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.

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

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]

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Ferric Complexes with Biguanides in the Spin Quartet Ground State

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Ferric complexes with biguanides (NH$_2$C(=NH)NHC(=NH)NH$_2$) and aryl (aryl = phenyl, *o*-chlorophenyl, and *p*-tolyl) biguanides of the composition [Fe(Big)$_2$Cl]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$_2$C(=NH)NHC(=NH)NH$_2$), [Fe(Big)$_2$Cl]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

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(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).

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*-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*-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

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

Table I[a]

	Chlorobis(biguanide)iron(III) Chloride, [ClFe(C$_2$H$_6$N$_5$)$_2$]Cl									
temp, K	302	260	240	200	180	160	140	120	100	90
χ_M(cor) × 10^6, cgs emu/mol	6056	6920	6250	8220	9130	10 280	12 700	13 700	17 500	20 100
μ_{eff}, μ_B	3.74	3.68	3.65	3.68	3.68	3.65	3.73	3.62	3.74	3.81

	Chlorobis(phenylbiguanide)iron(III) Chloride, [ClFe(C$_8$H$_{10}$N$_5$)$_2$]Cl											
temp, K	300	280	260	240	220	200	180	160	140	120	100	80
χ_M(cor) × 10^6, cgs emu/mol	6342	6800	7700	8600	9600	10 700	12 000	13 500	15 380	17 970	21 540	26 800
μ_{eff}, μ_B	3.90	3.90	4.00	4.06	4.11	4.13	4.15	4.15	4.15	4.15	4.15	4.14

	Chlorobis((o-chlorophenyl)biguanide)iron(III) Chloride, [ClFe(C$_8$H$_9$N$_5$Cl)$_2$]Cl										
temp, K	300	280	260	240	220	200	180	160	140	100	77
χ_M(cor) × 10^6, cgs emu/mol	7000	7414	8000	8700	9600	10 500	11 720	13 120	15 000	20 900	25 880
μ_{eff}, μ_B	4.10	4.08	4.08	4.08	4.11	4.10	4.11	4.10	4.10	4.09	3.99

[a] Diamagnetic correction is calculated from Pascal constants. Multiply numerical values of χ_M(cor) × 10^6 cgs emu/mol by 4π × 10^{-6} m^3 mol^{-1} to convert into SI units. χ_M and μ_{eff} have been calculated with use of relations given by Lahiry et al.[12]
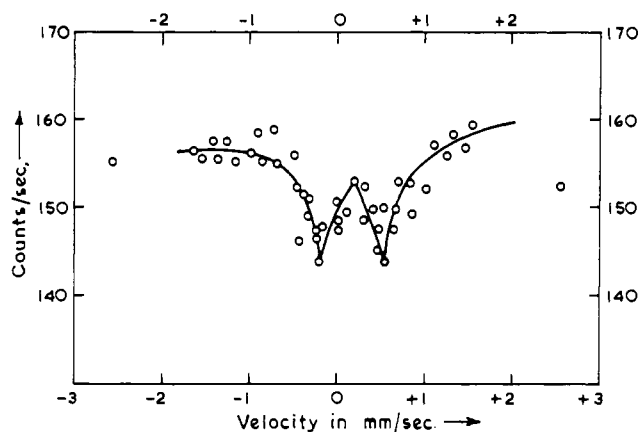

Figure 1. Mössbauer spectrum of chlorobis(phenylbiguanide)iron(III) chloride at room temperature (quadrupole splitting 0.75 mm/s; isomer shift 0.205 mm/s with reference to the Cu/^{57}Co source).

limited because of the insolubility of the compound.

The IR spectra exhibit unusually broad but strong bands in the complexes in the region 1600–1400 cm^{-1} with respect to well resolved bands in the free reagents, where the bands due to NH$_2$ (bending) and C=N are expected, suggesting pronounced effect of metal ion complexation. A fairly broad but strong band in the complexes in the region 3500–3300 cm^{-1} in place of two sharp and narrow bands at 3300 and ~3500 cm^{-1} in the free reagents appears; this is indicative of participation of NH$_2$ in bonding with the metal ion. These results are in fair agreement with the important valence-bond structures considered to account for the observed bond distances in the X-ray structure of nickel(II) bis(ethylbis(biguanide)) chloride.[9]

Temperature Variation Magnetic Results. The susceptibilities and magnetic moment values of compounds a, b, and d between 300 and 77 K, given in Table I, are perfectly consistent with the spin quartet ground state ($S = {}^3/_2$) of Fe(III); i.e., the symmetry around Fe(III) should be predominantly axial (with small orthorhombic component) and the

strength of the axial crystalline field should be large in order to explain the experimental magnetic moment results.[2,10]

Mössbauer Spectral Results. Compounds b and c do not exhibit any hyperfine structure and exhibit only a quadrupole doublet with quadrupole splitting $\Delta E = 0.75$ mm/s which is small (Figure 1) compared to $\Delta E = 0.288$ cm/s in some chlorobis(dialkyldithiocarbamato)iron(III) complexes where Fe(III) exists in the $S = {}^3/_2$ ground state.[5,6] It is well-known that the main contribution to quadrupole splitting[11] arises from $q_{valence}$ while $q_{lattice}$ contributes a little, where $q_{valence}$ and $q_{lattice}$ refer to valence and lattice electric field gradient (EFG). Since the compounds are insoluble, crystals cannot be grown for structural studies as well as for a detailed study of the electric field gradient tensor in these iron(III) complexes. Furthermore, detailed knowledge of relative separations of $^6A_1$, $^2T_2$, and $^4T_1$ (all in cubic field notation) is not available, and we can therefore offer the following tentative mechanism to explain the small values of quadrupole splitting in these complexes: (i) the symmetry of the complex is orthorhombic so that the ground state is a mixture of three orbital components of $^4T_1$ (neglecting mixing by spin–orbit interaction in the first approximation) and the value of the quadrupole splitting can be small depending, of course, on the values of coefficients of the three orbital components constituting the ground-state wave function, or (ii) the quadrupole splitting arises due to the lattice only. The small values of the isomer shift 0.205 mm/s with reference to the Cu/^{57}Co source are an indication of Fe^{3+} in strong crystal field. At room temperature, we could neither observe any EPR signal at X-band nor observe any paramagnetic hyperfine structure in Mössbauer spectrum, and therefore the paramagnetic relaxation time appears to be short and the ground Kramer's Zeeman levels following Wickman[12] may tentatively be considered as $M_s = |\pm^1/_2\rangle$, although EPR and Mössbauer studies at low temperatures would be desirable to establish the ordering of the Zeeman levels uniquely.

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