suggest that organisms may not be able to rigorously discriminate between iron and manganese.

Experimental Section

General Information. All manipulations involving reduced species were carried out in a continuously circulating Vacuum Atmospheres inert atmosphere box under He or N₂ (O₂, H₂O < 1 ppm). Most solvents (AR grade) were dried over molecular sieves and degassed inside the drybox using suction to bubble the inert atmosphere through a fritted gas dispersion tube for about 15 min. THF was distilled from sodium/benzophenone inside the drybox after predrying with CaH₂. Ligands were of commercial AR grade and were vacuum distilled (liquids) or recrystallized from hot toluene (solids) before use. Magnetic measurements at room temperature were done on a Cahn 7600 device adapted for anaerobic work with an argon flow glass inlet tube and an internal polonium Staticmaster strip (Nuclear Products Co.) to dispel static charge. Low-temperature data were taken on an SCT "squid" system by courtesy of Collman and Halbert. Magnetic moments were corrected for diamagnetism using diamagnetic susceptibilities estimated from measured values on closely related diamagnetic materials of similar composition. Infrared spectra were run on a Beckman IR20 as KBr disks hand-pressed inside the glovebox. Once pressed into a good disk such samples showed no aerobic decomposition for several hours. Visible spectra were run on a Beckman Acta MVI using rubber septum stoppered 0.2-mm path length cells. Aerobic decomposition was not normally detected within the first 10 min after removal from the drybox. ESR spectra were recorded on a Varian E11 spectrometer. Elemental analyses were done by the CalTech Analytical Facility and air-sensitive materials were loaded within an inert atmosphere box into preweighed airtight glass vials.

Quantitative GLC analyses for solvates and volatile ligands were done on a Hewlett-Packard 5712 A instrument. An accurately weighed sample (~20 mg) was dissolved (or aerobically decomposed) in an accurately weighed volume of stock solvent (~150 mg) in a small capped vial. The stock solvent was chosen for good solubility, manageable volatility, and convenient *R_f* and contained a precisely known weight fraction (~0.005) of a reference solvent. The weight fraction of the reference solvent was chosen to give similar peak heights (within a factor of ~4) to the solvent to be analyzed. Sample vs. reference weight ratios were calculated from peak height ratios using calibrated samples. Peak height ratios were found to be essentially linear with weight ratios and the experimental error for the complete determination was about 10%.

A typical experiment was the determination of toluene in Mn(TPP) \cdot *x*(toluene). The stock solution was benzene (28.671 g) with a *m*-xylene reference (0.245 g) and 0.2056 g was used to aerobically decompose 0.0277 g of Mn(TPP) \cdot *x*(toluene) in a small capped vial. After ensuring that all the complex had decomposed (~20 min) the solution was filtered through a tiny cotton wool plug in a shortened disposable pipet in order to minimize GLC syringe and column contamination. An average toluene/xylene peak height ratio of 4.42 (3) was obtained as quickly as possible from four separate injections. Calibration was done using accurately weighed aliquots of the stock solution and toluene. For example, stock solution (0.497 g) and toluene (0.0221 g) (giving a toluene/xylene weight ratio of 5.24) gave a peak height ratio of 7.43. Hence the weight of toluene in the sample was given by

$$\frac{5.24}{1} \times \frac{4.42}{7.43} \times \frac{0.2056}{1} \times \frac{0.245}{(28.671 + 0.245)} = 5.43 \times 10^{-3} \text{ g}$$

Hence *x* was calculated from the following weight ratio expression (MnTPP = 668, toluene = 92, molecular weight)

$$\frac{5.43 \times 10^{-3}}{0.0277} = \frac{92x}{668 + 92x}$$

$$x = 1.85$$

Hence *x* was taken to be 2.0 as confirmed by x-ray crystallography and elemental analysis.

MnCl(TPP), MnCl(OEP), CrCl(TPP), and CrCl(OEP) was prepared by the standard DMF method³⁶ and purified by column chromatography on alumina or silica gel. Single-spot TLC purity was achieved except with CrCl(TPP) and CrCl(OEP) which in our hands always gave two very similar compounds which we presume to be related by hydrolysis to hydroxy or aquo monomers or dimers of ill-defined formulas. The reduction reactions were not effected by these problems. Proton Sponge is *N,N,N,N*-tetramethyl-1,8-

naphthalenediamine available from Aldrich.

Mn(TPP) \cdot 2(toluene). MnCl(TPP) (1.0 g) in toluene (~20 mL) was heated almost to boiling. Cr(acac)₂ (~350 mg) was added until the color of the solution changed from green to claret. The hot solution was filtered quickly through a medium frit and heptane (~20 mL) was added. The crude product was filtered off after 1 h and the visible spectrum checked for the absence of Mn(III) at 475 nm. Recrystallization from hot toluene-heptane gave sparkling purple crystals (0.65 g, 55%).

Mn(OEP) was prepared similarly and isolated as fine purple needles (80%).

Mn(TPP) was also prepared by heating tetraphenylporphyrin (300 mg) with MnBr₂ (300 mg) and Proton Sponge (50 mg) in toluene (50 mL) and THF (30 mL) until the visible spectrum indicated complete reaction (lack of 750-nm band of protonated free porphyrin upon acidification). Degassed alumina (heated to 300 °C under vacuum) (10 g) was added and the solvents were carefully removed under reduced pressure. The product was chromatographed on a short alumina column (3 × 10 cm) and eluted with toluene-THF 4:1. Recrystallization from hot toluene-heptane gave purple Mn(TPP) \cdot 2(toluene) (200 mg, 55%).

Mn(TPP)L. These were prepared in good yield by addition of a slight excess of L (py, 1-MeIm) to a hot slurry of Mn(TPP) (150 mg) in toluene or THF (10 mL) followed by filtration and addition of heptane. For L = 2-MeIm, ethanol was used as well.

Mn(OEP)(1-MeIm) was prepared similarly.

Cr(TPP) \cdot 2(toluene). CrCl(TPP) (400 mg) in toluene (50 mL) and ethanol (1 mL) was heated with just enough Cr(acac)₂ (~800 mg) to turn the solution permanently brown. After filtration, ethanol (60 mL) was added and the solution set aside to crystallize. Recrystallization was done quickly from boiling toluene-ethanol-heptane (240 mg, 50%).

Cr(OEP). CrCl(OEP) (300 mg) in hot toluene (~150 mL) was heated with Cr(acac)₂ (300 mg) and the solution was filtered rapidly. A good yield of fine dark red needles quickly formed and further product was obtained by the addition of heptane.

Cr(TPP)L₂. These derivatives were prepared by addition of a slight excess of L (pyridine, 3-picoline, 4-picoline, 1-methylimidazole) to a toluene (5–10 mL) solution of Cr(TPP) \cdot 2(toluene) (100 mg). Good yields (~80%) of green-purple crystals were obtained upon addition of heptane.

Analyses and characteristic physical properties are tabulated in Table I.

Cr(TPP)(py) \cdot 2toluene. In a Schlenk tube zinc pellets were cleaned with dilute aqueous HCl followed by treatment with dilute aqueous HgCl₂, washed with degassed water, vacuum dried, and stored under nitrogen. CrCl(TPP) (2.0 g) and activated zinc (2.0 g) were stirred in a mixture of THF (200 mL), pyridine (20 mL), and water (30 mL) overnight. Completion of reduction was checked by the disappearance of 606- and 567-nm peaks due to CrCl(TPP). The crude blue-black crystals were collected by filtration and washed with a 1:1 mixture of THF and water. Recrystallization was achieved by dissolution in boiling toluene, filtration through a medium frit, and the addition of heptane (1.4 g, 60%).

Results and Discussion

The Chromous Reduction Method. The general reaction of eq 1 is most successful if certain conditions are met. First, the bright orange pyrophoric Cr(acac)₂ should be carefully synthesized and stored under strictly oxygen-free conditions. Even under the most ideal conditions it fails to react stoichiometrically and 2 or more equiv are usually necessary to effect complete reduction. This may be the result of preparative impurities or incomplete dehydration following its synthesis. An explanation might also lie in the presumed dimeric or trimeric nature of Cr(acac)₂ where possibly only one reducing equivalent per molecule is available. Second, the choice of solvents is important for yield optimization and purity. For many metalloporphyrins reduction in benzene followed by crystallization via ethanol addition exploits their low alcohol solubilities and has the added advantage that Cr(acac)₂ and its oxidation by-products are quite soluble in benzene/ethanol mixtures. For the more soluble compounds THF/heptane can be successful although coprecipitation of chromium impurities

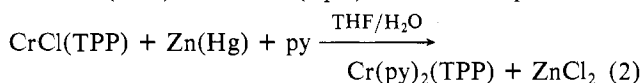
Table I. Characterization Data on New Complexes

compound	$\mu_{\text{cor}}, ^{25^\circ\text{C}}$ μ_{B}	anal., % ^f			solvate no. ^f	$\lambda_{\text{max}}, \text{nm}$ (in THF)
		C	H	N		
Mn(TPP)·2(toluene)	6.0	81.0 (81.7)	5.5 (5.2)	6.6 (6.6)	1.85 (2.0)	603, 566, 524, 434
Mn(OEP)	5.9	73.8 (73.6)	7.6 (7.6)	10.4 (9.5)		576, 541, 401
Mn(TPP)(1-MeIm)·0.8THF	6.3	76.0 (76.3)	5.5 (5.0)	10.5 (10.6)	0.71 (0.8)	614, 575, 530, 440
Mn(TPP)(py)	6.0	79.0 (78.8)	4.6 (4.5)	9.4 (9.4)		613, 575, 532, 440
Mn(TPP)(2-MeIm)·EtOH	6.0	75.5 (75.5)	5.4 (5.0)	10.4 (10.6)	0.85 (1.0)	610, 574, 530, 439
Mn(OEP)(1-MeIm)	5.9	70.9 (71.8)	7.7 (7.5)	12.7 (12.6)		576, 543, 404
Cr(TPP)·2(toluene)	4.9	<i>a</i>			1.6 (2.0)	655, 601, 516, 460 421, 402
Cr(OEP)	4.8	73.9 (74.0)	7.5 (7.6)	9.1 (9.6)		724, 642, 536, 531, 420, 402, 386
Cr(TPP)(py) ₂ ·toluene	2.93	79.9 (80.1)	5.3 (5.1)	8.3 (9.2)	0.99 ^b (1.0)	675, 610, 530, 455, 420
Cr(TPP)(3-pic) ₂ ·toluene	2.9	81.3 (81.3)	5.6 (5.6)	8.8 (8.1)	0.91 ^c (1.0)	725, 672, 541, 422, 400 ^e
Cr(TPP)(4-pic) ₂ ·toluene	2.9	79.9 (81.3)	5.4 (5.6)	8.8 (8.1)	1.3 ^d (1.0)	725, 672, 541, 422, 400 ^e
Cr(TPP)(1-MeIm) ₂ ·toluene	2.9	77.0 (76.9)	5.9 (5.3)	11.7 (12.2)	0.9 (1.0)	775, 682, 620, 532, 453, 423, 404

^a Air sensitivity prevented us from obtaining consistent satisfactory analyses. ^b Pyridine analysis: 1.96 (2.0). ^c 3-Picoline analysis: 1.80 (2.0). ^d 4-Picoline analysis: 1.75 (2.0). ^e In toluene solution. ^f Calculated analyses are given in parentheses.

can occur. If coordinating solvents (THF, alcohols, etc.) must be avoided then carrying out the reaction quickly in hot supersaturated toluene in the absence of excess Cr(acac)₂ is often successful.

Another reduction method of lower versatility was developed for CrCl(TPP) reduction (eq 2). The zinc pellets were



prepared in the manner of a Jones reductor and are conveniently removed from the reaction mixture by decanting. Judicious choice of solvent combinations (e.g., THF/H₂O) can give a situation where the desired product crystallizes out leaving the by-products in the solution.

Other successful literature methods of reduction (apart from the common aqueous dithionite method) include the use of NaBH₄,^{23,24} Pd/H₂,²⁵ and piperidine.²⁶ Also, direct incorporation of low-valent metals without subsequent oxidation can be achieved if suitably anaerobic conditions are employed. MBr₂ salts for M = Fe²⁷ and Mn have sufficient solubility for use in THF/toluene mixtures and surprisingly rapid incorporation into the free base porphyrin occurs. Presumably the poor solvation of MBr₂ by organic solvents entropically enhances the rate. A noncoordinating base such as "Proton Sponge" is usually added to take up the 2 equiv of liberated HBr.

Manganese(II) Porphyrins. Four-coordinate Mn(TPP) and Mn(OEP) were both prepared in good yield from their readily available manganese(III) complexes by the chromous reduction method or by direct Mn(II) incorporation. Unlike their closest analogues Mn(Pc) and Fe(TPP) which are intermediate spin, their solid-state magnetic moments (Table I) are consistent only with a high-spin configuration. This is confirmed by their ESR spectra in frozen dry toluene solution where characteristic ^{28,29} g_{\perp} (6.0) and g_{\parallel} (2.0) signals are observed (Figure 1). The small but significant difference in the hyperfine splitting of the $g = 2$ signal between Mn(TPP) in toluene and toluene containing a trace of ethanol suggests that the reported spectrum²⁴ of Mn(TPP) is actually that of Mn(EtOH)(TPP). The seven-line spectrum in the $g = 6$ region is unexpected but

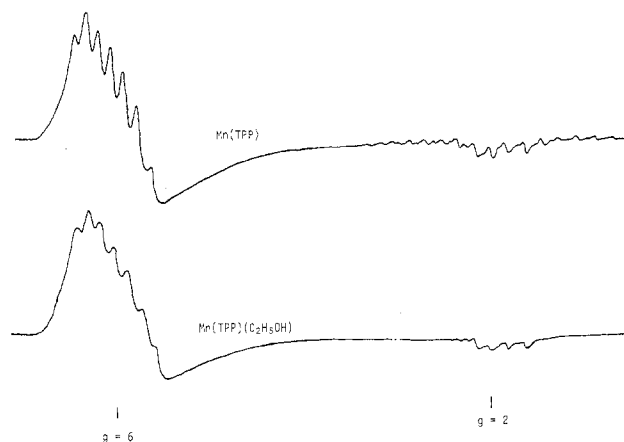


Figure 1. ESR spectra of Mn(TPP) and Mn(TPP)(C₂H₅OH) in toluene at 10 K. There is additional hyperfine splitting of the $g = 2$ signal in Mn(TPP) that is not observed in Mn(TPP)(C₂H₅OH).

not without precedent.^{37,38} The structural manifestation of the high-spin state is notable. The x-ray structure¹⁵ of Mn(TPP)·2(toluene) reveals a manganese(II) atom whose size is too large for accommodation in the plane of the porphyrin despite the severely dilated macrocycle. This size is more specifically understood in terms of single population of the $d_{x^2-y^2}$ orbital which is highly antibonding with respect to Mn-N σ bonding. Another interesting feature, which presumably stabilizes the lattice of Mn(TPP)·2(toluene), is a weak but significant π -complex interaction of the toluene molecules and the metalloporphyrin ring including the metal atom. This is also observed in Cr(TPP)·2(toluene) but not in Fe(TPP) which crystallizes solvate-free. The coordinatively unsaturated metal apparently confers its electron deficiency to the metalloporphyrin as a whole so that it can be viewed as the acceptor in a weak π complex with toluene.

The synthetic utility of the four-coordinate derivatives is exemplified by the ready introduction of axial ligands of choice. Oxygen donor solvents such as THF or EtOH coordinate both in solution and in isolable crystalline solids but are easily

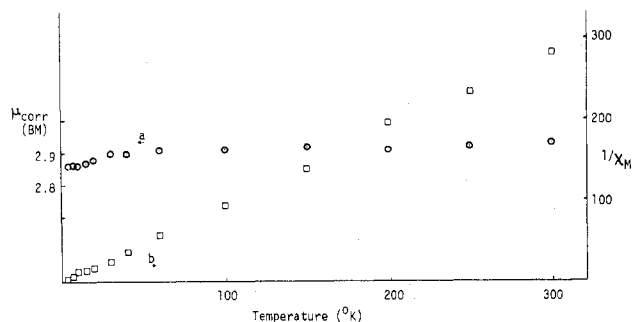


Figure 2. Temperature profile of (a) the magnetic moment (O) and (b) the reciprocal of the molar susceptibility (□) for Cr(TPP)(py)₂·toluene.

displaced by nitrogen donors such as pyridines or imidazoles. Only five-coordinate adducts Mn(TPP)L are isolated (Table I) despite attempts to force six-coordination with large excesses of a variety of ligands (L). The adducts have distinctive green colors in solution, display typical high-spin Mn(II) ESR spectra and have solid-state magnetic moments in the range ($\mu_{\text{cor}}^{25^\circ\text{C}} = 5.9\text{--}6.3 \mu_{\text{B}}$) expected of high-spin d^5 complexes. The crystal structure³⁰ of one derivative, Mn(TPP)(1-MeIm)·0.8THF reveals a manganese atom displaced 0.57 Å out of the mean porphyrin plane toward the axial ligand. We interpret the preference for five-coordination as the inability of a sixth ligand to closely approach the manganese atom; the limited expansion of the porphyrin core will not allow the metal atom to move to an in-plane position. By way of contrast, a low-spin manganese(II) atom is expected to be in-plane (or nearly so as in Mn(NO)(TPP)L³¹) and six-coordinate because $d_{x^2-y^2}$ and d_{z^2} , respectively, would be vacant. We believe previous reports of six-coordination should be reinterpreted.²³ Thus the preference for five-coordination can be traced to the inability of the ligands to cause adoption of a low-spin state. The contrasting case apparently occurs with the stronger field phthalocyanine (Pc) ligand where low-spin MnPc(py)₂ has been reported.³² The strong field ligand CO does not coordinate to Mn(TPP) or Mn(TPP)L presumably because of its intolerance to paramagnetism in metalloporphyrins even if it was capable of producing a low-spin complex. It should be pointed out that the d^5 configuration is the classic case of high-spin preference since electron exchange energy is maximized with five unpaired electrons and confers considerable stability to the half-filled d shell.

The visible spectra of the manganese(II) porphyrins are unexceptional except to mention that the complete absence of a band near 475 nm (due to manganese(III) porphyrins) is the best criterion of purity. Partial oxidation in samples has been noted in this manner previously.²⁹

Chromium(II) Porphyrins. Four-coordinate Cr(TPP) and Cr(OEP) were prepared by the Cr(acac)₂ reduction method and isolated as extremely air-sensitive, purple crystalline solids from their red-brown solutions. Magnetic moments measured under strictly anaerobic conditions indicate a high-spin d^4 state ($\mu_{\text{cor}}^{25^\circ\text{C}} = 4.9 \mu_{\text{B}}$). Since the Cr(III/II) reduction potential is very negative and is expected to be close to that of the porphyrin to porphyrin radical anion, we sought a variety of physical parameters which would establish the authenticity of the Cr(II) formulation as opposed to a chromium(III) porphyrin radical anion. First, cyclic voltammetry half-wave potentials are readily interpreted by chemically reasonable assignments based on a set of generalities developed by Fuhrhop et al.³³ as outlined in our earlier note.¹⁷ Second, the visible spectra have normal metalloporphyrin band energies and intensities³⁴; they do not show the broadening, red-shifted Soret, or the 800-nm bands which are believed to be characteristic of porphyrin radical anions.²

Nitrogen donor ligands L such as imidazoles or pyridines, but not CO, add to brown Cr(TPP) giving rise to greenish solutions from which purple six-coordinate crystalline adducts Cr(TPP)L₂ can be isolated (Table I). This corrects our previous formulation¹⁷ of Cr(TPP)(py)₂ as a five-coordinate complex. The extreme air sensitivity of these derivatives frequently led to unreliable absolute elemental analyses and moreover, C, H, and N ratios were misleading since solvate incorporation was common. This led us to routinely do solvate and volatile ligand analyses by quantitative GLC as outlined in the Experimental Section. Six-coordination confers a low-spin state on Cr(II) with a (t_{2g})⁴ configuration. This has been rigorously established by variable-temperature magnetic susceptibility measurements with Cr(TPP)(py)₂·toluene which shows Curie law behavior (Figure 2). The magnetic moment ($\mu_{\text{cor}}^{\text{eff}} = 2.93 \mu_{\text{B}}$ at 300 K) is essentially invariant with temperature (Figure 2). Our magnetic results compare favorably with those of Tsutsui et al.³⁴ who did the first definitive work with chromium(II) porphyrins. That Cr(II)(MPIXDME) is high spin in solution but low spin in the solid state³⁴ leads to the suggestion that intermolecular axial ligation occurs, possibly via the ester functionality of MPIXDME. A compound formulated as Cr(TPP)·4H₂O has been reported³⁵ but since its visible spectrum differs from ours and since a tetrahydrate is extremely unlikely for a hydrophobic tetraphenylporphyrin complex we suggest that this formulation be treated with some caution.

Acknowledgment. This research was supported by the National Science Foundation (CHE-75-03648), the Research Corp., and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Note Added in Proof. The x-ray crystal structure of Co(acac)₂ has been reported. It reveals weakly associated planar monomers: F. A. Cotton, C. E. Rice, and G. W. Rice, *Inorg. Chim. Acta*, **24**, 213 (1977).

Registry No. Mn(TPP)·2(toluene), 56189-58-3; Mn(OEP), 51321-25-6; Mn(TPP)(py), 57034-31-8; Mn(TPP)(1-MeIm), 56082-02-1; Mn(OEP)(1-MeIm), 67113-82-0; Cr(TPP)·2(toluene), 65150-27-8; Cr(OEP), 67113-83-1; Cr(TPP)(py), 60298-97-7; Cr(TPP)(py)₂, 67113-84-2; Cr(TPP)(3-pic)₂, 67113-85-3; Cr(TPP)(4-pic)₂, 67113-86-4; Cr(TPP)(1-MeIm)₂, 67113-87-5; Mn(TPP)(2-MeIm), 67180-30-7; Mn(TPP)(C₂H₅OH), 67113-88-6.

References and Notes

- (1) Alfred P. Sloan Fellow 1976-1978; Camille and Henry Dreyfus Teacher-Scholar Grant Awardee 1976-1981.
- (2) J.-H. Fuhrhop, *Struct. Bonding (Berlin)*, **18**, 1 (1974).
- (3) J. P. Collman, J. L. Hoard, N. Kim, G. Lang, and C. A. Reed, *J. Am. Chem. Soc.*, **97**, 2676 (1975).
- (4) L. J. Radonovich, A. Bloom, and J. L. Hoard, *J. Am. Chem. Soc.*, **94**, 2073 (1972).
- (5) (a) J. P. Collman, N. Kim, J. L. Hoard, G. Lang, L. J. Radonovich, and C. A. Reed, Abstracts, 167th Meeting of the American Chemical Society, Los Angeles, Calif., April 1974, No. INOR 29; (b) D. A. Buckingham, J. P. Collman, J. L. Hoard, G. Lang, L. J. Radonovich, C. A. Reed, and W. T. Robinson, to be submitted for publication.
- (6) P. Madura and W. R. Scheidt, *Inorg. Chem.*, **15**, 3182 (1976).
- (7) P. N. Dwyer, P. Madura, and W. R. Scheidt, *J. Am. Chem. Soc.*, **96**, 4815 (1974).
- (8) W. R. Scheidt, *J. Am. Chem. Soc.*, **96**, 84 (1974).
- (9) W. R. Scheidt, *Acc. Chem. Res.*, **10**, 339 (1977).
- (10) J. L. Hoard in "Porphyrins and Metalloporphyrins", K. M. Smith, Ed., Elsevier, Amsterdam, 1975, p 317.
- (11) C. A. Reed in "Metal Ions in Biological Systems", Vol. 7, H. Sigel, Ed., Marcel Dekker, New York, N.Y., 1978, Chapter 7.
- (12) Abbreviations used in this paper: acac = anion of acetylacetonate; TPP = dianion of meso-tetraphenylporphyrin; THF = tetrahydrofuran; py = pyridine; OEP = dianion of octaethylporphyrin; EtOH = ethanol; MPIXDME = dianion of mesoporphyrin IX dimethyl ester.
- (13) I. A. Cohen, C. Jung, and T. Governio, *J. Am. Chem. Soc.*, **94**, 3003 (1972).
- (14) C. A. Reed and W. R. Scheidt, *Inorg. Chem.*, **17**, 710 (1978).
- (15) J. F. Kirner, C. A. Reed, and W. R. Scheidt, *J. Am. Chem. Soc.*, **99**, 1093 (1977).
- (16) B. Gonzalez, J. Kouba, S. Yee, C. A. Reed, J. F. Kirner, and W. R. Scheidt, *J. Am. Chem. Soc.*, **97**, 3247 (1975).
- (17) S. K. Cheung, C. J. Grimes, J. Wong, and C. A. Reed, *J. Am. Chem. Soc.*, **98**, 5028 (1976).

- (18) B. M. Hoffman, Q. H. Gibson, C. Bull, R. C. Crepeau, S. J. Edelstein, R. G. Fisher, and M. J. McDonald, *Ann. N.Y. Acad. Sci.*, **244**, 174 (1975).
 (19) P. A. Loach and M. Calvin, *Biochemistry*, **2**, 361 (1963).
 (20) D. C. Borg and G. C. Cotzias, *Nature (London)*, **182**, 1677 (1958).
 (21) R. G. V. Hancock and K. Fritze, *Bioinorg. Chem.*, **3**, 77 (1973).
 (22) L. R. Ocone and B. P. Block, *Inorg. Synth.*, **8**, 125 (1966).
 (23) H. Kobayashi and Y. Yanagawa, *Bull. Chim. Soc. Jpn.*, **45**, 450 (1972).
 (24) B. B. Wayland, L. W. Olson, and Z. U. Siddiqui, *J. Am. Chem. Soc.*, **98**, 94 (1976).
 (25) W. S. Brinigar and C. K. Chang, *J. Am. Chem. Soc.*, **96**, 5595 (1974).
 (26) L. M. Epstein, D. K. Straub, and C. Maricondi, *Inorg. Chem.*, **6**, 1720 (1967).
 (27) J. P. Collman and T. R. Halbert, personal communication.
 (28) L. Boucher, *Coord. Chem. Rev.*, **7**, 289 (1972).
 (29) B. M. Hoffman, C. J. Weschler, and F. Basolo, *J. Am. Chem. Soc.*, **98**, 5473 (1976).
 (30) J. F. Kirner, C. A. Reed, and W. R. Scheidt, *J. Am. Chem. Soc.*, **99**, 2557 (1977).
 (31) P. L. Piciulo, G. Rupprecht, and W. R. Scheidt, *J. Am. Chem. Soc.*, **96**, 5293 (1976).
 (32) L. K. Philips, Ph.D. Thesis, University of California, Berkeley, 1968, reported in ref 28.
 (33) J. H. Fuhrhop, K. M. Kadish, and D. G. Davis, *J. Am. Chem. Soc.*, **95**, 5140 (1973).
 (34) M. Tsutsui, R. A. Velapoldi, K. Suzuki, F. Vohwinkel, M. Ichikawa, and T. Koyano, *J. Am. Chem. Soc.*, **91**, 6262 (1969).
 (35) N. J. Gogan and Z. U. Siddiqui, *Can. J. Chem.*, **50**, 720 (1972).
 (36) A. D. Adler, F. R. Longo, F. Kampas, and J. Kim, *J. Inorg. Nucl. Chem.*, **32**, 2443 (1970).
 (37) Y. Yonetani, H. R. Drott, J. S. Leigh, G. H. Reed, M. R. Waterman, and T. Asakura, *J. Biol. Chem.*, **245**, 2998 (1970).
 (38) R. D. Dowsing and D. J. E. Ingram, *J. Magn. Reson.*, **1**, 517 (1969).

Notes

Contribution from the Istituto di Chimica Generale ed Inorganica, Università, Laboratorio C.N.R., Florence, Italy

Electron Spin Resonance Investigation of the Mixed-Valence Dinuclear Tetra(μ -1,8-naphthyridine-*N,N'*)-bis(bromonickel) Tetrphenylborate Complex

A. Bencini, D. Gatteschi, and L. Sacconi*

Received December 10, 1977

The interest in the magnetic interactions among metal atoms in polymeric transition-metal complexes is increasing,¹⁻¹¹ from both an experimental and a theoretical point of view. By far, the most common examples of reported complexes are those where an even number of electrons are present. Recently, we reported the synthesis and the characterization of some mixed-valence nickel complexes with the ligand 1,8-naphthyridine (napy),¹² where a copper acetate-type dimer is present containing three unpaired electrons.

We report now the single-crystal ESR spectra of one of these complexes and interpret the magnetic interactions between the metal ions using an angular overlap parameterization of the orbital energies we have suggested recently.¹³

Experimental Section

The $[\text{Ni}_2\text{Br}_2(\text{napy})_4]\text{B}(\text{C}_6\text{H}_5)_4$ complex was prepared as previously described.¹² Single crystals were obtained by slow evaporation of acetone solutions. The crystals were found by Weissenberg techniques to conform to the X-ray structure report.¹² They can be described as prisms, with the (100) face most developed.

X-band (9-GHz) ESR spectra were run with the apparatus described previously,¹⁴ and Q-band (35-GHz) ESR spectra were run with a Varian V-4651 microwave bridge.

Results

The room-temperature polycrystalline powder spectra of $[\text{Ni}_2\text{Br}_2(\text{napy})_4]\text{B}(\text{C}_6\text{H}_5)_4$ recorded at Q-band and X-band frequencies are shown in Figure 1.³³ They are quite similar to each other as regards both the position and the shape of the lines. They can be interpreted by using an effective Hamiltonian with $S = 1/2$ and axial symmetry. The corresponding g' values are shown in Table I. We recorded also X-band frozen-solution spectra, by pouring directly the chloroform solution into liquid nitrogen, in order to prevent crystallization.¹⁵ The close similarity of the latter spectra to the powder spectra suggests that the crystal g' values correspond quite closely to the molecular g' values.

Table I. g' Values for $[\text{Ni}_2\text{Br}_2(\text{napy})_4]\text{B}(\text{C}_6\text{H}_5)_4$

	X band		Q band powder
	powder	glass	
$g'_{ }$	2.19 ± 0.03	2.20 ± 0.03	2.22 ± 0.03
g'_{\perp}	4.30 ± 0.03	4.30 ± 0.03	4.27 ± 0.03

The single-crystal spectra showed only one signal for most orientations in the magnetic field, and the line shape was found to be Lorentzian to a good approximation. In the case of spectra recorded with the static field in the (010) plane, in some orientations at X-band frequency the line appeared markedly asymmetric and unusually broad. Q-band spectra showed that the origin of this behavior is the presence of two signals of differing intensities. In the original structure report it was observed that the X-ray reflections were split into two separate peaks largely different in intensity,¹² as a consequence of the poor quality of the crystals, and we interpret the appearance of two signals in the ESR experiment as due to the same cause. Repeated attempts to find better crystals were unsuccessful. The best results were obtained with small crystals, $0.05 \times 0.3 \times 0.7$ mm being the typical dimensions of the ones we used.

The spectra recorded with the magnetic field parallel to the monoclinic b crystal axis yielded the g_{yy}' value of 4.25 ± 0.02 at X-band frequency and 4.12 ± 0.02 at Q-band frequency. The main origin of the large uncertainty on the value of g' is associated with orientation errors of the crystal in the magnetic field. By rotating around the b axis a dramatic dependence of the line width on the orientation in the magnetic field was observed. At Q-band frequency it was observed to vary between 16 and 120 mT, the narrower line being observed in correspondence to the higher g' value, $g_{xx}' = 4.28 \pm 0.02$, while the wider line was observed in correspondence to the lowest g' value, $g_{zz}' = 2.26 \pm 0.03$. In the X-band spectra the signal could be followed only in a range of about $\pm 60^\circ$ from the x direction. Approaching closer to the z direction caused washing out of the signal. We interpret the difference observed at the two different frequencies as due to the higher sensitivity of the Q-band experiment, which allowed us to detect the signals of small crystals. The g_{zz}' value in the X-band experiment was obtained by extrapolating the angular dependence of the g'^2 values at the z direction. It is $g_{zz}' = 2.24 \pm 0.03$ that is in accord with both the powder and the Q-band spectra.

At X-band frequency the spectra were run also down to liquid helium temperature, and although a sharpening of the lines was observed, it was not possible to record any signal in the z direction. Spectra were run also up to 400 K, and no