accompanied by simultaneous increase in $A_{\parallel}^{N}$ and $A_{\perp}^{N}$ values. This signifies that the σ bonding (M–N) is slightly more covalent. The origin of this can be traced to either an increase in the π-electron density on nitrogens or an increase in the electronic charge on copper in the complex relative to CuTPP.[21b]

The emission studies of the macrocycles indicates that the TNB strongly quenches the fluorescence of the donor due to the possible formation of the exciplex. The Stern–Volmer plot corrected for ground-state complexation gave reasonably good straight lines at lower acceptor concentrations (Figure 6). The emission data presented in Table III indicate that the values of K_{sv} decreases as Zn(pheo) > Zn(phth) > ZnTPP. On the assumption that the lifetimes of M(TPP)'s are of the order of nanoseconds, the bimolecular quenching constants were calculated and they are of the order of the diffusion-controlled rate. Lopp et al.[23] have studied the quenching of excited-state metalloporphyrins with various electron-deficient nitro aromatics and concluded that the possible mechanism for quenching of the excited state of the donor include either the formation of the excited-state complex (exciplex) or electron transfer from donor to acceptor to form the radical ion. Since the values of K_q^s are of the order of the diffusion-controlled rate, quenching occurs through formation of a collision complex. The fact that K_{sv} changes only slightly on increasing the solvent polarity suggests formation of a exciplex with some polar character rather than a complete electron transfer as the quenching mechanism. Further, the acceptor concentration required to quench the porphyrin fluorescence is very much less than the concentration of the same acceptor required to decrease the optical density of the donor in the ground state, suggesting that the TNB forms an exciplex with donors strongly in the excited state rather than in the ground state.[24] The absence of any separate emission for the complex implies extremely fast radiationless deactivation of the exciplex possibly by intersystem crossing as observed for the TNB complex of anthracene.[25]

The ^{1}H NMR spectra of the diamagnetic Ni^{II}TPP and Zn^{II}TPP and paramagnetic Co^{II}TPP complexes have shown that the aryl proton resonances of TNB occur in a shielded region (δ 0.8–1.08) relative to the acceptor alone. It is seen that both pyrole and aryl protons of the M(TPP)'s are shifted upfield in the spin-free Co(II) case while an upfield shift (for pyrole protons) and a downfield shift (for aryl protons) are observed for Ni(II) and Zn(II) complexes. These observations are essentially in agreement with the earlier study[4,5] wherein a time-averaged structure for the complex was proposed in which TNB is positioned near the pyrrole moiety with one of its $>NO_2$ groups projected away from the metal ion. We tend to believe that a similar structure previals in the solution of these complexes, however, further work is necessary to explain the metal-dependent K values.

Acknowledgment. T.K.C. is thankful to the University Grants Commission, New Delhi, for the award of a fellowship.

Registry No. TNB, 99-35-4; Zn(pheo), 15739-11-4; Zn(phth), 14320-04-8; Zn(TPP), 14074-80-7; Co(TPP), 14172-90-8; Cu(TPP), 14172-91-9; Ni(TPP), 14172-92-0; Cd(TPP), 14977-07-2; VO(TPP), 14705-63-6; Pd(TPP), 14187-13-4.

---

(22) The α^2 values is calculated with use of the procedure described by: Kivelson, D.; Neiman, R. *J. Chem. Phys.* **1961**, *35*, 149. The α^2 value (CuTPP–Cu(TPP)TNB) is –0.0097 and compares favorably with that of Cu(OEPO)TNB (see ref 21b).

(23) (a) Lopp, I. G.; Hendren, P. W.; Wides, P. D.; Whitten, D. G. *J. Am. Chem. Soc.* **1970**, *92*, 6440. (b) Whitten, D. G.; Lopp, I. G.; Wides, P. D. *Ibid.* **1968**, *90*, 7196.

(24) The ground-state complexation in all the cases contributes only to the extent of 20–25% while the percent quenched is in the order of 60–65%.

(25) Kleineraman, M.; Azarraga, L.; McGlynn, S. P. "Luminescence of Organic and Inorganic Systems"; Wiley: New York, 1962.

Contribution from the Chemical Physics Group, Tata Institute of Fundamental Research,
Colaba, Bombay 400005, India

Effect of Axial Interaction in High-Spin Iron(III) Porphyrins. Paramagnetic Anisotropy and Zero-Field Splitting in (Tetraphenylporphyrin)iron(III) Thiocyanate and Iodide

D. V. BEHERE, ROSHUN BIRDY, and SAMARESH MITRA*

Received October 20, 1980

Magnetic anisotropy measurements in the 80–300 K temperature range on the single crystals of high-spin (tetraphenylporphyrin)iron(III) thiocyanate and iodide are reported, and the data have been used to deduce the zero-field splitting parameter (D) of the ferric ion. The variation in D for the prophyrin series follows the sequence $D_{NCS} < D_{Cl} < D_{Br} < D_{I}$.

Introduction

(Tetraphenylporphyrin)iron(III) complexes, (TPP)FeX (X = NCS, Cl, Br, I) form a series of high-spin ($S = {}^5/_2$) synthetic iron(III) porphyrins which are very similar to natural heme systems.[1,2] The ferric ion is coordinated to the four pyrrole nitrogen atoms of the essentially planar porphyrin macroring, the halide ion occupying an axial position to give approximately square-pyramidal geometry around the iron(III) atom (Figure 1). The iron is however not coplanar with the porphinato core or with the four nitrogen atoms but is displaced (by ca. 0.4–0.6 Å) in the direction of the axial ligand. The ferric ion is thus under the influence of a crystal field generated by the basal porphyrin ring and the axial halide.

Table I. X-ray Structural Data for the (TPP)FeX Series

compd	Fe–N, Å	Fe–X, Å	Ct–M (Δ), Å
(TPP)Fe(NCS)	2.065	1.957	0.55
(TPP)FeCl	2.060	2.192	0.39
(TPP)FeBr	2.069	2.348	0.56
(TPP)FeI	2.066	2.554	0.53

We are currently investigating by single-crystal magnetic study the effect of variation of the apical ligand on the electronic ground-state properties of the ferric ion in the (TPP)FeX series.[3-6] There are several advantages in choosing the

---

(1) Hoard, J. L. *Ann. N.Y. Acad. Sci.* **1973**, *206*, 18.

(2) Scheidt, W. R. *Acc. Chem. Res.* **1977**, *10*, 339.

(3) Behere, D. V.; Marathe, V. R.; Mitra, S. *J. Am. Chem. Soc.* **1977**, *99*, 4149.

(4) Behere, D. V.; Mitra, S. *Inorg. Chem.* **1979**, *18*, 1723.

(5) Behere, D. V.; Mitra, S. *Indian J. Chem., Sect. A* **1980**, *19A*, 505.

(6) Behere, D. V.; Date, S. K.; Mitra, S. *Chem. Phys. Lett.* **1979**, *68*, 544.

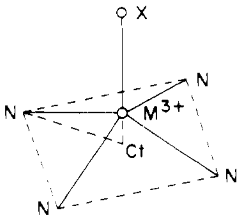

Figure 1. Coordination polyhedron in (TPP)$M^{III}X$. M is Fe, and Ct is the center of the square formed by the four nitrogen atoms.

(TPP)FeX series for such a study, an important one being the availability of complete structural data on all members of the series.[7-10] Equally important is the fact that large single crystals of sufficiently high quality for magnetic anisotropy measurements are more easily grown for the TPP series than for complexes of less symmetrically substituted porphyrins. Table I shows that the structural parameters of the ((TPP)-Fe)$^+$ unit are virtually constant as the axial ligand changes; the series therefore provides a good opportunity to study the effect on the ferric ion of variations in axial halide coordination, uncomplicated by an concomitant changes in the basal geometry.[11,12]

The magnetic properties of iron(III) porphyrins with $^6A_1$ ground state can be described by the spin Hamiltonian[13]

$$\mathcal{H} = DS_z^2 + g\beta H\cdot S \tag{1}$$

We have recently determined very accurately the ZFS in (TPP)FeCl[3-5] and (TPP)FeBr[6] from single-crystal magnetic studies and have established that $D_{Cl} < D_{Br}$. To establish further trends in the variation of D with apical halogen and to seek the origin of this variation, we have extended our measurements to other members of the series. This paper reports magnetic measurements, and analysis of the data between 80 and 300 K, on single crystals of two members of the (TPP)FeX series, namely, (TPP)Fe(NCS) and (TPP)FeI, thus covering the entire range of the halide ligands from NCS to I. A knowledge of the single-crystal susceptibilities of these complexes has also been very helpful in the interpretation and analysis of the isotropic shifts in their ^{1}H NMR spectra.[14]

Experimental Section

(TPP)Fe(NCS) and (TPP)FeI were prepared and purified by literature methods.[15] The compounds were analysed for C, H, and N, and their identity and purity were further checked by electronic spectra. Large, well-developed crystals of the thiocyanato complex, weighing between 5 and 10 mg, were grown by very slow evaporation of a benzene solution over a period of several weeks. The iodide crystals were obtained by allowing pentane to diffuse slowly into a chloroform solution. This process gave well-developed crystals weighing up to 4 mg in 2–3 weeks.

An examination of the (TPP)Fe(NCS) crystals by X-ray diffraction established them to be tetragonal. (TPP)FeI crystals belong to the monoclinic system and are isomorphous with (TPP)FeBr.[9,10] The crystal anisotropies in the 80–300 K temperature ranges were measured by the null-deflection method[16] using equipment described elsewhere.[17] The molecular anisotropies were calculated as described for (TPP)FeCl and (TPP)FeBr. The experimental molecular anisotropies were corrected for the diamagnetic anisotropy of the porphyrin ring with use of the known value of the diamagnetic anisotropy for (TPP)Ni.[18] The corrected data are shown in Figures 2 and 3, in terms of principal moments μ_i where $\mu_\perp^2 - \mu_\parallel^2 = 7.997(K_\perp - K_\parallel)T$. The parallel and perpendicular subscripts refer to the quantities parallel and perpendicular to the symmetry axis of the molecule which is approximately along the Fe–X direction.

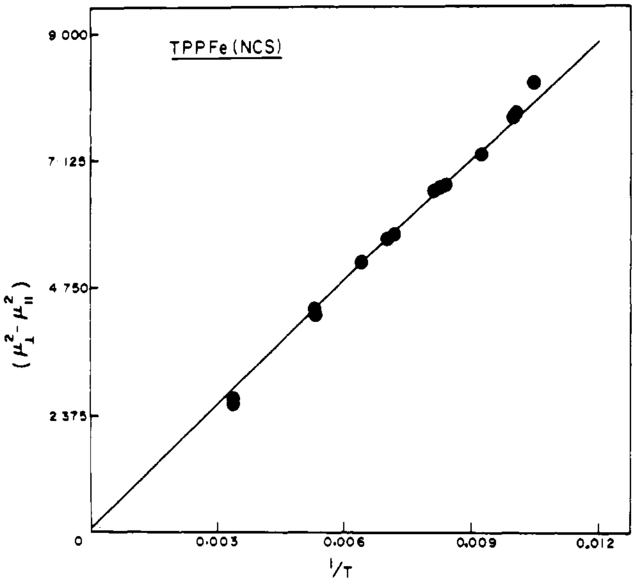

Figure 2.. Temperature dependence of $\mu_\perp^2 - \mu_\parallel^2$ in (TPP)Fe(NCS). The asterisks are the experimental data, and the solid line is the theoretical plot for D = 5.0 cm^{-1}.

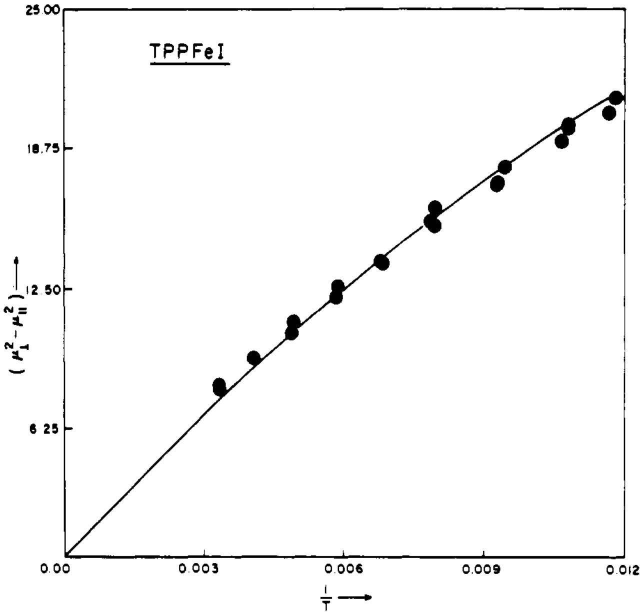

Figure 3. Temperature dependence of $\mu_\perp^2 - \mu_\parallel^2$ in (TPP)FeI. The asterisks are the experimental data, and the solid line is the theoretical plot for D = 13.5 cm^{-1}.

Results and Discussion

With use of eq 1, the expressions in eq 2 for principal

$$\mu_\parallel^2 = \frac{3}{1 + e^{-2x} + e^{-6x}}(1 + 9e^{-2x} + 25e^{-6x})$$

$$\mu_\perp^2 = \frac{3}{1 + e^{-2x} + e^{-6x}}\left[\left(9 + \frac{8}{x}\right) - \left(\frac{11}{2x}\right)e^{-2x} - \left(\frac{5}{2x}\right)e^{-6x}\right] \tag{2}$$

---

(7) The structure of (TPP)Fe(NCS) was presented: Bloom, A.; Hoard, J. L., paper presented at the 173rd National Meeting of the American Chemical Society, New Orleans, 1977.

(8) Hoard, J. L.; Cohen, G. H.; Gillick, M. D. *J. Am. Chem. Soc.* **1967**, *89*, 1992.

(9) Skelton, B. W.; White, A. H. *Aust. J. Chem.* **1977**, *30*, 2655.

(10) Hatano, K.; Scheidt, W. R. *Inorg. Chem.* **1979**, *18*, 277.

(11) Tang, S. C.; Koch, S.; Papaefthymiou, G. C.; Foner, S.; Frankel, R. B. Ibers, J.; Holm, R. H. *J. Am. Chem. Soc.* **1976**, *98*, 2415.

(12) Dolphin, D. H.; Sams, J. R.; Tsin, T. B.; Wong, K. L. *J. Am. Chem. Soc.* **1978** *100*, 1711.

(13) Weissbluth, M. *Struct. Bonding (Berlin)* **1967**, *2*, 1.

(14) Behere, D. V.; Birdy, R.; Mitra, S., to be submitted for publication.

(15) Alder, A. D.; Longo, F. R.; Kampas, F.; Kim, J. *J. Inorg. Nucl. Chem.* **1970**, *32*, 2443 and ref 7 and 10 therein.

(16) Mitra, S. *Transition Met. Chem.* **1972**, *7*, 183.

(17) Ganguli, P.; Marathe, V. R.; Mitra, S. *Inorg. Chem.* **1975**, *14*, 970.

(18) Murray, K. S.; Sheahan, R. M. *Aust. J. Chem.* **1975**, *28*, 2623.

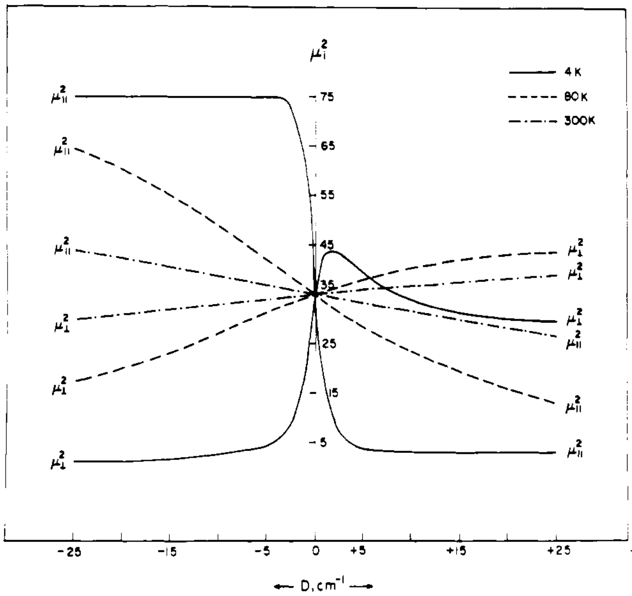

Figure 4. Variation of principal magnetic moments with the ZFS (D): —, 4 K; ---, 80 K; -·-, 300 K.

magnetic moments can be easily deduced,[3] where $x = D/kT$. Here $g_\parallel = g_\perp = 2$ following all available results.[19-21] A plot of eq 2 as a function of D at three representative temperatures is shown in Figure 4. It is seen that D is positive for $\mu_\perp > \mu_\parallel$ and that the temperature dependence of $\mu_\perp^2 - \mu_\parallel^2$ in the 80–300 K temperature range is sensitive enough to determine D accurately. For both the iodide and thiocyanate crystals, $\mu_\perp > \mu_\parallel$; hence D is positive in both cases. A least-squares fit of the data to eq 2 was then attempted which gave $D = 5.0 \pm 0.2$ and 13.5 ± 0.5 cm^{-1}, respectively, for (TPP)Fe(NCS) an (TPP)FeI. The solid lines in Figures 2 and 3 show the quality of the fit. The cited error margins reflect mainly the uncertainty in the fitting; the actual error in D may be slightly higher, particularly in (TPP)Fe(NCS) in view of the relatively low value of the anisotropy and the consequently greater importance of the diamagnetic anisotropy correction.

Table II. ZFS in Iron(III) Porphyrins

compd	D, cm^{-1}	ref
(TPP)FeCl	6.0 ± 0.1	3, 4
	6.5	32
	11.3	36
(TPP)FeBr	12.5 ± 0.5	6[c]
	4.9	36
(TPP)FeI	13.5 ± 0.5	this work
(TPP)Fe(NCS)	5.0 ± 0.2	this work
	9.8	36
(DPDME)FeCl[a]	8.95	21
(DPDME)FeBr	11.8	
(DPDME)FeI	16.4	
(PPDME)FeCl[b]	6.9	21
(PPDME)FeBr	9.75	
(PPDME)FeI	14.5	

[a] DPDME = deuteroporphyrin dimethyl ester. [b] PPDME = protoporphyrin dimethyl ester. [c] A revised value obtained after a refitting of the magnetic anisotropy and particularly the magnetization data in ref 6.

The zero-field splittings in high-spin iron(III) porphyrins and heme proteins have been the subject of extensive investigation by a variety of methods such as ESR,[22-26] ME,[12,27-29] far-infrared spectroscopy,[21,30-32] magnetic susceptibility,[20,33-37] and magnetic anisotropy[38-40] and even high-resolution NMR in solution.[41] The ZFS of the $^6A_1$ ground state in the TPPFeX series has also been determined by several method, and the values are listed in Table II. The ZFS was originally deduced by Maricondi et al.[36] for several members of this series (X = Cl, Br, NCS) from the temperature dependence of their average magnetic susceptibilities, but all later measurements have shown their results to be grossly in error.

The value of D for (TPP)FeI is close to the values available for the analogous protoporphyrin and deuteroporphyrin derivatives (see Table II). No accurate value of D for the thiocyanate derivative is available for comparison, the only published data being that of Maricondi et al.

The results of our measurements on the (TPP)FeX series reveal that the ZFS parameter increases in the order (though D_{Br} is rather close to D_I)

$$D_{NCS} < D_{Cl} < D_{Br} < D_I$$

This trend differs from that obtained earlier by Maricondi et al. but is in agreement with that observed in deutero- and protoporphyrin series for which accurate values are known from far-infrared spectroscopy.[20] It is interesting that a similar variation in D was also observed in a series of five-coordinated square-pyramidal $S = {}^3/_2$ (dithiocarbamato)iron(III) halides.[16]

This discrepancy with the work of Maricondi et al. may be due largely to the insensitivity of the average susceptibility to the zero-field splitting (a feature also observed recently in manganese(III) porphyrins[42]) and, to some extent, to unwarranted approximations in their theoretical analysis of the data.[43]

Although several possible mechanisms have been suggested to account for the ZFS in high-spin Fe(III) compounds,[19,44,45] it is now agreed, following the work of Griffith,[46] Harris,[47] and

---

(19) Abragam, A.; Bleaney, B.; Electron Paramagnetic Resonance of Transition Ions; Oxford University Press: Oxford, 1970.

(20) Kotani, M. *Suppl. Prog. Theor. Phys.* 1961, *17*, 4; *Rev. Mod. Phys.* **1963**, *35*, 717.

(21) Brackett, G. C.; Richards, P. L.; Caughey, W. S. *J. Chem. Phys.* **1971**, *54*, 4383.

(22) Ingram, D. J. E. "Biological and Biochemical Applications of ESR"; Adam Hilger Ltd.: London, 1969.

(23) Sato, M.; Rispin, A. S.; Kon, H. *Chem. Phys.* **1976**, *18*, 211.

(24) Alpert, Y.; Couder, Y.; Tuchendler, J.; Thome, H. *Biochim. Biophys. Acta* **1973**, *322*, 34.

(25) Slade, E. F.; Farrow, R. H. *Biochim. Biophys. Acta* **1972**, *278*, 450.

(26) Slade, E. F.; Ingram, D. J. E. *Proc. R. Soc. London, Ser. A* **1969**, *A312*, 85.

(27) Johnson, C. E. *Phys. Lett.* **1966**, *21*, 491.

(28) Lang, G. *Q. Rev. Biophys.* **1970**, *3*, 1.

(29) Fitzsimmons, B. W.; Sams, J. R.; Tsin, T. B. *Chem. Phys. Lett.* **1976**, *38*, 588.

(30) Feher, G.; Richards, P. Proceedings of the International Conference of Magnetic Resonance on Biological Systems, Stockholm, 1967.

(31) Richards, P. L.; Caughey, W. S.; Eberspaecher, H.; Feher, G.; Malley, M. *J. Chem. Phys.* **1967**, *47*, 1187.

(32) Uenoyama, H. *Biochim. Biophys. Acta* **1971**, *230*, 479.

(33) Tasaki, A.; Otsuka, J.; Kotani, M. *Biochim. Biophys. Acta* **1967**, *140*, 284.

(34) Iizuka, T.; Kotani, M. *Biochim. Biophys. Acta* **1969**, *181*, 275.

(35) Iizuka, T.; Kotani, M. *Biochim. Biophys. Acta* **1969**, *194*, 351.

(36) Maricondi, C.; Swift, W.; Straub, D. K.; *J. Am. Chem. Soc.* **1969**, *91*, 5205.

(37) Sullivan, S.; Hambright, P.; Evans, B. J.; Thorpe, A.; Weaver, J. A. *Arch. Biochem. Biophys.* **1970**, *137*, 51.

(38) Mitra, S. *Prog. Inorg. Chem.* **1978**, *22*, 309.

(39) McKim, F. R. *Proc. R. Soc. London, Ser. A* **1961**, *A262*, 287.

(40) Uenoyama, H.; Iizuka, T.; Morimoto, H.; Kotani, M. *Biochim. Biophys. Acta* **1968**, *160*, 159.

(41) LaMar, G. N.; Eaton, G. R.; Holm, R. H.; Walker, F. A. *J. Am. Chem. Soc.* **1973**, *95*, 63.

(42) Behere, D. V.; Mitra, S. *Inorg. Chem.* **1980**, *19*, 992.

(43) Marathe, V. R.; Mitra, S. *Chem. Phys. Lett.* **1973**, *21*, 62.

(44) Sharma, R. R.; Das, T. P.; Orbach R. *Phys. Rev.* **1967**, *155*, 338.

(45) Sharma, R. R.; Das, T. P.; Orbach, R. *Phys. Rev.* **1968**, *171*, 378.

(46) Griffith, J. S. *Biopolym. Symp.* **1964**, *1*, 35.

(47) Harris, G. *J. Chem. Phys.* **1968**, *48*, 2191.

(48) Koenig, D. F. *Acta Crystallogr.* **1965**, *18*, 663.

Kotani,[20] that in the present heme systems the major contribution to *D* arises from the inequivalence of the axial and equatorial ligand fields, all other interactions being insignificant. Harris[47] has argued that the ligand field acting on the ferric ion can be considered to a good approximation as consisting of two parts: the basal porphyrin part ($Fe-N_4$ core) and the axial (halogen) ligand (Fe–X). Table I summarizes relevant structural data from the single-crystal X-ray analyses on the (TPP)FeX series. It readily emerges from Table I that the mean Fe–N bond length remains almost constant throughout the series, as does the displacement (Δ) of the iron from the porphyrin core or the N_4 core, except for the (TPP)FeCl whose low value of Δ appears anomalous since this value is nearly constant at ca. 0.54 Å in other members of the TPPFeX series and is also about 0.54 Å in the related chlorohemin.[49] The Fe–X bond length however increases from the thiocyanate to the iodide.

These structural data may appear to suggest that the equatorial ligand field in the (TPP)FeX series remains nearly the same and that the variation in *D* follows the spectrochemical series for the halides (e.g., NCS > Cl > Br > I). Caughey[49] has however attempted to explain a similar variation in *D* in the analogous iron(III) protoporphyrin and deuteroporphyrin series on the basis that a change in the axial halide may produce a concomitant change in the Fe–N bonding, resulting in the above variation in *D*. Though the X-ray structural data do not show any significant and systematic variation in Fe–N bond length in the (TPP)FeX series, a small variation in the equatorial ligand field, which need not necessarily be reflected in the structural parameters, may not be ruled out. Such a variation in ligand field has in fact been theoretically anticipated.[47]

Registry No. (TPP)Fe(NCS), 25482-29-5; (TPP)FeI, 25482-28-4.

Supplementary Material Available: Tables of magnetic anisotropic parameters (3 pages). Ordering information is given on any current masthead page.

(49) Caughey, W. S. *Inorg. Biochem.* **1973**, *2*, 797.

Contribution from the Department of Chemistry,
University of Delhi, Delhi-110007, India

Ferric Complexes with Biguanides in the Spin Quartet Ground State

S. LAHIRY* and V. K. ANAND

Received October 15, 1980

Ferric complexes with biguanides ($NH_2C(=NH)NHC(=NH)NH_2$) and aryl (aryl = phenyl, *o*-chlorophenyl, and *p*-tolyl) biguanides of the composition $[Fe(Big)_2Cl]Cl$ (BigH = a molecule of biguanide) have been prepared; their temperature variation magnetic susceptibilities between 300 and 77 K are in accord with the spin quartet ground state of Fe(III). Isomer shift with respect to $Cu/^{57}Co$ source and quadrupole splitting in Mössbauer spectrum at room temperature are 0.205 and 0.75 mm/s, respectively.

Fe(III) in spin quartet ($S = {}^3/_2$) ground state is known to occur in ferric porphyrin chloride[1,2] and in chloro- or bromobis(dialkyldithiocarbamate)iron(III), where dialkyl = dimethyl, diethyl, etc.).[3] The latter compounds have been studied extensively[4-6] by X-ray, temperature-variation magnetic susceptibility, Mössbauer, and EPR techniques. We report the preparation and characterization of a few new Fe(III) complexes with biguanides and aryl-substituted biguanides where Fe(III) is shown to exist in the spin quartet ground state.

Experimental Section

Preparation of Reagents. The simple biguanide acid sulfate was prepared following Ray,[7] and the free base was obtained by the interaction of the acid sulfate with sodium ethoxide. The aryl-substituted biguanide bases were prepared by the interaction of hydrochlorides with sodium ethoxide.

Preparation of Complexes. The complex of Fe(III) with simple biguanide ($NH_2C(=NH)NHC(=NH)NH_2$), $[Fe(Big)_2Cl]Cl$ was prepared by adding 1.6 g of anhydrous ferric chloride to a clear solution of 2 g of biguanide base in dry acetone. Then a light brown precipitate which separated out was filtered and washed a few times with dry acetone. The compound was stable. It was insoluble in common organic solvents such as chloroform, acetone, carbon tetrachloride, alcohols, etc.

Other Fe(III) complexes with aryl-substituted (such as phenyl, *p*-tolyl and *o*-chlorophenyl) biguanides were prepared as above and analyzed.

Anal. Calcd for $[ClFe(Big)_2]Cl$: Fe, 16.68; N, 42.80; partial Cl^-, 10.89; total Cl^-, 21.72. Found: Fe, 16.80; N, 4.20; partial Cl^-, 11.04; total Cl^-, 22.00.

Anal. Calcd for $[ClFe(PhBig)_2]Cl$: Fe, 11.60; N, 28.56; partial Cl^-, 7.40; total Cl^-, 14.83. Found: Fe, 11.75; N, 28.00; partial Cl^-, 7.80; total Cl^-, 15.15.

Anal. Calcd for $[ClFe(p\text{-tolBig})_2]Cl$: Fe, 10.75; N, 27.50; partial Cl^-, 7.51; total Cl^-, 13.95. Found: Fe, 11.05; N, 27.00; partial Cl^-, 7.51; total Cl^-, 14.43.

Anal. Calcd for $[ClFe((o\text{-ClPh})Big)_2]Cl$: Fe, 9.98; N, 25.40; partial Cl^-, 6.44; total Cl^-, 25.75. Found: Fe, 9.87; N, 25.30; partial Cl^-, 6.72; total Cl^-, 26.00.

The oxidation state of iron was confirmed iodometrically. The amount of chloride (not participating in coordination) was estimated, after the compound was dissolved in $ARHNO_3$, as silver chloride. The total amount of chloride was estimated, after the compound was fused with sodium carbonate, as silver chloride. Magnetic susceptibilities between 300 and 77 K were measured in a Gouy balance (at NPL, Delhi). Mössbauer data were collected following the procedure of Bhide and Multani[8] (at NPL, Delhi).

Results and Discussion

On the basis of analytical results it appears that one of the two biguanide units in the complexes behaves as a bidentate ligand, satisfying the oxidation state of the metal ion through C=N—M, but does not become protonated as it occurs with other biguanide metal complexes;[8] this is indeed tentative in the absence of X-ray and other critical studies which become

---

(1) J. F. Gibson, D. J. E. Ingram, and D. Schonland, *Discuss. Faraday Soc.*, **26**, 72 (1958).

(2) J. S. Griffith, *Discuss. Faraday Soc.*, **26**, 81 (1958); "The Theory of Transition Metal Ions"; Cambridge University Press, New York, 1961.

(3) R. L. Martin and A. H. White, *Inorg. Chem.*, **6**, 712 (1967).

(4) B. S. Hoskins, R. L. Martin, and A. H. White, *Nature (London)*, **211**, 621 (1966).

(5) H. H. Wickman and A. M. Trozzolo, *Inorg. Chem.*, 7, 63 (1968).

(6) H. H. Wickman and C. F. Wagner, *J. Chem. Phys.*, **51**, 435 (1969); H. H. Wickman, M. P. Klein, and D. A. Shirley, *Phys. Rev.*, **152**, 345 (1965).

(7) P. Ray, *Chem. Rev.*, **61**, 314 (1961).

(8) V. G. Bhide and M. S. Multani, *Phys. Rev. A*, **139**, 1983 (1963).

0020-1669/81/1320-2789$01.25/0